Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium

by

Timothy Crowtz

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia
August 2017

For Mom and Dad

Table of Contents

List of Tables

List of Figures

Abstract

One of the remaining challenges driving polymer electrolyte membrane hydrogen fuel cell research is the durability of the Pt oxygen reduction reaction (ORR) catalyst. Pt is inherently unstable; minute amounts (in the order of $ng\,cm^{-2}$) are dissolved every time the fuel cell is started, goes from idle to load, or shut-down. In addition, corrosion of carbon-based materials (ubiquitous inside fuel cells) occurs during the start-up and shut-down, and also contributes to the steady decline of fuel cell performance. Adding oxygen evolution reaction (OER) catalysts, of which only Ru and Ir are stable in the acidic conditions of the fuel cell, can decrease Pt loss and carbon corrosion by mitigating the degradation mechanism which occurs during the start-up and shut-down phases. There are two challenges in developing this materials solution (there are other solutions, based on hardware systems) to the fuel cell durability problem: 1) finding the right mixture of Ru and Ir, (Ru is cheaper, more active, but less stable than Ir), and 2) balancing an increase of OER activity with a loss of ORR activity due to Pt coverage by the Ru and Ir.

A spread of compositions containing various amounts of Ir or Ru on 85 $\mu g\,cm^{-2}$ of Pt were sputter deposited on a nanostructured thin film state-of-the art catalyst support made by 3M. The nanostructured thin film was grown by 3M on glassy carbon disks designed for a rotating disk electrode, which was used to simulate what happens to a fuel cell cathode during repeated start-up, operation, and shut-down. Experimental difficulties of glassy carbon disk corrosion were overcome with the application of high vacuum silicone grease (silicone oil and fumed silica) to the glassy carbon disk. The silicone grease did not affect the ORR activity. Ir was found to be better at protecting the ORR activity than Ru, and an Ir on Pt sputter deposition scheme was found to be better than a Ir intermixed with Pt scheme.

The second study looked for ways to visualize the OER and ORR durability of ~50 ternary (Ir on Ru on Pt) compositions. Increasing Ir loading improved the durability of both ORR and OER activity. Various Ru loadings provided little benefit except when combined with 10 $\mu g\,cm^{-2}$ Ir. There was a large amount of scatter in the data. In particular some of the experiments attained a stable ORR activity, something which should not be possible given the nature of electrochemical Pt dissolution. Further work on identifying the source of these problems is needed before another catalyst screening study is done.

List of Abbreviations and Symbols Used

$\boldsymbol{\Delta \bar{g}}$ molar specific Gibbs energy

$\boldsymbol{\Delta_{\mathrm{rxn}} \bar{g}^{\circ}}$ molar specific Gibbs reaction energy at standard conditions

$\boldsymbol{\Delta_{\mathrm{rxn}} \bar{s}^{\circ}}$ molar specific reaction entropy at standard conditions

$\boldsymbol{\alpha_a}$ anodic transfer coefficient

$\boldsymbol{\alpha_c}$ cathodic transfer coefficient

AST accelerated stress test

$\boldsymbol{b}$ Tafel slope

$\boldsymbol{b_a}$ anodic Tafel slope

$\boldsymbol{b_c}$ cathodic Tafel slope

$\boldsymbol{\beta}$ symmetry parameter between 0 and 1 (almost always 0.5)

CCM catalyst coated membrane

COR carbon oxidation reaction

CV cyclic voltammogram

$\boldsymbol{E}$ electrical potential difference

ECSA electrochemical surface area

$\boldsymbol{E_{eq}}$ equilibrium potential

$\boldsymbol{E^{\circ}_{eq}}$ equilibrium potential at standard conditions

$\boldsymbol{E_{iRcorr}}$ electrode potential corrected for ohmic loss

$\boldsymbol{E_{raw}}$ measured electrode potential

$\boldsymbol{\eta}$ over-potential (deviation away from E_{eq})

$\boldsymbol{F}$ Faraday’s constant (96485 $C\,mol^{-1}$)

FCCJ Fuel Cell Conference of Japan

GDL gas diffusion layer

$\mathbf{H_{UPD}}$ underpotential deposited hydrogen

HER hydrogen evolution reaction

HOR hydrogen oxidation reaction

$Q_{H_{UPD,des}}$ $\mathrm{H_{UPD}}$ desorption charge

$\boldsymbol{i}$ areal current density

i_{Ar} current density in Argon saturated electrolyte

ICE internal combustion engine

ICP-MS inductively coupled plasma mass spectrometer

i_d diffusion limited current density for a given rotation rate

i_{fara} Faradaic current density

$i_{fara(ORR)}$ current density due only to the ORR

i_k kinetic current density

i_k^{Pt} Pt specific kinetic current density

i_o exchange current density

$i_{\mathrm{O_2}}$ current density in oxygen saturated electrolyte

i_{raw} measured current density

$\boldsymbol{I}$**-**$\boldsymbol{V}$ current voltage

MEA membrane electrode assembly

MSE mercury/mercurous sulfate electrode

$\boldsymbol{n}$ number of electrons transferred in the electrochemical half-reaction considered for the electrode

NSTF nanostructured thin film

$\boldsymbol{n_t}$ total number of electrons transferred in the overall electrode reaction

OER oxygen evolution reaction

ORR oxygen reduction reaction

$\boldsymbol{P}$ partial pressure

PEM polymer electrolyte membrane

PFSA perfluorosulfonic acid

PGM platinum group metals

Pt\C carbon supported platinum

$\mathfrak{R}$ universal gas constant

$\boldsymbol{r}$ number of electrons transferred in the rate determining step

RCDM reverse current decay mechanism

RDE rotating disk electrode

$\boldsymbol{R}$ electrical resistance

RHE reversible hydrogen electrode

s total number of electrons transferred before the rate determining step (in the cathodic direction)

A_{geo} geometric (sometimes called planar) surface area of the electrode

SEF surface enhancement factor

SHE standard hydrogen electrode

SU/SD start-up and/or shut-down

T temperature (in Kelvin)

TEM transmisison electron microscope

USDOE United States Department of Energy

v stoichiometric number for the rate determining step (i.e. the number of times the rate determining step has to occur to make the whole mechanism occur once)

XPS X-ray photoelectron spectroscopy

Acknowledgements

The first and foremost acknowledgement goes to my supervisor Jeff Dahn. I am deeply thankful to him for providing me this opportunity and for his continued trust and support throughout the project. I would also like to acknowledge Robbie Sanderson for teaching me about sputtering and helping me to fix broken equipment. Others who deserve credit are David Stevens, Tim Hatchard, Jessie Harlow, and Gary Lui for creating the rotating disk electrode experimental set-up and showing me how to use it. Simon Trussler and Nils Bosch were also indispensable in creating the experimental set-up. In addition, many summer students made a significant contribution through their help with the experiments.

I would also like to thank the following Dahn Lab members for their friendship: Deijun Xiong, Eric McCalla, Laura (Downie) McCalla, Lin Ma, Jian Xia, Leah Ellis, Stephen Glazier, Kathlyene Nelson, Jim Lee, John Camardese, Remi Petibon, Patrick Bonnick and Aaron Rowe. A special mention goes to Ramesh Shunmugasundaram for many discussions about materials science, self improvement, and doing what you love to do.

Chapter 1

Introduction

This chapter provides a description of the reasons this thesis project was undertaken, and highlights basic principles of hydrogen fuel cells and electrocatalysis.

1.1 Project Motivation

The research described in this thesis arose from an arrangement between Dalhousie University and 3M to develop a materials based solution to polymer electrolyte hydrogen fuel cell degradation caused by start-up and/or shut-down (SU/SD) events. Funding was provided by a grant awarded by the United States Department of Energy (USDOE) to the 3M Fuel Cell Division in 2009 to improve catalyst durability. This project was initiated by the discovery that traditional fuel cell catalyst materials are inherently unstable (*Stevens and Dahn* (2005) and *Ferreira et al.* (2005)), and that the degradation mechanism provided a way to address the problem by hindering and promoting certain catalytic reactions within the fuel cell (*Reiser et al.*, 2005). An understanding of this mechanism lead to the conclusion that adding Ru and/or Ir (oxygen evolution catalysts) to Pt (an oxygen reduction catalyst) in the fuel cell cathode would enhance its durability (*Atanasoski*, 2009).

Dalhousie University was subcontracted by 3M to provide high-throughput catalyst screening. The Dahn lab at Dalhousie was a natural fit for partnering with 3M on fuel cell research because of preexisting cooperation agreements on Li-ion battery and carbon respirator materials research. The Dahn Lab also operated two combinatorial sputtering machines, necessary for the synthesis of fuel cell catalyst materials on nanostructured thin film (NSTF), a unique electrocatalyst support material patented by 3M. In addition, methods for high-throughput screening of oxygen reduction electrocatalysts on NSTF had already been refined in the Dahn Lab for a prior USDOE funded subcontract. (This work resulted in numerous publications and two thesis works concerned with the effect of various alloy compositions (*Bonakdarpour*, 2007) and de-alloying pretreatment strategies (*Liu*, 2011).) The work presented in this thesis represents a small but important fraction of the work prepared for 3M under the second award, pertaining to catalyst durability.

Pursuing the strategy of including Ru and/or Ir on an ordinary NSTF supported Pt catalyst follows a sequence of questions: How will Ru and Ir behave on NSTF? Will there be durability issues for the oxygen evolution reaction (OER) catalysts like there is for Pt, and if so what is the nature of the instability? What are the best sputtering conditions for Ru and Ir on NSTF? What is the best manner of sputtering deposition for Ru and Ir when combined with Pt on NSTF? Will adding Ru and Ir compromise the catalytic activity of the Pt? Attempting to answer these questions resulted in the experiments and data analysis techniques explained in Chapters 2 through 5.

1.2 What is a Fuel Cell?

1.2.1 Fuel Cells vs. Batteries

A fuel cell is an electrochemical galvanic cell where the reductant (i.e. the fuel) is stored outside the anode, and oxygen in the air is the oxidant on the cathode. This is in contrast to most other galvanic cells, like a common electrochemical storage battery , where both electrodes contain, or are primarily composed of, the chemical species which undergo the oxidation/reduction reactions. Thus a fuel cell has an inherent advantage over batteries, because the species to be reduced (oxygen) does not contribute to the weight of the cell (with the exception of metal/air chemistries). This property, and the energy density of the various liquid and gaseous fuels used by fuel cells, means the energy density of fuel cell systems surpasses even the most mature rechargeable battery chemistries available, namely Li-ion. Figure 1.1 shows a chart in the style of *Ragone* (1968) produced by *Srinivasan* (2008) from “product data sheets”, which shows a fuel cell has about three times the energy density of a Li-ion battery. It is understood that Ragone charts like the one shown in Figure 1.1 should be viewed with scepticism, as the factors which determine the energy density may be alternatively considered, and the technologies are constantly advancing. But other Ragone plots like Figure 1.1 consistently show fuel cell systems above all battery chemistries on the energy axis, and one could easily argue the margin for improvement in fuel cell systems is much greater than that for batteries. Thus fuel cell systems will likely always have an energy density advantage over rechargeable battery systems, barring commercial maturation of one of the metal-air cell chemistries, or the emergence of a ‘beyond-Li-ion’ chemistry such as Mg-ion. This energy density advantage however, is influenced more by the fuel type or storage technology, rather than the fuel cell technology itself. Given the energy density advantage, it is prudent to list the core disadvantages of fuel cells:

- Forced convection of fuel and/or air streams is often required, introducing additional equipment requirements and energetic losses.
- The catalytic reduction of di-oxygen on the cathode is not a thermodynamically efficient process.
- High ohmic losses often accompany fuel cells.

In short, fuel cells are generally inefficient and more complicated to operate compared to batteries.

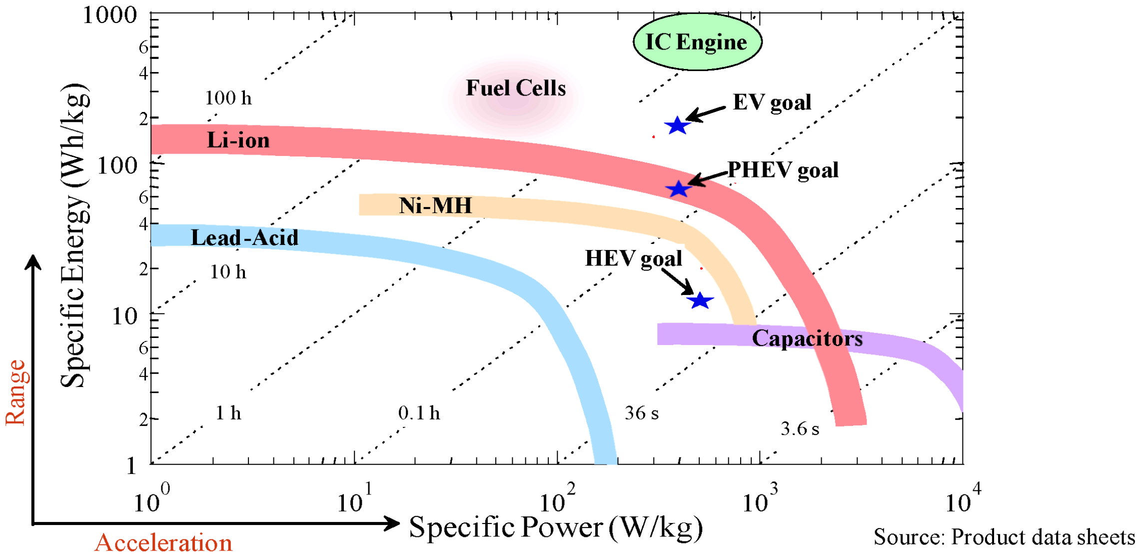


Figure 1.1: The gravimetric energy and power ranges of various energy storage technologies. Reproduced from Srinivasan, V. Batteries for Vehicular Applications, in AIP Conference Proceedings 1044, 283-296 (AIP Publishing, 2008), with the permission of AIP Publishing (*Srinivasan*, 2008).

1.2.2 The Hydrogen Fuel Cell

The distinguishing feature of a fuel cell is its electrolyte, which must take the form of a membrane which keeps the fuel and air separate. The electrolyte/membrane must be either:

- a solid matrix, usually a polymer, containing immobilized counter ions,

- a liquid electrolyte wicked into a porous solid matrix, or
- a solid state electrolyte.

Figure 1.2 shows six types of fuel cells with their corresponding fuel(s) and ionic charge carrier. This thesis project is concerned with polymer electrolyte membrane (PEM) fuel cells where a perfluorosulfonic acid (PFSA) polymer (an immobilized counter ion electrolyte) comprises the membrane, and hydrogen gas is the fuel. The PEM fuel cell was selected by the USDOE as the prime candidate for an emissions and petroleum-free technology to supplant internal combustion engines (ICEs) in the vast number of transport vehicles. The hope is that wide spread deployment of hydrogen fuel cells in the transport sector would ease the transition to other energy sources[1] which have a smaller carbon footprint. The PEM fuel cell in particular was selected over other hydrogen fuel cell types because 1) the low operating temperature would enable quick starts and require no thermal shielding and 2) PEM fuel cell systems were comparatively volumetrically and gravemetrically dense with respect to both energy and power. There was, and still is, much room for energy and power density improvements. The PEM fuel cell's volumetric power density is actually quite impressive. It is a direct result of its geometric current density, which stands among the highest of any electrochemical cell, achieving up to 2 $A\,cm^{-2}$ at 0.6 V (*Debe*, 2013) and surpassed only by its electrolytic water splitting analog, which has been shown to achieve up to 4 $A\,cm^{-2}$ at 1.9 V (*Siracusano et al.*, 2015). The high current densities are possible because reactants and products are delivered to and from the catalyst surface in the gas phase instead of the liquid phase. Only the proton from the hydrogen gas (the ionic current) is transferred in liquid water (absorbed by the PFSA), and proton mobility in water is extremely fast due to the *de Grotthius* (1806) mechanism.

---

[1] Hydrogen itself is not an energy source, but better considered as an energy carrier. It can be made via electrochemical processes (such as electrolysis of water or ammonia), thermal water dissociation, thermochemical processing of coal, hydrocarbons or biomass (i.e. steam reforming, plasma gasification etc), anaerobic bio-processes and photocatalytic water splitting. It can be used in many types of fuel cells, and any combustion process such as internal combustion engines and gas turbines. This great flexibility is in part what lead to the excitment about a so-called hydrogen economy, prompting popular futuristic books from *Hoffmann* (2002) and *Rifkin* (2003). A more sobering perspective is provided in *Romm*'s (2005) book "The Hype About Hydrogen".

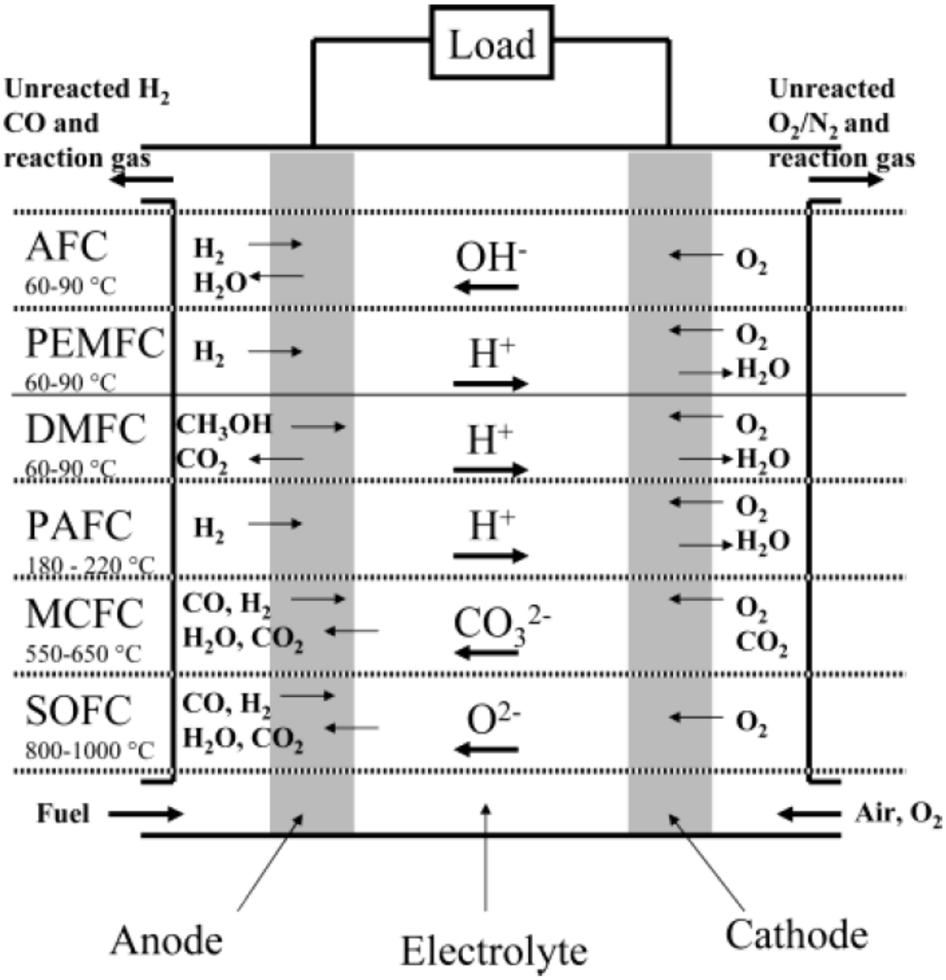


Figure 1.2: Six types of fuel cells (AFC: alkaline fuel cell, PEMFC: polymer electrolyte membrane fuel cell, DMFC: direct methanol fuel cell, PAFC: phosphoric acid fuel cell, MCFC: molten carbonate fuel cell, SOFC: solid oxide fuel cell) showing their respective electrolyte charge carriers, fuels (anode), oxidizers (cathode) and operating temperatures. Reprinted with permission from Winter, M. & Brodd, R. J. What Are Batteries, Fuel Cells, and Supercapacitors? Chem. Rev. 104, 4245-4270 (2004). Copyright (2004) American Chemical Society (*Winter and Brodd*, 2004).

When a boundary between the catalyst and electrolyte meets a gaseous void, the three phases which support the current meet, and all mass flows can occur at the maximum rates. Figure 1.3 shows a transmisison electron microscope (TEM) image of a three phase boundary formed by the catalyst platinum, a solid PFSA electrolyte, and a pore.

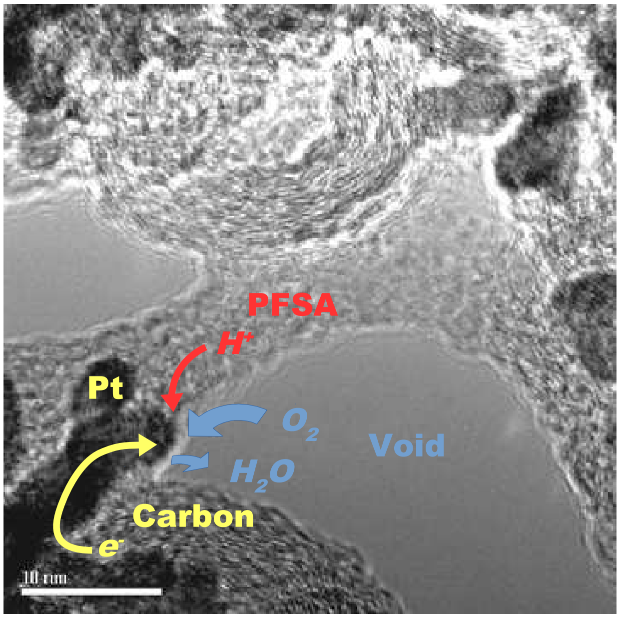


Figure 1.3: TEM micrograph of a three phase boundary crucial to fuel cell operation. With Permission of Springer (*Li*, 2008).

Also labelled in Figure 1.3 is carbon, or more specifically carbon black, known by the trade names Ketjenblack (made by AkzoNoble) and Vulcan (made by Cabot Corporation). High surface area carbon was first used as a catalyst support by alkaline fuel cell pioneers (Davtyan (1946), in *Bacon* (1953), Kordesch and Marko (1951) in *Chen* (2002)) due to its high surface area, electrical conductivity, electrochemical stability, and cost effectiveness. For the acidic PEM fuel cell, carbon supported platinum (Pt\C) was augmented by *Raistrick* (1986) to include PFSA which reduced the amount of platinum required for a PEM by an order of magnitude. *Wilson and Gottesfeld* (1992), working at the same lab, made further improvements by mixing a PFSA/ethanol solution into Pt\C to make a catalyst 'ink'. Their technique of casting and drying the ink onto a PFSA sheet to make a membrane electrode assembly (MEA), has since been the mainstay of PEM fuel cell catalyst materials because of the high density of three-phase boundary sites. However, work by *Stevens and Dahn* (2005), *Ferreira et al.* (2005), and *Reiser et al.* (2005), exposed high surface area carbon black as a less-than-ideal candidate material for supporting Pt, resulting in the increased investigation of alternative, more stable Pt supports such as high surface area graphitized carbon and electrically conductive porous metal oxides. A particularly unique alternative catalyst support is an organic material discovered by 3M, originally developed outside the scope of fuel cell research as "a novel alternative approach to plasma etching and photo lithography for producing nanostructured surfaces with new properties"(*Debe and Poirier*, 1994). This material is the basis of all catalyst materials presented in this thesis, and is given a detailed description in Section 2.2.

A typical PEM fuel cell is made by sandwiching the MEA between carbon fibre mats and electrically conductive flow field plates. Figure 1.4 shows all the basic components and reactions in a PEM fuel cell. Not shown in Figure 1.4, is a carbon micro-porous layer that goes between the catalyst layer and the carbon fibre mat, or gas diffusion layer (GDL) and acts to improve the mass transport (i.e. water management) properties (*Gostick et al.*, 2009). For a practical application, multiple cells are connected in series to create a stack with higher voltage, introducing engineering challenges which make the field of fuel cells very multidisciplinary. The low operating temperature, stack architecture, and high areal current density of a PEM fuel cell stack creates engineering challenges pertaining to cooling, reactant/product gas conveyance, and ohmic loss respectively. The biggest operational challenge of PEM systems is managing the humidity to prevent dry-out (maintain liquid water) in the membrane and prevent condensation (flooding) on the cathode catalyst. This operational challenge is referred to as water management and has proved a formidable, though not insurmountable challenge in the field of PEM fuel cell development. The complexity of the water management challenge is apparent in the first isothermal, one-dimensional, steady-state (i.e. probably the simplest) model for a PEM fuel cell by *Springer* (1991), which required twelve parameters to define fuel cell operation. This 'simple' model requires the humidity, pressure, and stoichiometric ratio (relating inlet mass flow to electrical current) of the fuel and air stream. These parameters, in addition to cell operating temperature and five materials properties (catalyst and membrane), determine the steady state current voltage (I-V) curve, and at what voltage the current will severely attenuate due to flooding or dry-out Anyone who uses this simplest of PEM fuel cell models soon realizes that keeping the fuel cell operation optimized is no easy task. Humidifiers, blowers, heat exchangers, and pumps are required to maintain conditions conducive to neither dry-out nor flooding, and these balance-of-plant components impose mandatory electrical loads which decrease efficiency beyond inherent ohmic and catalytic losses.

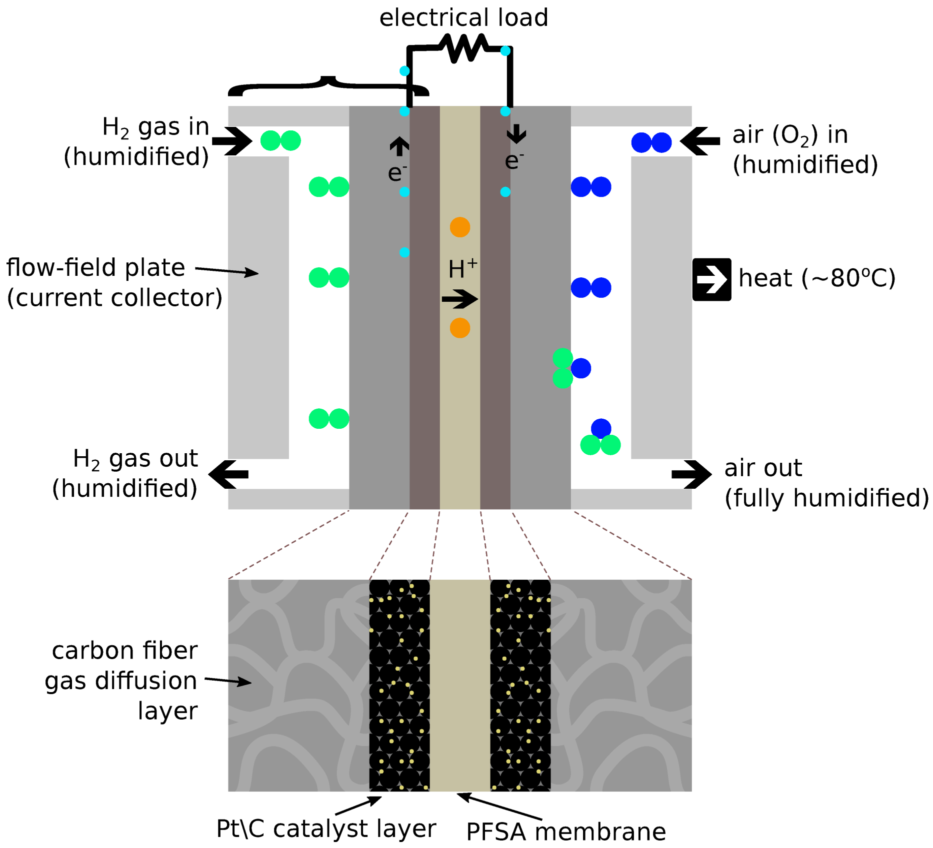


Figure 1.4: The various components and mass flows of a typical PEM fuel cell. Not shown is a carbon micro-porous layer that goes between the catalyst layer and the carbon fibre layer.

The *I*-*V* curve of a single cell can be used to visually highlight the non-balance-of-plant losses. Figure 1.5 shows a fictitious fuel cell power curve, along with the three types of losses that are incurred. These losses are:

1. activation polarization, or kinetic loss, which is principally due to the electro-reduction of di-oxygen to water on the cathode (*Nørskov et al.*, 2004),
2. ohmic losses, which are due to electrical and ionic resistance, governed by Ohm's law, and
3. concentration polarization, or mass transport loss, due to a less-than-maximum rate

of reactants arriving and/or products leaving the catalytic sites. Electric current is limited by a mass transport resistance, but energy is not dissipated as heat as in the previous two types of losses.

Figure 1.5 will be referred to in the next section which explores the sources of these losses.

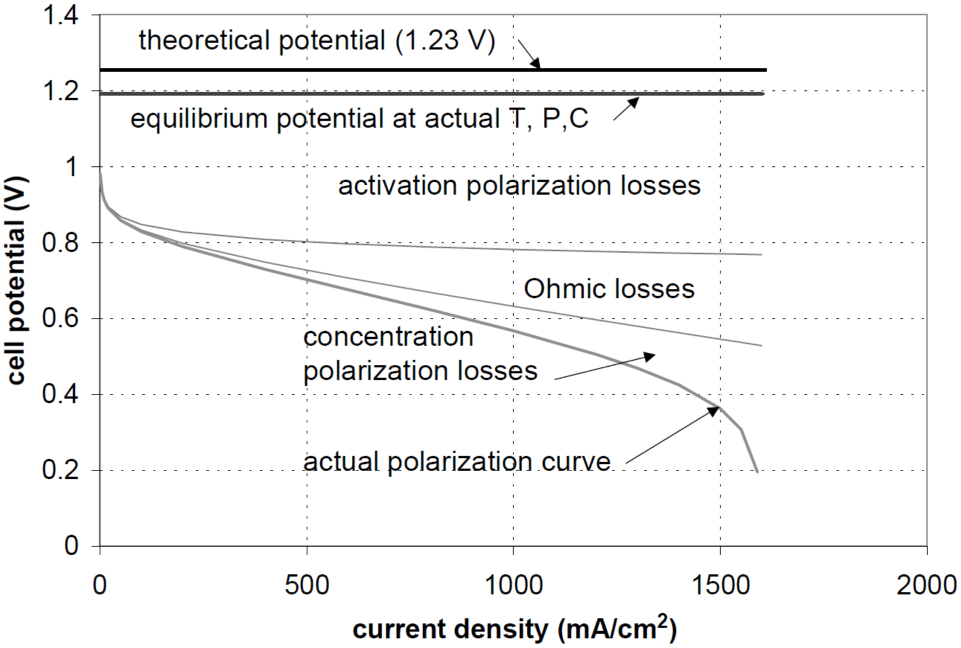


Figure 1.5: A fictitious *I*-*V* curve illustrating how the three types of electrical potential losses (activation polarization, ohmic, and concentration polarization) change with the current drawn from the cell. “T”, “P”, and “C” stand for temperature, pressure, and concentration respectively. (Including concentration could be seen as redundant since it can be expressed at a partial pressure.) “theoretical potential” is the equilibrium potential at standard conditions (with H_2 and O_2 pressures both at 1 *atm*). Reprinted from PEM Fuel Cells, Barbir, F., Chapter 3 Fuel Cell Electrochemistry, pg. 50, Copyright (2005) with permission from Elsevier (*Barbir*, 2005).

Other aspects of PEM fuel cells are worth mentioning. Hydrogen fuel is highly explosive so tanks and refuelling systems must be designed to ensure public safety. Hydrogen gas storage tanks pressurized to 700 *bar*, or cryo-compressed to 350 *bar* will be used to achieve driving ranges on-par with ICE technology, according to *Boeriu* (2015) at BMW. Hydrogen storage materials offer an alternative to ultra high pressure systems, but suffer from worse gravimetric energy density. PEM fuel cells are also very sensitive to contaminants in the hydrogen supply, and often require additional purification for hydrogen produced from hydrocarbons. In addition to the carbon support susceptibility already mentioned (pg. 7), another serious problem affecting PEM fuel cell durability is PFSA membrane degradation which is mostly due to hydrogen peroxide, a by-product of the oxygen reduction on the cathode. All these aspects are areas of active hydrogen fuel cell research.

The platinum requirement is also problematic because of its scarcity and cost, but great strides have been made in this regard. The least disruptive approach would be to achieve a Pt requirement described by researchers at GM:

> "The future prices of platinum group metals (PGMs) cannot be accurately predicted; therefore, to ensure that the fuel cell garners a nontrivial place in the automotive market, it seems advisable to target total PGM costs no higher than those needed for catalytic converters for advanced internal combustion engines meeting ever-tighter efficiency and emissions standards." –*Wagner et al.* (2010)

The total PGM cost referred to in the above quotation works out to about $212 USD per vehicle, and this translates to a cap of about 4.4 g Pt per vehicle, based on 2013 data.[2] A cost analysis by *Spendelow and Marcinkoski* (2014) for USDOE, which is based on actual state-of-the-art data, assumes 16.8 g Pt will be required for a modest (80 kW_{net}) vehicle system. Even though this is about four times higher than the non-disruptive target, it may be acceptable to auto manufacturers, provided Pt prices do not skyrocket. For instance, the latest fuel cell vehicle from Toyota contains about 30 g Pt in the stack, which is down from 100 g for initial prototypes (*Shirouzu et al.*, 2014). So what is this state-of-the-art technology used in USDOE's financial model? It is the previously mentioned (pg. 1 and 7) organic catalyst support invented and manufactured by 3M Inc. This unique catalyst support material is described in Section 2.2. It is now prudent to re-examine Figure 1.5 which will provide starting points to cover the basics of fuel cell electrochemistry.

---

[2] From *Cowley* (2013), global autocatalyst consumption was $24.6Mg_{Rh} + 97.2Mg_{Pt} + 217Mg_{Pd} = 339Mg_{TotPGM}$, and to find the weighted price for autocatalyst PGM: $24.6Mg_{Rh}/339Mg_{TotPGM} * \$3.28g_{Rh}^{-1} + 97.2Mg_{Pt}/339Mg_{TotPGM} * \$48.23g_{Pt}^{-1} + 217Mg_{Pd}/339Mg_{TotPGM} * \$23.47g_{Pd}^{-1} = \$29.1g_{TotPGM}^{-1}$. From *Loferski* (2015), USA autocatalyst demand/consumption for 2013 was: $5,650kg_{Rh} + 19,800kg_{Pt} + 55,200kg_{Pd} = 80,650kg_{TotPGM}$ (Rh estimated by assuming USA accounts for 23% of global autocatalyst consumption, which is based on USA Pt/Pd consumption divided by global consumption data from *Cowley* (2013).) From *OICA* (2013), there were 11,066,432 car and commercial vehicles produced in the USA. Therefore: $80,650,000g_{TotPGM}/11,066,432 * \$29.1g_{TotPGM}^{-1} = \$212/vehicle$, divided by the price of Pt ($\$48.23g_{Pt}^{-1}$) is $4.4g_{Pt}/vehicle$.

1.3 Fuel Cell Electrochemistry

1.3.1 Equilibrium Potential

A good starting point for any research concerning energy efficiency is the theoretical maximum, indicated in Figure 1.5 as the theoretical potential of 1.23 V. Figure 1.5 shows the maximum cell voltage is slightly lowered to ~1.2 V by practical operating temperature and reactant pressures. Where do these numbers come from? The overall reaction of hydrogen gas and oxygen gas at standard conditions is:

$$\tfrac{1}{2}\mathrm{O_2(g)} + \mathrm{H_2(g)} \longrightarrow \mathrm{H_2O(l)} \quad \Delta_{\mathrm{rxn}}\bar{g}^\circ = -237.2\ kJ\,mol^{-1} \tag{1.1}$$

where $\Delta_{\mathrm{rxn}}\bar{g}^\circ$ is the molar specific Gibbs reaction energy at standard conditions.[3] The electrical potential difference corresponding to a Gibbs energy is given by:

$$E = \frac{-\Delta\bar{g}}{nF} \tag{1.2}$$

where $\Delta\bar{g}$ is the molar specific Gibbs energy, E is the electrical potential difference, n is the number of electrons transferred in the electrochemical half-reaction considered for the electrode, and F is Faraday's constant (96485 $C\,mol^{-1}$). De-constructing reaction 1.1 into the electrochemical half reactions on a PEM fuel cell anode and cathode gives:

$$\text{anode:} \qquad \mathrm{H_2(g)} \longrightarrow 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \tag{1.3}$$

$$\text{cathode:} \qquad \tfrac{1}{2}\mathrm{O_2(g)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2O} \tag{1.4}$$

It is clear that two electrons are transferred, hence the maximum voltage a hydrogen fuel cell should provide at standard conditions can be calculated:

$$\frac{-(-237,200\ J\,mol^{-1})}{2 * 96485\ C\,mol^{-1}} = 1.229\ V \tag{1.5}$$

---

[3] A method for determining the $\Delta_{\mathrm{rxn}}\bar{g}^\circ$ should be found in most physical chemistry textbooks. The steps specific to reaction 1.1 can be found in Appendix 1 of *Larminie and Dicks* (2003).

A fuel cell does not operate at standard conditions. For instance, a PEM fuel cell typically operates at $80°C$. The reactant concentrations (or partial pressures) also affect the maximum voltage of a fuel cell. The effects of temperature and pressures on the maximum, or equilibrium, potential of a fuel cell can be quantitatively determined according to a modified form of Nernst equation (*O'Hayre et al.*, 2009), which for reaction 1.1, is:

$$E_{eq} = E^{\circ}_{eq} + \frac{\Delta_{\mathrm{rxn}}\bar{s}^{\circ}}{nF}(T - 298) + \frac{\Re T}{2F} \ln\left(\frac{P_{H_2}\, P^{1/2}_{O_2}}{P_{H_2O}}\right) \tag{1.6}$$

where E_{eq} is the fuel cell equilibrium potential, E°_{eq} is the fuel cell equilibrium potential at standard conditions, $\Delta_{\mathrm{rxn}}\bar{s}^{\circ}$ is the molar specific reaction entropy at standard conditions ($44.34\ J\,mol^{-1}\,K^{-1}$)[4], $\Re$ is the universal gas constant, T is the temperature (in Kelvin), F is Faraday's constant ($96485\ C\,mol^{-1}$), and P is the partial pressure[5] in *atm* of hydrogen, oxygen, and water vapour. If liquid water is produced, as would be the case for a fuel cell operating at $80°C$, P_{H_2O} is 1. The exponents in the logarithm argument are taken from the stoichiometric factors in reaction 1.1. Note that the equilibrium potential is based only on thermodynamics and calorimetric data of hydrogen, oxygen, and water. Dissolved hydrogen gas in the PFSA membrane migrates over to the cathode; this effect is called hydrogen crossover. Therefore, a fuel cell's practical operating voltage at zero load is also affected (lowered) due to the presence of a small amount of hydrogen gas on the cathode. Further lowering of the voltage is due to activation polarization and mass transport limitations.

1.3.2 Activation Polarization

1.3.2.1 Electrochemical Kinetics: Theoretical Background

Electrochemical kinetics involving a single step reaction is described by:

$$i = i_o\left(e^{\frac{(1-\beta)nF\eta}{RT}} - e^{\frac{-\beta nF\eta}{RT}}\right) \tag{1.7}$$

where i is the areal current density, β is the symmetry parameter between 0 and 1 (almost always 0.5), η is the over-potential (deviation away from E_{eq}), and i_o is the exchange current

---

[4] Calculating $\Delta_{\mathrm{rxn}}\bar{s}^{\circ}$ is a preliminary step for determining $\Delta_{\mathrm{rxn}}\bar{g}^{\circ}$. See footnote 3

[5] The Nernst equation is defined in terms of 'activities', but concentrations or partial pressures often suffice.

density, which represents the forward (reduction or cathodic) or backward (oxidation or anodic) current of the half reaction at the equilibrium potential. Electrochemical kinetics involving multi-step reactions, where one of the steps is significantly slower than the rest, is described by the Butler-Volmer[6] Equation:

$$i = i_o\left(e^{\frac{\alpha_a F\eta}{RT}} - e^{\frac{-\alpha_c F\eta}{RT}}\right) \tag{1.8}$$

where α_a is the anodic transfer coefficient, and α_c is the cathodic transfer coefficient. The transfer coefficients are determined by:

$$\text{anodic (oxidaiton):} \qquad \alpha_a = \frac{n_t - s}{\nu} - r\beta \tag{1.9}$$

$$\text{cathodic (recution):} \qquad \alpha_c = \frac{s}{\nu} + r\beta \tag{1.10}$$

where s is the total number of electrons transferred before the rate determining step (in the cathodic direction), n_t is the total number of electrons transferred in the overall electrode reaction, r is the number of electrons transferred in the rate determining step, v is the stoichiometric number for the rate determining step (i.e. the number of times the rate determining step has to occur to make the whole mechanism occur once). For more explanation of the transfer coefficient formulae (Equations 1.9 and 1.10), see *Bockris and Nagy* (1973).

When only considering one reaction direction, as is the case for work in this thesis, Equation 1.8 can be simplified to the Tafel equation:

$$\eta = b\log\left(\frac{i}{i_o}\right) \tag{1.11}$$

where b is known as the Tafel slope. Accordingly, theoretical Tafel slopes for multi-step reactions can calculated:

$$\text{anodic:} \qquad b_a = \frac{RT}{\log(e)\alpha_a F} \tag{1.12}$$

$$\text{cathodic:} \qquad b_c = -\frac{RT}{\log(e)\alpha_c F} \tag{1.13}$$

---

[6] Despite being named as such in in English language electrochemistry texts, British electrochemist John A. V. Butler did not directly contribute to the development of the equation (*de Levie* (2000) and *Inzelt* (2011)).

where b_a is the anodic Tafel slope, and b_c is the cathodic Tafel slope. Cathodic Tafel slopes are negative by IUPAC convention for electrochemical current, but are commonly reported as positive. Commonly observed theoretical Tafel slopes at room temperature, with their respective approximate namesakes, are 118.3 (120) $mV\,decade^{-1}$, 59.1 (60) $mV\,decade^{-1}$, 39.4 (40) $mV\,decade^{-1}$, and 29.6 (30) $mV\,decade^{-1}$.

Exchange current density (i_o) should not be regarded as an intrinsic materials property which could be determined from first principles. It is a property of the temperature, the electrode and the concentrations[7] of products and reactants in solution. For gas electrodes like the hydrogen or oxygen electrode, if the dissolved gas is always held at saturation concentration with purging, i_o is a property of the temperature, catalyst material, and catalytic surface area. There is an intrinsic materials property that describes catalytic activity, known as turn-over frequency, which would be proportional to i_o (at defined reactant and product concentrations and temperature) divided by the number of 'active sites' (i.e. atoms, or groups of atoms which catalyse the reaction). Therefore i_o's can be reported normalized to some parameter which estimates the number of active sites, which is often the catalytically active surface area.

The only two parameters which relate to material properties appear in the Tafel equation and the Butler-Volmer equation, are the Tafel slope and the exchange current density. These two key parameters describe the properties of a catalyst material for a given electrocatalytic reaction. The Tafel slope relates to the reaction mechanism, and the exchange current density can be viewed as a potential independent descriptor of activity. In light of catalysis, what is desirable with regards to these two parameters? Primarily a high exchange current density and low Tafel slope, but it depends on the application considerations such as a maximum allowable potential or current. Figure 1.6 is a Tafel style plot (current on log-scale abscissa) which shows two catalysts: (a) has a higher i_o and Tafel slope than (b). It is plain to see that at a current or potential higher than the intersection of the two lines, the (b) catalyst with the lower i_o, actually becomes more energy efficient. Therefore, at a current and potential above the intersection point, (b) is the more active catalyst, but for values of current and potential below the intersection point, (a) is the more active catalyst.

---

[7] As per footnote 5 (pg. 12), it should read activity instead of concentration, but this terminology, is avoided so as to not clash with activity used in the catalytic context, which is widely used throughout this report

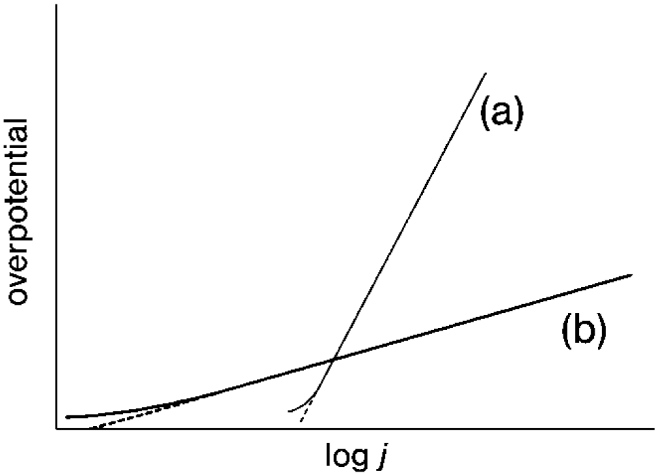


Figure 1.6: Tafel style plot of two catalysts with different exchange current densities and Tafel slopes. With Permission of John Wiley and Sons (*Guerrini and Trasatti*, 2009).

1.3.2.2 Electrochemical Kinetics for Hydrogen Fuel Cells and Electrolyzers

The H_2 and O_2 Gas Electrodes

The gas electrode reactions that pertain to fuel cells and electrolyzers are:

$$\text{hydrogen electrode:} \qquad 2\,H^+(g) + 2\,e^- \underset{\text{HOR}}{\overset{\text{HER}}{\rightleftharpoons}} H_2(aq) \qquad E^\circ_{eq} = 0\ V_{SHE} \tag{1.14}$$

$$\text{oxygen electrode:} \quad O_2(g) + 4\,H^+(aq) + 4\,e^- \underset{\text{OER}}{\overset{\text{ORR}}{\rightleftharpoons}} 2\,H_2O \quad E^\circ_{eq} = 1.229\ V_{SHE} \tag{1.15}$$

where E°_{eq} is the equilibrium potential at standard conditions, which is always vs. the standard hydrogen electrode (SHE)[8]. The forward reaction for the hydrogen electrode is the hydrogen evolution reaction (HER) and the backward reaction is the hydrogen oxidation reaction (HOR). Likewise for the oxygen electrode, the forward reaction is the oxygen reduction reaction (ORR) and the backwards reaction is the oxygen evolution reaction (OER).

The i_o for the cathodic and anodic (or forward and backward) hydrogen reactions are generally the same, but the i_o for the oxygen reactions are different. The generalized theory of electrochemical kinetics, the Butler-Volmer Equation (1.8), implies that i_o should be

---

[8] The SHE is a platinum electrode immersed in 1 [H^+] electrolyte at 25°*C* saturated with hydrogen gas at 1 *atm*.

the same for both forward and reverse reactions, but this is only if the mechanisms are symmetric. This is not the case for an oxygen gas electrode in acid, even on the same catalyst. In fact, these two reactions are extremely complicated and continue to attract careers devoted to their elucidation.

Since the invention of the PEM fuel cell by *Grove* (1842), Pt has been used as a catalyst for both the HOR on the anode and the ORR on the cathode. No other pure element has proven active or stable enough in acidic electrolyte to take the place of Pt. Pt is also an excellent catalyst for the HER in acid, but not for the OER in acid. A detailed background on OER catalysis in acid is given in Section 2.3.1.

The HOR and HER on Pt in acid is extremely fast. So fast in fact, that there are essentially no HOR activation losses from a Pt anode in a fuel cell *Sheng et al.* (2010). All the activation loss illustrated in Figure 1.5 is due to the ORR on the cathode. The ORR mechanism is complicated and was the subject of a great deal of research before significant attention was devoted to it via funding for PEM fuel cells. For instance, *Kinoshita* (1992) lists sixteen proposed ORR reaction mechanisms.

Tafel Slopes for the OER

The assignment of a specific reaction mechanism based on Tafel slope is not so simple when:

1. more than one step is rate determining (i.e. all reactions but one are NOT in quasi-equilibrium), and
2. reactions are catalytic because the coverage of catalytically active sites by intermediate species changes with the reaction rate (i.e. electrode potential).

Determining theoretical Tafel slopes for multi-step catalytic reactions (such as the ORR or OER) requires a full kinetic model, based on a particular mechanism, which uses a modified form of Equation 1.7 for each step. Exchange current density and β are missing, but the equation contains the more intrinsic standard rate constants (k°, akin to the previously mentioned turn-over frequency, pg. 14) for the reduction (forward) and oxidation (backward) reaction. Other additional and necessary constants are oxygen concentration, pH, the number of catalytic sites, and the surface coverage percentages of intermediate species. A full kinetic model avoids the so-called quasi-equilibrium assumption, which states that all but one of the reactions composing a multi-step mechanism are in equilibrium. (The quasi-equilibrium assumption leads to Equations 1.8, 1.9 and 1.10). *Marshall and Vaisson-Béthune* (2015) have implemented a full kinetic model for a commonly proposed OER mechanism (*Bockris*, 1956) with some interesting results.[9] Figure 1.7, taken from their study, shows that five Tafel slopes are attainable by exploring values for the second and third equilibrium constants (used to determine surface coverages of adsorbed participating species) of a three step reaction.

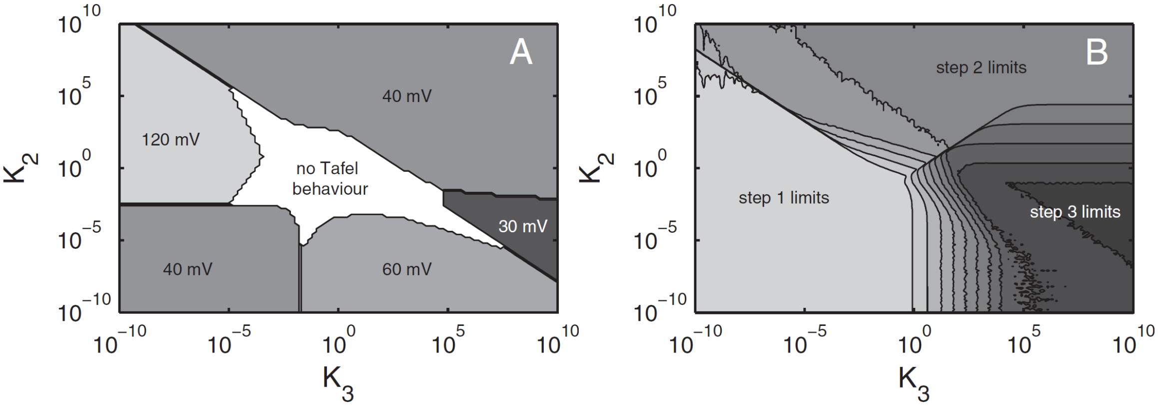


Figure 1.7: Tafel slopes (**A**) and rate-determining-step (**B**) for a full kinetic model, with coverage of active sites considered for the OER electrochemical oxide mechanism (*Bockris*, 1956) within a space of values for the second and third equilibrium constants (K_2 and K_3). Other parameters are $k^{\circ}_{\mathrm{S+H_2O \rightarrow S–OH+H^+ +e^-}} = 10\ L\,s^{-1} mol^{-1}$, $k^{\circ}_{\mathrm{S–OH \rightarrow S–O+H^+ +e^-}} = 10\ s^{-1}$, $k^{\circ}_{\mathrm{S–O \rightarrow S+O_2}} = 100\ s^{-1}$, $T = 298.15K$, $C_{O_2} = 1\ bar$, and $pH = 0$ (where k°'s are standard rate constants, and C_{O_2} is O_2 partial pressure. Reprinted from Electrochemistry Communications, 61, Marshall, A. T. & Vaisson-Bethune, L., Avoid the Quasi-equilibrium Assumption When Evaluating the Electrocatalytic Oxygen Evolution Reaction Mechanism by Tafel Slope Analysis, pg. 25, Copyright (2015) with permission from Elsevier (*Marshall and Vaisson-Béthune*, 2015).

The model predicts some interesting things, clearly visible in Figure 1.7:

1. non-Tafel behaviour, particularly when none of the reaction steps are rate limiting (Tafel behaviour is defined as a slope remaining the same (within ± 1 mV) for approximately 1 decade in current density.)
2. multiple Tafel slopes for a quasi-equilibrium scenario (there are three possible Tafel slopes (120, 40, and 60 $mV\,dec^{-1}$) when reaction (step) 1 is limiting,
3. Tafel behaviour when only one step is in quasi-equilibrium (e.g. 60 $mV\,dec^{-1}$ straddles the space where both step 1 and step 3 are rate limiting).

---

[9] *Shinagawa et al.* (2015) have written a very similar, but less concise study.

Furthermore, many model scenarios (not shown in Figure 1.7) predict two Tafel slopes, one for low current densities and one for high, with non-Tafel behaviour in between. Figure 1.7 shows only the Tafel slopes at low current densities. Thus the emergence of Tafel behaviour for electrocatalytic multi-step reactions where changing coverage is considered, is not straightforward. Therefore, *Marshall and Vaisson-Béthune* (2015) criticize those who use experimental Tafel slopes to justify inventing new multi-step reaction mechanisms[10] based on the quasi-equilibrium assumption. The lesson from their work is any discussion on how an experimental Tafel slope relates to a proposed catalytic multi-step mechanism should consider a full kinetic model (i.e. one that considers changing coverage) of the proposed mechanism. For this reason, consideration and discussion of reaction mechanisms for the ORR and OER are beyond the scope of this thesis due to the time and effort required in implementing and analyzing full kinetic models.

Exchange Current Density and the ORR

The exchange current density (i_o) for a fuel cell catalyst of interest is vary rarely reported in the fuel cell literature. Instead, catalysts are compared with I-V curves, Tafel style plots (Figure 1.6), and current at a specified potential (or vice-versa). Given the exponential relationship of over-potential to current, small ($< 10\%$) experimental errors in the Tafel slope could lead to large (order of magnitude) scale variation in i_o because the extrapolation must extend ~$300 mV$ beyond the measured data. It is probably better to base a comparative performance metric on actual data, rather than an extrapolated parameter.

1.3.3 Electrochemical Surface Reactions on Pt

Determining the two fundamental electrochemical properties (Tafel Slope and exchange current density) of a Pt-based fuel cell catalyst is a numerically intensive multistep process which is explained in Chapter 3. Some of the knowledge relevant to that process, the surface reactions on Pt, is presented here because it is also relevant to certain sections in Chapter 2. Figure 1.8 shows a cyclic voltammogram (CV) of polycrystalline Pt measured with the rotating disk electrode (RDE) (explained in Section 3.1.2).

---

[10] For a summary of commonly proposed OER mechanisms based on the quasi-equilibrium assumption, see Tables 2-1 and 2-2 in *Thuv* (2015)

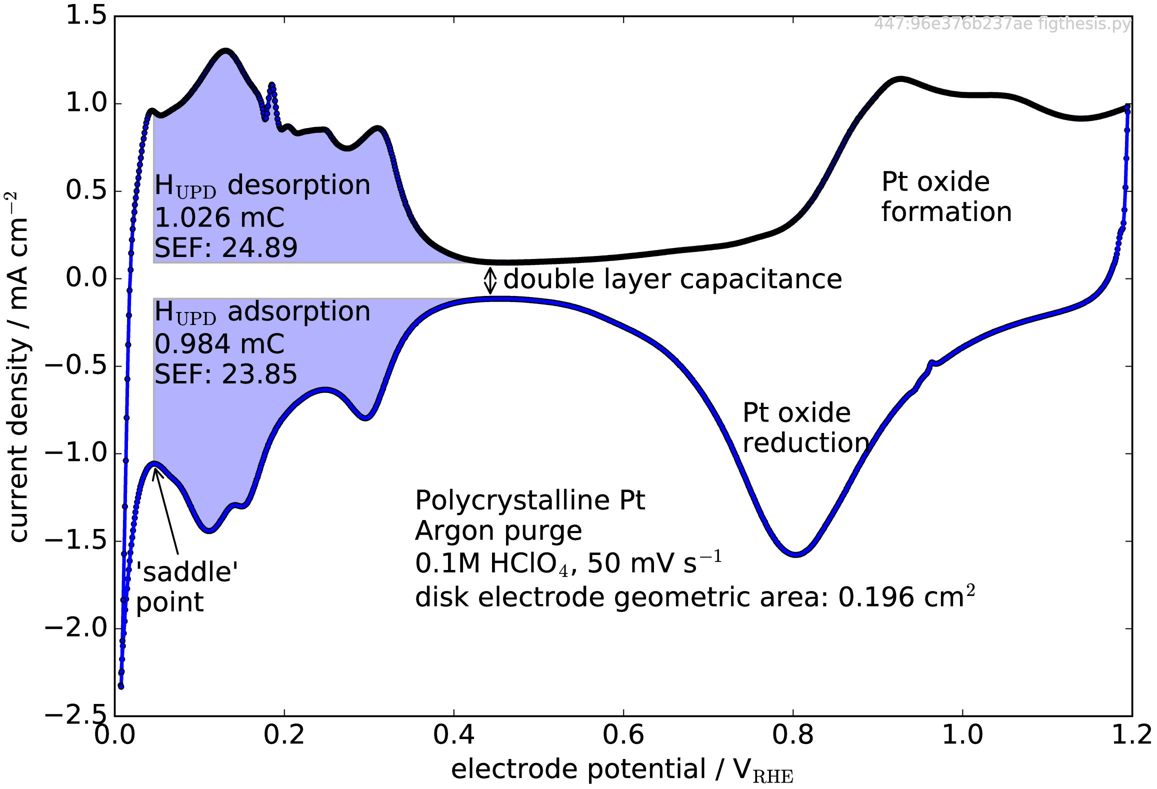


Figure 1.8: CV of polycrystalline Pt in acid, with important features labelled.

It is well known that surface reactions on Pt in either acid or alkaline electrolyte are responsible for the voltammetric features, or ‘waves’ seen in the CV. There is a potential range, ~0.35 to 0.5 V vs. the reversible hydrogen electrode (RHE)[11], in which no surface reactions occur. The current in this range is due only to charging/discharging of the electrochemical double-layer[12]. In the lower potential range (0 to 0.4 V_{RHE}), the cathodic (negative) current comes from the underpotential deposition of hydrogen on the metallic Pt surface. It is widely accepted that each surface metal atom can adsorb one hydrogen atom. For example

---

[11] The RHE is a reference electrode that is similar to the SHE, except it is immersed in the same electrolyte as the cell. Therefore the potential vs. RHE deviates from that vs. SHE according to the Nerstian response due to pH, i.e. increasing it by $\frac{R(298\mathrm{K})}{\log e\, F}$ ($e = 2.71828...$) at room temperature for every integer increase in pH ($V_{RHE} = V_{SHE} + 0.059 * pH$). Reporting vs. the RHE, even when a different reference electrode is actually used, is very common because with the RHE, the thermodynamic limits of water stability will always be 0 and 1.23 V_{RHE} regardless of the electrolyte pH. For this reason, the RHE is sometimes called “pH independent” (for example, by *van der Vliet et al.* (2012)), though others have called the SHE “pH independent” (*Burke and Lyons*, 1986). It depends on one’s perspective.

[12] The term “double-layer” was given by *Helmholtz* (1879) for the hypothetical arrangement of ions and polar solvent molecules adjacent to an electrode surface. The polarization of the double-layer results in a current and enables change transfer into or out of an electrode without chemical oxidation or reduction reactions, known as “Faradaic current” An IUPAC document (*Meites et al.*, 1985) contains definitions of these and other types of current in electrochemistry.

Bett et al. (1973) verified a unity ratio for underpotential deposited hydrogen (H_{UPD}) desorption atoms to surface Pt atoms. This H_{UPD} could be thought of as a precursor step to the evolution of hydrogen. H_{UPD} adsorbs on the negative-going sweep (cathodic/negative current) and desorbs on the positive-going (anodic/positive current) sweep. For a detailed discussion on the physical interpretation of the peaks within the H_{UPD} region, see *Solla-Gullón et al.* (2013).

The positive area under the H_{UPD} feature or negative area above the H_{UPD} feature has units of charge when divided by the sweep rate and is proportional to the atomically rough Pt surface area if the charge due to the double-layer capacitance is subtracted. The H_{UPD} adsorption area (negative) is usually avoided because as the potential nears 0 V_{RHE}, it appears as though hydrogen evolution starts earlier than 0 V_{RHE}. This extra current leads to a higher charge than that determined by the H_{UPD} desorption area. To obtain a value for the Pt surface area, first the charge due to double-layer charging must be excluded. A horizontal line corresponding to the minimum anodic (positive) current in the double-layer region serves as the bottom delimitation for determining the area. Then the Pt surface area can be obtained by dividing the H_{UPD} desorption charge by the widely accepted constant for polycrystalline Pt, 210 $\mu C\, cm^{-2}$ (originally determined by Frumkin in *Delahay and Tobias* (1963)). This is called the electrochemical surface area (ECSA). In some studies, the method is refined to also include a left vertical delimitation on the area, corresponding to the potential at the maximum cathodic (negative) current on the saddle shape in the H_{UPD} adsorption region, which forms just before the potential scan reverses direction (*Fournier et al.* (1997) and *Binninger et al.* (2014)). With this method, the area formed within the bounds of the H_{UPD} desorption area agrees better with the area formed within the bounds of the H_{UPD} adsorption area. An area ratio called the surface enhancement factor (SEF) is also determined with the ECSA, which relates the atomic Pt surface area to the geometric surface area of the disk electrode. An equation expressing this relation (3.3) is presented later in Chapter 3 (pg. 96). Figure 1.8 shows the charges and SEFs for both H_{UPD} adsorption and desorption. The other surface reaction is Pt oxide formation and reduction. The review by *Conway* (1995) presents the details and intricacies of the oxidation and reduction of Pt by oxygen species in great detail. Figure 1.8 shows where H_{UPD} is adsorbed and desorbed, and where Pt oxide is formed and reduced.

1.4 Structure of this Thesis

This chapter provided only the basics of PEM fuel cells and the basic theory for fuel cell electrochemistry. An outline of the remaining chapters is provided below.

Chapter 2 contains three main sections of knowledge relevant to this project: 1) the properties and degradation mechanisms of fuel cell materials, 2) a detailed description of 3M's nanostructured thin film (NSTF) catalyst support, and 3) the properties of OER-in-acid catalysts Ru and Ir. This third section contains original data and attempts to answer a question from the *Project Motivation* section: "How will Ru and Ir behave on NSTF?" A fourth, smaller, section adresses the uniqueness of this project, and clarifies a characterization related consequence of using the RDE to test catalysts supported on NSTF.

Chapter 3 explains how catalyst samples were synthesized, measured, and numerically analyzed. In addition to the normal descriptions of the instrumentation and data processing methods used, rationale is given for the use of the RDE instead of the fuel cell, and for the design of the durability testing protocol. Not all numerical data processing methods are covered in this chapter; methods specific to Chapter 4 and 5 are described in the respective chapters.

Chapter 4 shows the results of a study which was published in The Journal of the Electrochemical Society (*Crowtz et al.*, 2014). This study followed previous Dahn Lab fuel cell durability studies (*Stevens et al.* (2010) and *Hatchard et al.* (2011)) and used a novel constant current pulse durability testing protocol developed at the Dahn Lab (*Stevens et al.*, 2013). Part of the dataset in Chapter 4 (the OER portion, no ORR analysis) appeared earlier in *Harlow et al.* (2013). Despite it's position as the fifth published study from the USDOE/3M durability contract, it should still be viewed as a learning experience, because there were problems: there was a known issue with glassy carbon disk corrosion, and some data analysis shortcomings were found after its publication. It should be seen as a first attempt at getting the USDOE/3M durability project done properly. Many aspects of the study not included in *Crowtz et al.* (2014) are also discussed in this chapter.

Chapter 5 is the principle result of the project; a screening study of over 50 different compositions of Ir and Ru on Pt.

Chapter 6 (the conclusion) lists the important lessons (what should be done differently) and makes recommendations for the continuation of the work.

Chapter 2

Fuel Cell Durability, 3M's Nanostructured Thin Film and Electrochemistry of Ir and Ru

This chapter provides relevant background information on the chemical and electrochemical mechanisms which determine the lifetime of a fuel cell, 3M's catalyst support material, and some relevant electrochemical properties of Pt, Ir and Ru in acid electrolyte. There are three important causes of fuel cell degradation which are beyond the scope of this report and will not be discussed:

1. The PFSA membrane can be degraded due to attack by free radicals probably originating from electrochemically generated hydrogen peroxide (*Healy et al.*, 2005).
2. Fuel impurities can 'poison' Pt (i.e., absorb and block catalysis) in the anode (*Wood et al.*, 2007).
3. Air contaminants can poison, and in the case of chloride or other complexing agents, promote corrosion of, Pt-based catalysts in the cathode (*Wood et al.*, 2007).

2.1 The Principle Causes of Fuel Cell Catalyst Degradation

As mentioned earlier (pg. 6), the combination of PFSA and Pt\C was first developed by *Raistrick* (1986) and improved by *Wilson and Gottesfeld* (1992), who are generally credited for ushering in the age of the PEM fuel cell with their MEA made by casting a catalyst ink. The Nafion imbibed Pt\C catalyst material was synonymous with PEM fuel cells for over a decade, with much research devoted to improving the Pt utilization efficiency. Much of this progress is summarized in the highly cited review paper by *Gasteiger et al.* (2005). As it turned out, 2005 was an important year for PEM fuel cell research, because of the publication of three other highly cited studies that changed perspectives on the de-facto Nafion plus Pt\C catalyst layer material. The three studies, along with prior and follow-up research supporting their conclusions, are respectively presented in the next three sections.

2.1.1 Pt Instability

Ferreira et al. (2005) showed unambiguously that Pt in a fuel cell is subject to dissolution and precipitation via two mechanisms: Ostwald ripening and reduction of soluble Pt species with H_2 in the ionomer. Ostwald ripening occurs on the nanometer scale and leads to the coarsening of Pt particles in the catalyst layer. Migration of soluble Pt species also occurs on the micrometer scale and results in the precipitation of metallic Pt in both the cathode ionomer phase and the membrane, depending on H_2 crossover flux. Pt precipitated in this way is electrically disconnected from the electrode and therefore lost.

2.1.1.1 Thermodynamic Considerations of Pt Stability

Pt is considered to be a noble metal, completely resistant to corrosion. Pt was known to be only soluble in a solution composed of both a strong complexing agent and oxidizing agent. Aqua regia, a 3:1 mixture of concentrated hydrochloric acid (complexing agent) and concentrated nitric acid (oxidizing agent), is probably the best example of a reagent known for dissolving noble metals such as Pt. Pt was also considered to be electrochemically stable except in a narrow range of high potential (~1.0 V_{SHE}) and low pH (0 to 1), where Pt may be susceptible to electrochemical dissolution (*Pourbaix*, 1966). Figure 2.1 shows a *Pourbaix* (1945) diagram for Pt. Figure 2.1a) shows all the substances considered for the Pt-water system and their regions of predominance. Figure 2.1b) shows a small region around 1.0 V and pH $= -1$ in which Pt will corrode because Pt^{2+} ($\geq 10^{-6}$ M) is thermodynamically favourable. Pourbaix diagrams are predictors of thermodynamic stability only. They gives no indication of kinetics, i.e. how fast a substance will become predominant given a change in pH or potential. *Pourbaix et al.* (1959b) constructed Figure 2.1 using calorimetrically determined Gibbs energies, and an estimation of the Gibbs energy for Pt^{2+} provided by *Latimer* (1952). Also seen in Figure 2.1 are lots of question marks. Pourbaix expresses a lot of uncertainty about:

1. The existence of soluble Pt ions: $Pt(OH)^{3+}$, PtO^{2+}, ${PtO_4}^{2-}$ and ${PtO_3}^{2-}$. These species were not considered in the calculations but were "shown in the diagram in their approximate positions" –*Pourbaix et al.* (1959b). It is not clear how these positions were deduced.
2. The positions of the lines for enclosing $PtO_2 \cdot xH_2O$ because "the exact amount of

> hydration is unknown and thus their thermodynamic properties are known very approximately.” –*Pourbaix et al.* (1959b)

He also doubts the existence of Pt^{2+}, (citing Marie in *Pourbaix* (1966)), hence his label “CORROSION ?” in Figure 2.1b). He also emphasized that the nature of dissolved Pt is to be in a complexed form (Charlot in *Pourbaix* (1966)), and furthermore, the dissolved species can be more complexed than the ionic species of the salt (Pascal in *Pourbaix* (1966)).

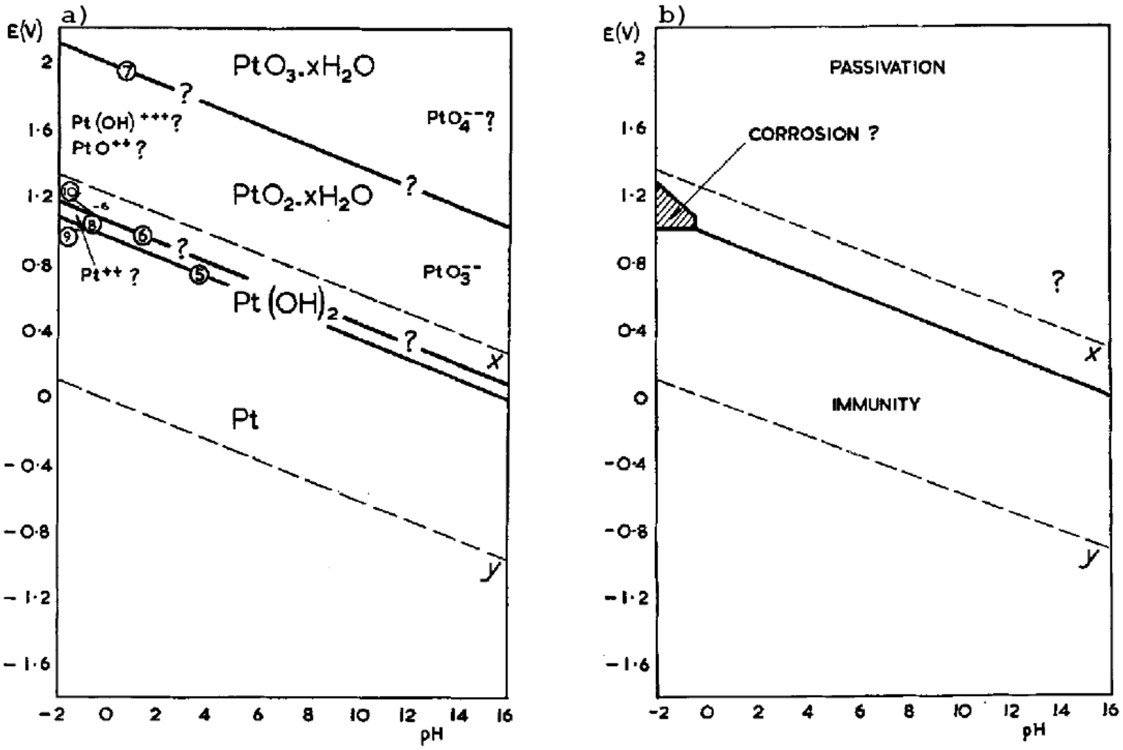


Figure 2.1: The potential-pH, or Pourbaix, diagram for Pt. Lines enclosing the shaded region marked “CORROSION ?” delineate the predominance of $\geq 10^{-6}$ *M* Pt^{2+}. Dotted lines labelled “x” and “y” enclose the stability region for water. Potentials are vs. SHE. Published by Johnson Matthey, reproduced under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (*Pourbaix et al.*, 1959b).

Figure 2.2 shows a Pourbaix diagram by *Lee* (1981) calculated with a Gibbs formation energy for Pt^{2+} from *Wagman et al.* (1969). The region of instability ($Pt^{2+} \geq 10^{-6}M$) is larger than for Pourbaix’s original plot. Pourbaix suggested Pt will corrode, but cast plenty of doubt. Lee’s diagram suggested Pt may be more susceptible to corrosion than previously thought. Other studies, some of which are cited by *Ferreira et al.* (2005), experimentally demonstrated mild electrochemical instability of Pt within the region noted in the Pourbaix diagram. For instance, Figure 2.3 shows how the equilibrium concentrations of Pt vary with potential from several studies.

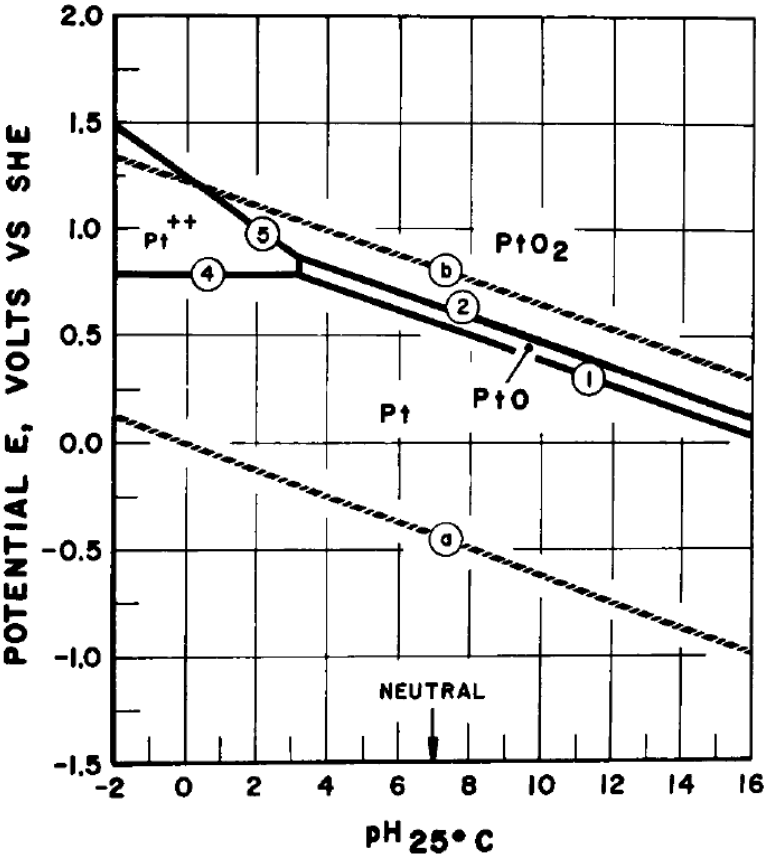
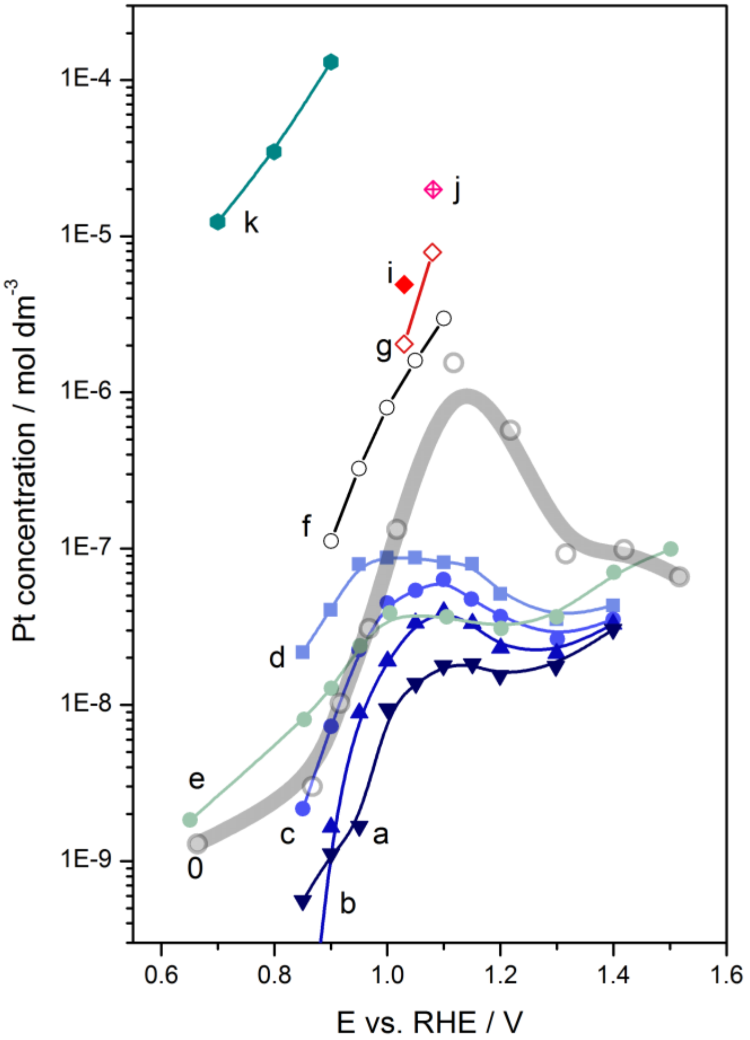


Figure 2.2: Pourbaix diagram for Pt. Lines enclosing Pt^{2+} delineate the predominance of $> 10^{-6}$ *M* Pt^{2+}. Reproduced with permission from NACE International, Houston, TX. All rights reserved, ©NACE International 1981. Lee, J. B., Elevated Temperature Potential-pH Diagrams for the Cr-H_2O, Ti-H_2O, Mo-H_2O, and Pt-H_2O Systems, Corrosion 37, 8, 1981 (*Lee*, 1981).

Given all the prior art on Pt, what *Ferreira et al.* (2005) showed should come as no surprise. However, they conclusively demonstrated the mobility of Pt in an operating fuel cell, and the seriousness of the problem to the fuel cell community. But what *Ferreira et al.* (2005) did not show is the mechanism by which the dissolution occurs. It would take the work of *Topalov et al.* (2012) working under Karl Mayrhofer at the Max Planck Institute for Iron Research to fully elucidate the nature of electrochemical Pt corrosion. Details of Topalov's studies are subsequently presented.



curve	*Electrolyte (M,type)*	*Pt type*	*Particle size (nm)*	*T (°C)*
0	0.57 $HClO_4$	Pt poly	N/A	room
a	"	Pt\C	12.7	"
b	"	"	7.1	"
c	"	"	3.2	"
d	"	"	1.9	"
e	"	"	2.6	"
f	0.5 H_2SO_4	"	2-3	80
g	1.0 H_2SO_4	Pt black	~10	23
i	"	"	"	76
j	"	"	"	51
k	19 H_3PO_4	Pt\C	4-5	206

Figure 2.3: The equilibrium Pt concentration dependence on potential in acidic electrolyte in contact with Pt nano particles of various sizes (lines ‘a’ though ‘k’) and bulk polycrystalline Pt (line ‘0’) at various temperatures in various electrolytes. Reprinted from Nano Energy, 29, Cherevko, S., Kulyk, N. & Mayrhofer, K. J. J., Durability of Platinum-Based Fuel Cell Electrocatalysts: Dissolution of Bulk and Nanoscale Platinum, pgs. 275-298, Copyright (2016) with permission from Elsevier (*Cherevko et al.*, 2016d).

2.1.1.2 The Nature of Electrochemical Pt Dissolution

Many studies on electrochemical Pt dissolution revealed that a changing potential, as opposed to a static potential, accelerated the dissolution process. The most extreme example is from *Benke and Gnot* (2002) who obtained a considerable 11 $g\,L^{-1}$ of Pt via electrochemical dissolution and proposed it as a viable and faster method of Pt salt production from solid Pt metal. Most studies probed minute concentrations of electrochemically dissolved Pt. The exact nature of this dissolution was speculated upon but remained a mystery. There was also disagreement among the early studies as to the effect of potential scan direction, and the resulting oxidation state of the solvated Pt. The mystery of dynamic dissolution was only recently shown by Angel *Topalov* (2014) in his PhD research. His lab's innovation of a flow-through electrochemical cell coupled to an inductively coupled plasma mass spectrometer (ICP-MS) (*Klemm et al.*, 2011) revealed in real time how dissolving Pt responds to changes in potential. The profound importance of this new technique to the fuel cell community was emphasized by *Schmickler* (2013) in an article devoted entirely to the implications of Topalov's first publication (*Topalov et al.*, 2012). Although Topalov did not speculate on the nature of dissolved Pt species (e.g. oxidation state, complexed or not), his work is of tremendous importance to PEM fuel cell research and therefore is briefly described here.

Figure 2.4 shows an ICP-MS response to an applied potential cycling regime, where the lower potential is 0.1 V_{RHE} and the upper potential increases by 50 mV every second cycle from 1.0 to 1.8 V_{RHE}. This figure shows a complete lack of dissolution when the upper potential is below 1.1 V_{RHE}. Each potential cycle corresponds to two spikes in dissolved Pt, the first much smaller than the second. These two dissolution events correspond to the anodic up-sweep and cathodic down-sweep, respectively. Therefore Topalov described the Pt loss in the first peak as "anodic dissolution" and in the second peak as "cathodic dissolution".

Figure 2.5 shows an ICP-MS response to an applied potential cycling regime, where the upper potential was constantly 1.55 V_{RHE} and the lower potential steadily increases from 0.05 V_{RHE} to 1.05 V_{RHE} and back. Figure 2.5 shows a complete lack of dissolution when the lower potential reaches 1.05 V_{RHE}. Figures 2.4 and 2.5 show that platinum dissolution is a dynamic process, i.e. it is due to a changing potential. More specifically, when taken in the context of knowledge about Pt surface electrochemistry (which can be garnered by

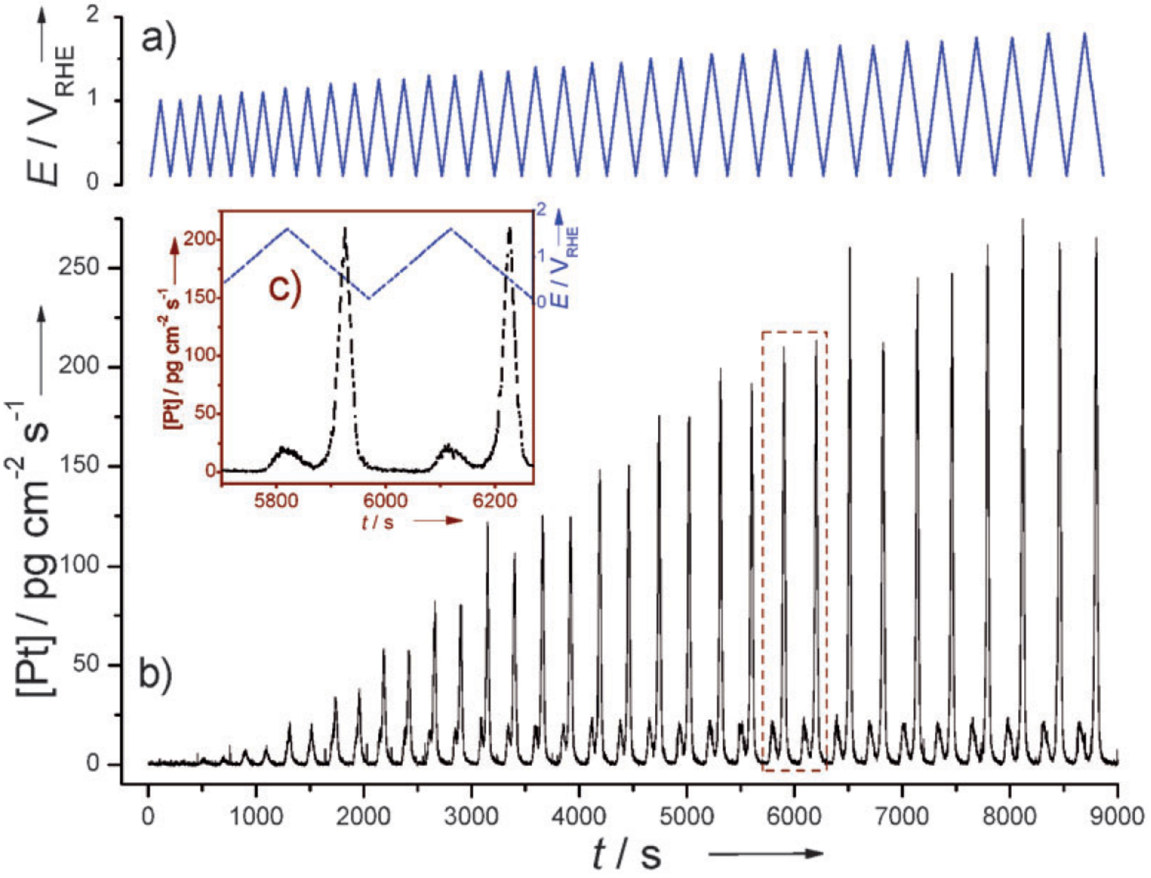


Figure 2.4: An in-situ, real-time ICP-MS response to electrochemical control of a Pt working electrode in a three-electrode flow-through cell with a carbon counter electrode: **a)** the potential of the Pt electrode (10 $mV\ s^{-1}$), and **b)** the Pt concentration in the electrolyte stream which is fed directly into the ICP-MS. Electrolyte: 0.1 M $HClO_4$. With Permission of John Wiley and Sons (*Topalov et al.*, 2012).

reviewing a Pt CV (see Figure 1.8, pg. 19)), Figures 2.4 and 2.5 show the dissolution occurs only in conjunction with oxidation and reduction of Pt. For instance, Figure 1.8 shows on the down (negative going) sweep of a Pt CV, oxide reduction starts at $\sim 1\ V_{RHE}$. This potential corroborates well with the lower potentials and dissolution amounts in Figure 2.5; the obvious conclusion is that there is no Pt dissolution if there is no reduction of Pt oxide to metallic Pt.

The onset potential for Pt oxide formation ($\sim 0.8\ V_{RHE}$ in Figure 1.8) does not correspond well with the upper potential for the dissolution amounts ($\sim 1\ V_{RHE}$) in Figure 2.4. Why? Also, why is there a far greater amount of Pt dissolved on the negative going potential sweep, during the a reduction of electrochemically formed Pt oxide? The most

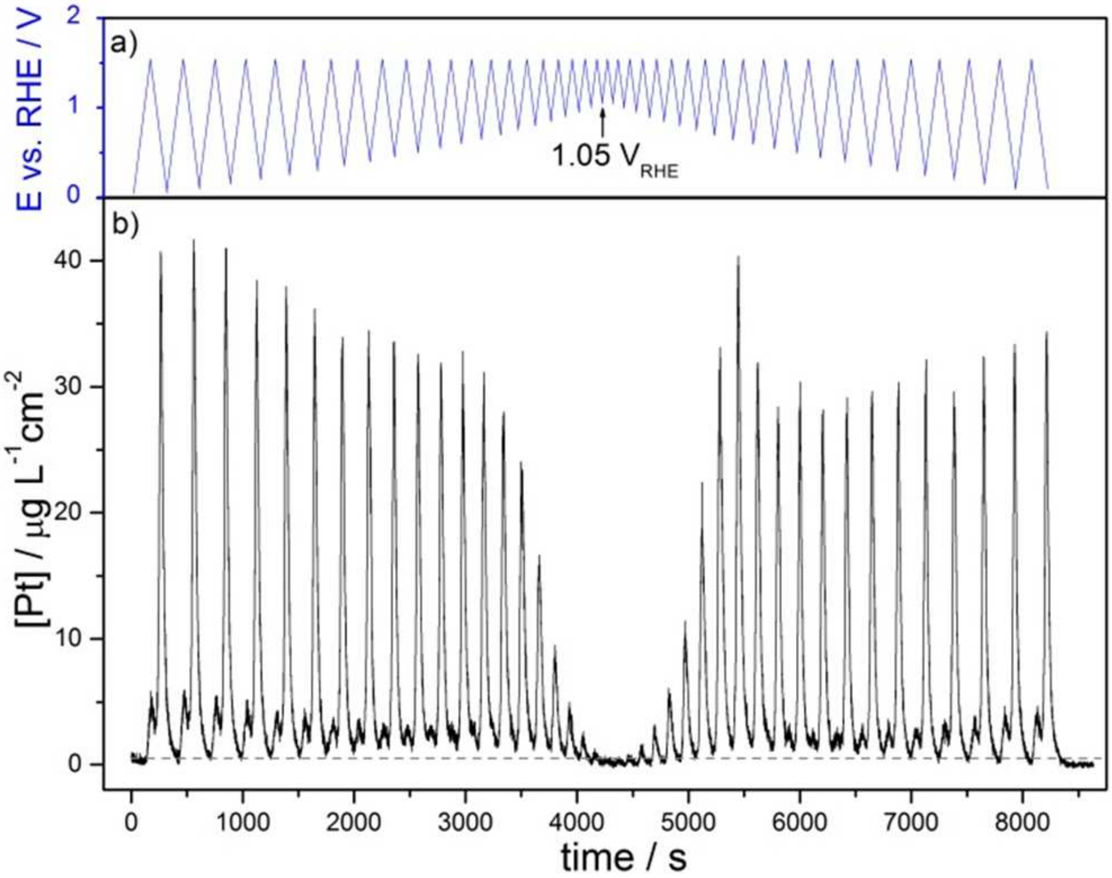


Figure 2.5: An experiment with conditions the same as Figure 2.4, with upper potential limit fixed at 1.55 V_{RHE}. Published by The Royal Society of Chemistry, reproduced under the Creative Commons Attribution 3.0 Unported Licence (*Topalov et al.*, 2013).

likely explanation for both observations lies in the repulsive interaction of chemisorbed oxygenated species (presumably OH and O) which at some critical coverage, energetically favours the oxygen in subsurface sites, a process known as place-exchange. *Topalov et al.* (2013) claims place-exchanged Pt atoms are intimately connected to the dynamic nature of Pt dissolution. Concerning the greater amount of cathodic dissolution,

> "...the amount of dissolved Pt scales ... with the amount of oxidized, but passivated (place-exchanged Pt) atoms in the initial state before a negative going scan. During the reduction of the surface those sites become exposed to the electrolyte and can then potentially be dissolved. Due to the large amount of formed place-exchanged atoms at high potentials, the cathodic dissolution rate is generally higher than the anodic one." –*Topalov et al.* (2013)

Concerning the anodic dissolution onset occurring at a higher potential than the oxide formation onset, place-exchanged Pt atoms also likely play a key role because the place-exchange process also starts at some point after the oxide formation onset, when that critical coverage of surface adsorbed oxygen species is reached. When a Pt atom exchanges sites with an oxygen species, that Pt atom is no longer protected by a passivation layer and dissolution becomes thermodynamically favourable if the potential is high enough.

Figure 2.6 shows a schematic of the anodic and cathodic dissolution mechanisms which illustrates some proportion of place-exchanged Pt atoms dissolving, and how more place-exchanged Pt atoms appear during the negative going sweep. This basic mechanism translates to practically observable correlations between dissolution amounts and electrochemical controls or observations of the Pt electrode. For instance *Topalov et al.* (2013) showed that the amount of dissolution depends on the potential sweep rate and also confirmed that the amount of cathodic dissolution corresponds directly to the reduction charge. Figure 2.7 shows both of these expected and important correlations.

Other research groups have adopted a similar approach to studying electrochemical Pt stability, developing their own versions of the ICP-MS flow cell technique. *Jovanovivc et al.* (2014) have studied Pt nano particles, namely Pt black and Pt\C, and found Pt\C to be much less stable for similar mass loadings. *Lopes et al.* (2016) studied Pt single crystals and found the (110) facet to be significantly more susceptible to cathodic dissolution.

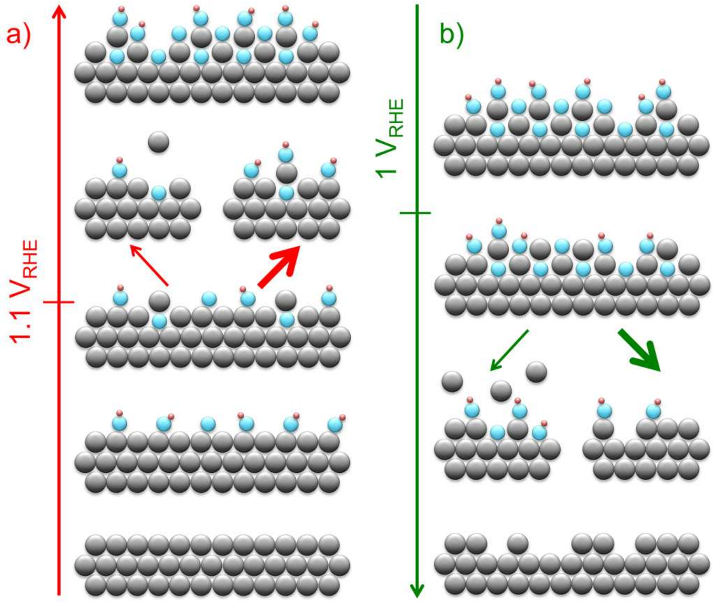


Figure 2.6: A dynamic Pt dissolution mechanism mediated by place-exchange of Pt atoms (large grey balls) and oxygen species (medium blue balls = oxygen atoms, tiny red balls = hydrogen atoms). Time-step dissolution processes are envisaged for both the **a)** anodic, oxide forming sweep, and the **b)** cathodic, oxide reducing sweep. Published by The Royal Society of Chemistry, reproduced under the Creative Commons Attribution 3.0 Unported Licence (*Topalov et al.*, 2013).

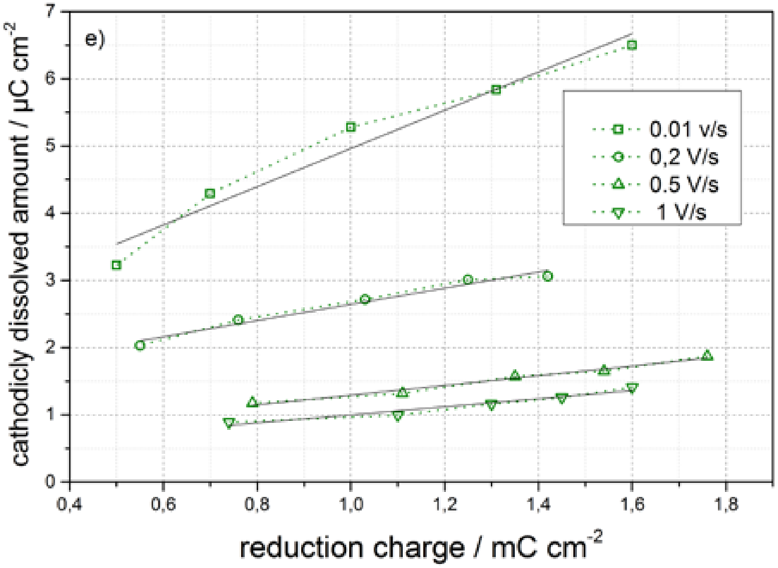


Figure 2.7: The effect of sweep rate and extent of Pt oxidation (quantified as reduction charge) on the amount of Pt lost to the electrolyte (0.1 M $HClO_4$) during the cathodic (negative going) scan of a 0.05 to 1.5 V_{RHE} CV. Though not indicated in the original work, solid lines are assumed to be the linear regression of the data points (squares) which are connected with dotted lines. Published by The Royal Society of Chemistry, reproduced under the Creative Commons Attribution 3.0 Unported Licence (*Topalov et al.*, 2013).

2.1.1.3 The Effect of Alloying/Decoration on Pt Loss

Very little research has been done regarding the effect of alloying on Pt loss. The study by *Burke and O'Sullivan* (1980) is one notable exception, especially given its age. From that study, Figure 2.8 shows that 10 wt% Rh in Pt has a large impact on reducing the amount of Pt loss. This result somewhat contradicts ICP-MS flow cell work from (*Cherevko et al.*, 2014) which shows Rh is less stable than Pt (see Figure 2.9). However, *Burke and O'Sullivan* (1980) used base, while (*Cherevko et al.*, 2014) used acid.

Cherevko et al. (2016c) is perhaps the only other study devoted to assessing the effect of a bi-metallic material on Pt loss. They analyzed the Pt loss from sub-monolayer Pt on Gold foil using the ICP-MS flow cell technique in an effort to investigate the reputed enhanced stability of carbon dispersed Au-Pt core-shell catalysts (for example *Xing et al.* (2010) and *Wang et al.* (2011)). The equilibrium concentration, or "quasi-steady-state" dissolution of Pt was lower for Pt-on-Au than for pure polycrystalline Pt. But Pt surface area normalized Pt loss was much higher for Pt-on-Au for the transient-potential type of dissolution (like Figures 2.4 and 2.5), making the verdict on Au-enhanced Pt stability inconclusive.

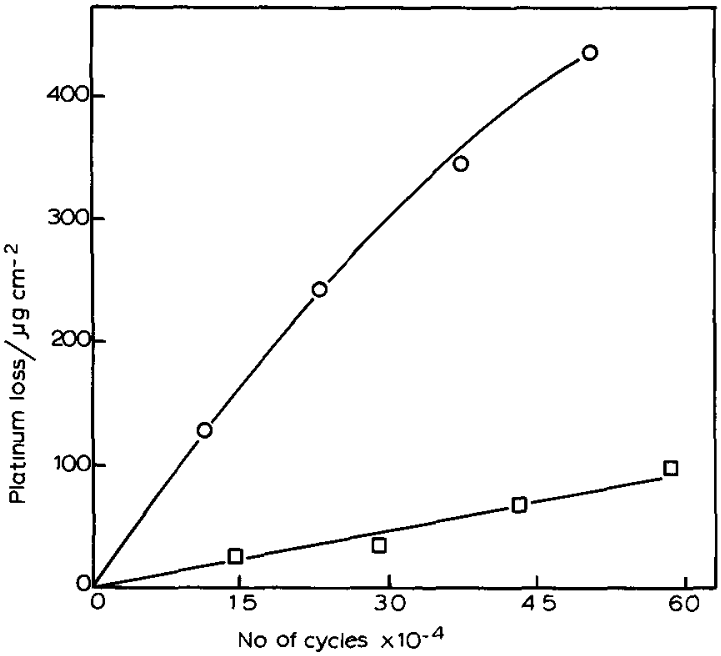


Figure 2.8: The effect of 10 wt% Rh in Pt (squares) compared to pure Pt (circles) on the amount of Pt lost to the electrolyte (0.1 M NaOH) with number of cycles (10^{-4} should be 10^{4}) during potential cycling (0.0 to 1.5 V_{RHE}, 6 $V\,s^{-1}$. With Permission of Elsevier (*Burke and O'Sullivan*, 1980).

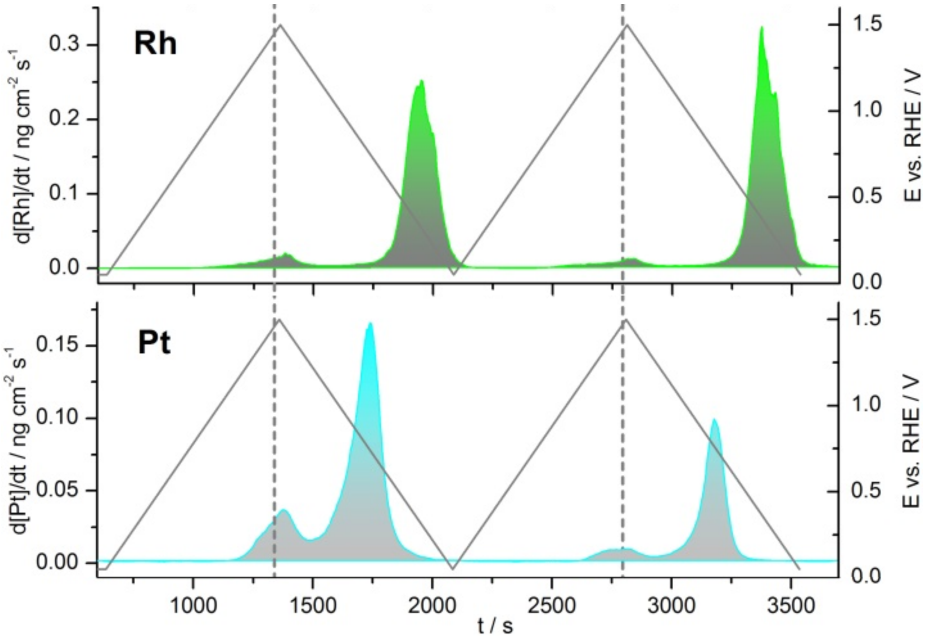


Figure 2.9: Dissolution of polycrystalline Rh and Pt in 0.1 M H_2SO_4 caused by potential sweeps (2 $mV\,s^{-1}$) between 0.05 and 1.5 V_{RHE}. Reprinted from ChemCatChem, 6, S. Cherevko, A. R. Zeradjanin, A. A. Topalov, N. Kulyk, I. Katsounaros, and K. J. J. Mayrhofer, Dissolution of Noble Metals during Oxygen Evolution in Acidic Media, pg. 2219-2223, Copyright (2014) with permission from Elsevier (*Cherevko et al.*, 2014).

2.1.2 Carbon Instability

Stevens and Dahn (2005) showed that commercially available Pt\C made from high surface area carbon is unstable in a fuel cell cathode. At temperatures and humidity common in PEM fuel cells, Pt\C loses mass with increasing carbon surface area, temperature and Pt loading, most likely due to catalytic combustion. A follow up study (*Stevens et al.*, 2005) showed the mass loss is also exacerbated by humidity. *Roen et al.* (2004) also demonstrated carbon corrosion occurs in a fuel cell under normal operating conditions and increases with Pt mass fraction. The corrosion of carbon in a fuel cell should come as no surprise because of the equilibrium potential of the electrochemical reactions involving water and carbon. Figure 2.10 shows the standard reduction potentials of three electrochemical reactions involving carbon and water: 1) the carbon oxidation reaction (COR), 2) the electrochemical analogue of the water gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$) and 3) the electrochemical oxidation of carbon to carbon monoxide.

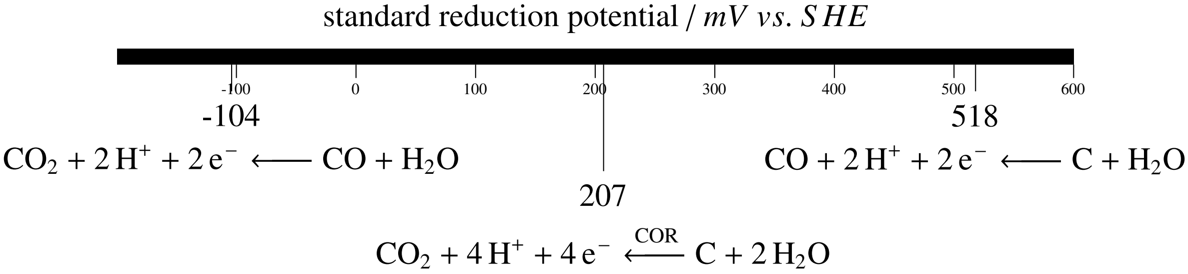


Figure 2.10: The standard reduction potentials of electrochemical half reactions involving carbon and water at standard conditions (data from *Bratsch* (1989)).

All these standard reduction potentials are lower than typical fuel cell cathode potentials (0.6 to 0.9 V_{RHE}), so the oxidation reaction (i.e. the direction of the arrows in Figure 2.10) should proceed during normal fuel cell operation. This should raise alarm, given that carbon is ubiquitous in fuel cells. However, the kinetics of electrochemical carbon oxidation were thought to be too slow for these reactions to be of any concern. Carbon is often viewed as an electrochemically stable material, pursuant to its use in many other electrochemical devices. The carbon corrosion rate in a fuel cell is very small, at or below a typical fuel cell open circuit voltage ($\sim$0.9 V). However gaseous carbon species are detectable and, over time, can amount to a sizable loss of carbon. On-line mass spectrometry studies of operating fuel cells have revealed that CO yield is approximately an order of magnitude lower than for CO_2 (*Maass et al.* (2008) *Kim et al.* (2009)). The much lower concentration of

CO is in agreement with the relative position of the standard reduction potentials involving water, carbon, CO_2, and CO. The oxidation of CO to to CO_2 is more thermodynamically favourable than the creation of CO from carbon. Therefore CO in the cathode should be readily oxidized to CO_2 (assuming the kinetics for these reactions, do not wildly differ). In addition, CO strongly adsorbs to Pt and poisons the catalyst by blocking the activity of the ORR. Copious amounts of CO in either the anode or cathode would preclude a viable Pt\C based fuel cell.

In light of the aforementioned studies and that by *Reiser et al.* (2005) (discussed in the next section) it suddenly became apparent that having carbon in a PEM fuel cell is a bad idea, which was a shock considering that all the electric current collecting materials in a PEM fuel cell (the catalyst support, the micro-porous layer, and gas diffusion layer, and the bi-polar flow-fields) were traditionally made of carbon. This spurred interest in non-carbon supports and and other non-carbon, corrosion-resistant current collectors. However it should be stated that carbon, per-se, is not the problem. Highly graphitized forms of carbon can be used without significant corrosion or performance losses, as shown by *Yu et al.* (2006) and others listed in the reviews by *Yu and Ye* (2007), *Shao et al.* (2007), *Antolini* (2009), and *Cao et al.* (2014). The problem is that on graphite powders, Pt does not form small, well dispersed particles as it does on high surface area carbon blacks. Figure 2.11 shows this effect with TEM images. Thus Pt on graphite powders requires a higher Pt loading to achieve an ORR activity comparable to the more common Pt\C made with carbon black. The review on Pt\C by *Antolini* (2009) provides an excellent synopsis on different types of Pt\C and how important properties, such as surface area, and electrical conductivity compare.

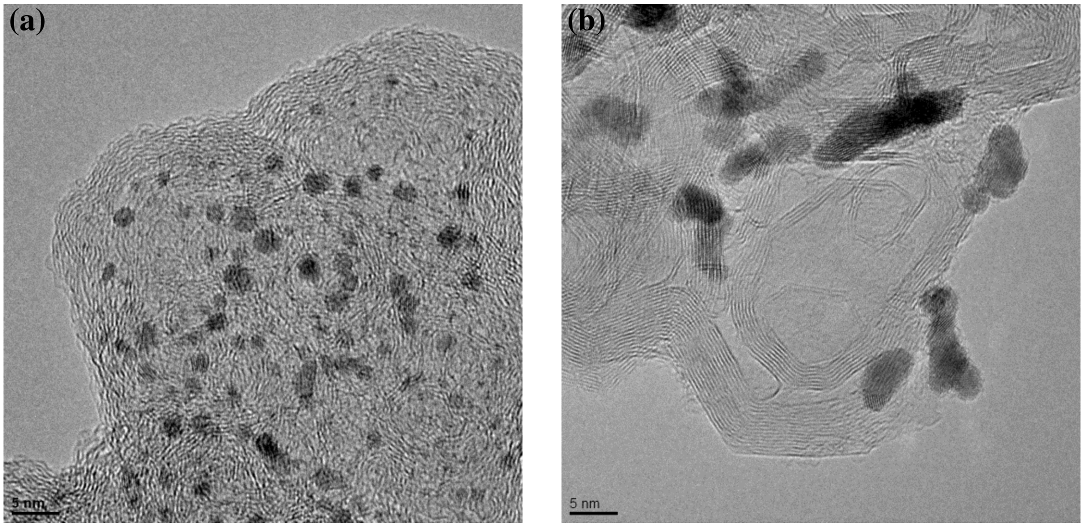


Figure 2.11: TEM images showing Pt\C made using **(a)** carbon black, and **(b)** graphite powder. Reprinted with permission from ECS Meeting Abstracts MA2012-02, 1313-1313 (2012). Copyright 2012, The Electrochemical Society (*More et al.*, 2012).

2.1.3 Localized Fuel Starvation

Reiser et al. (2005) showed that the performance of a fuel cell declines with time due to the presence of both air and hydrogen in the anode which happens during start-up and/or shut-down (SU/SD) of the cell. During a shut-down event, air diffuses back into the anode after the flow of hydrogen is stopped. During a start-up event, air is already in the anode flow field, and is pushed out by the hydrogen gas. During either event, the current through the membrane in the region where hydrogen is absent is reversed. This is driven by the spontaneous/galvanic action of the available hydrogen on the fuel cell anode and oxygen on the cathode. The electrochemical corrosion of carbon, also known as the carbon oxidation reaction (COR) satisfies this current, which is completely internal to the cell. Figure 2.12 shows these four reactions (along with a fifth reaction, addressed in the next section) and their locations within the fuel cell. *Reiser et al.* (2005) called this phenomenon the reverse current decay mechanism (RCDM). They modelled it with a charge conserving differential equation (which was incorrect according to *Sidik* (2009)) and verified it with an experiment which showed significant shrinkage of the Pt\C layer adjacent to the hydrogen starved region in the anode. Though not directly stated, the obvious conclusion was that fuel cell performance degradation was due to the collapse of the porous structure of the carbon black. Figure 2.13 shows a TEM image from their study.

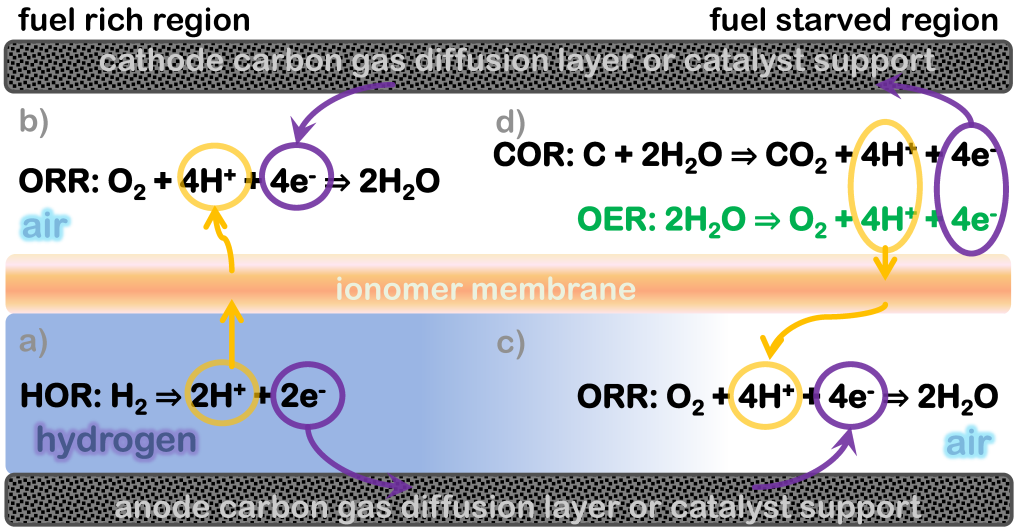


Figure 2.12: The electrochemical reactions involved in the RCDM, their respective ionic/electronic current paths, and their locations within a cell during SU/SD. Reproduced with permission from J. Electrochem. Soc., 161, F961-F968 (2014). Copyright 2014, The Electrochemical Society (*Crowtz et al.*, 2014).

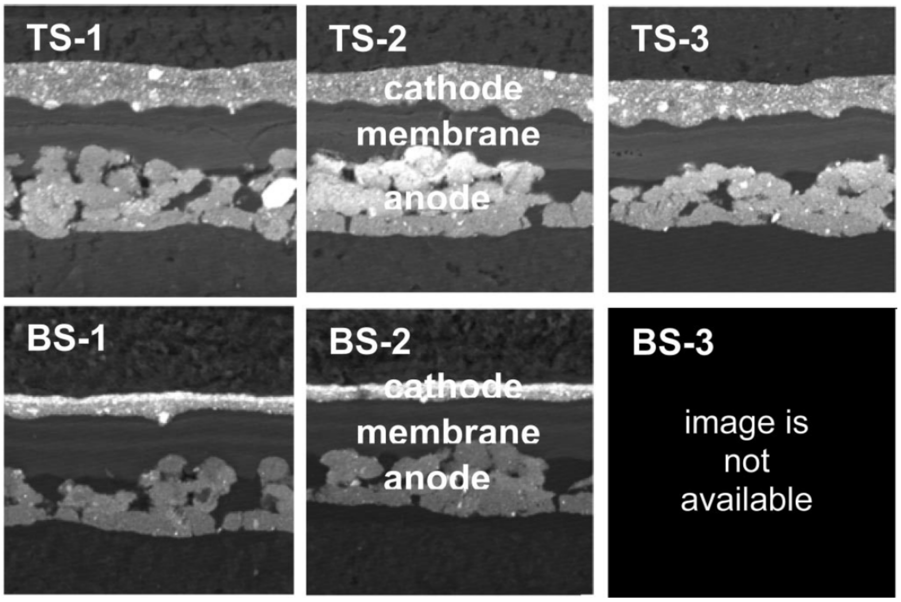


Figure 2.13: Cross-sectional images of a PEM fuel cell MEA post-RCDM taken with an electron microprobe. **BS-1** and **BS-2** show a thinned catalyst layer from the fuel starved region and c)) due to the RCDM. **TS-1/2/3** show the catalyst layer in the fuel-rich region is unaffected by the RCDM. Reprinted with permission from Electrochem. Solid-State Lett. 8, A273-A276 (2005). Copyright 2005, The Electrochemical Society (*Reiser et al.*, 2005).

2.1.3.1 A Materials Solution to the RCDM

Reiser et al. (2005) listed three strategies to mitigate the RCDM, citing three patents they applied for five years earlier. These patents are mechanical engineering approaches to the problem as they involve either gas conveyance modifications or carefully timed electrical loads. Indeed, most stack manufacturers responded to the RCDM problem with similar types of systems engineering fixes. *Yu et al.* (2012) lists 100 patents of this nature for mitigating damage due to the RCDM. The other major response was modifications to the carbon support in the Pt\C, namely graphitization, and incorporation of other elements like S (*Higgins et al.*, 2014) and N (*Sidik et al.*, 2006) into the carbon structure. However, an understanding of Figure 2.12 reveals two possible materials science approaches of an electrocatalytic nature to fix the RCDM problem.

Ⓐ Promote the OER in the cathode. Figure 2.12d) shows the COR and OER as competing reactions in the fuel cell cathode fuel starved region (these are anodic reactions so the term "fuel cell cathode" is used). Both reactions can supply the necessary oxidative current necessary to complete the RCDM.

Ⓑ Hinder the ORR in the anode. In this way, the RCDM will proceed more slowly.

Figure 2.14 shows hypothetical Tafel models for all five reactions of the RCDM on a Tafel-style plot (i.e. current on a log-scale abscissa), and it is clear that for either strategies Ⓐ or Ⓑ, or for both Ⓐ and Ⓑ, the potential on the fuel cell cathode is lowered. This is very important to mitigating the damage done to a fuel cell during these events. Both strategies were the crux of 3M's proposal that secured the USDOE funding (*Atanasoski*, 2009) for most of the original research shown in this thesis project. 3M's publications on this materials approach developed the tagline "always on" to set it apart from the plethora of other systems engineering approaches.

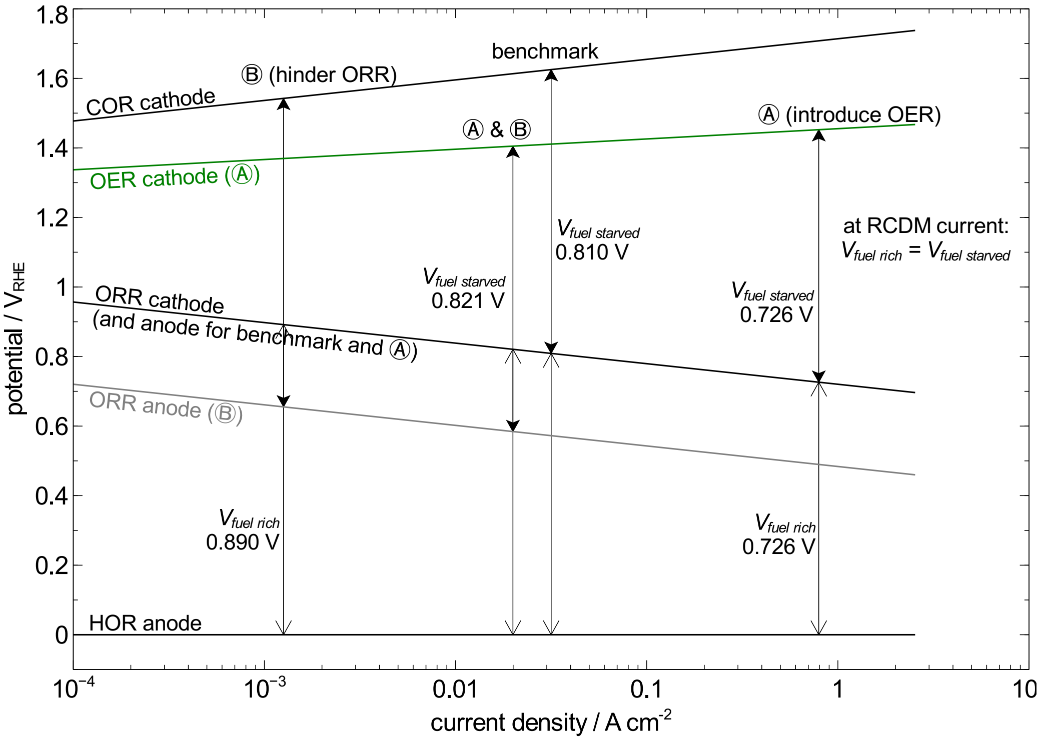


Figure 2.14: Tafel equation models of four different catalyst scenarios for the RCDM: 1) the benchmark case, 2) increase the cathode OER activity (Ⓐ), 3) decrease the anode ORR activity (Ⓑ) and 4) both Ⓐ and Ⓑ. The RCDM current is determined when the voltage of the fuel starved region is the same as the voltage of the fuel rich region (see Figure 2.12). According to *Sheng et al.* (2010), there is virtually no activation loss from the anode in a PEM fuel cell, therefore the HOR line is flat.

3M's NSTF is a non-carbon support, so will not corrode due to the RCDM. NSTF was actually in development prior to the carbon susceptibility or localized fuel starvation revelations so was well positioned as a state-of-the-art non-carbon support to be part of the solution to the carbon instability/RCDM problem. However, even with non-carbon supported catalysts, other carbon parts comprise the current collector components, these being the carbon-based microporous layer and gas diffusion layer. These carbon parts, especially the micro-porous layer, are susceptible. The following quote is taken from an ageing study of NSTF fuel cells by researchers at GM:

> "NSTF-based fuel cells are not entirely immune to high potentials. It should be noted that in our unpublished work it has been shown that an extensive high cell potential (> 1.5 *V*, (1 $mA\,cm^{-2}$), for several hours) led to corrosion of the micro-porous layer adjacent to the cathode catalyst layer and hence higher gas transport resistances. Therefore, unintentional high voltage excursion should be avoided as possible." –*Kongkanand et al.* (2011)

More details later emerged from the same research group at GM which showed significant loss in the *I*-*V* curve after a 1.5 *V* hold for only 10 *min* (*Kongkanand et al.*, 2014). Therefore even for non-carbon black catalyst supports like NSTF, it seems advisable to implement a strategy to mitigate against the RCDM, and the materials strategy could be a unique, simple and cost effective cure to the problem. NSTF deserves a special description, as all original research presented in this thesis report is based on this special material.

2.2 Nanostructured Thin Film

The common organic dye N,N-di(3,5,xylyl)perylene-3,4:9,10bis(dicarboximide), known commonly as perylene red, pigment red 149 or PR149, can be annealed to form vertically oriented, crystalline, nanoscale whiskers after thermal deposition as a thin film. This material was patented by 3M (*Debe*, 1989) prior to the first publications of the material by *Debe and Poirier* (1994) and *Debe and Drube* (1995). The electrochemical application of this material as an electrode support in fuel cells and sensors was also patented by *Parsonage and Debe* (1994) almost a decade before it was published as a state-of-the-art catalyst support in the scientific PEM fuel cell literature (*Debe*, 2003).

Figure 2.15 shows a collage of micrographs with panel (c) highlighting the important physical characteristics of NSTF whiskers. NSTF whiskers are dimensionally similar to a multi-walled carbon nanotube, but faceted and flat like a lath, and are packed with a density of about 3 to $5{\times}10^9\ cm^{-2}$ (*Debe*, 2003). The substrate NSTF is grown on is a polyimide (Kapton®) film with a saw toothed surface which is coated with one or more layers of sputtered transition metals, presumably to enhance adhesion or growth properties of the NSTF whiskers. Figure 2.15(b) shows a cross section of the substrate with NSTF whiskers grown on the saw-toothed side. The saw-toothed surface increases surface area by a factor of $\sqrt{2}$ and enables the film to be stored as a roll, which facilitates roll-to-roll manufacturing of an MEA, also called catalyst coated membrane (CCM) by 3M. The NSTF whiskers are sputter coated with catalyst metal(s) to any desired loading. The number of different elements comprising the catalyst film is limited only by the number of targets the sputtering machine can accommodate. More on sputtering can be found in Section 3.2.3. The sputter coated NSTF whiskers are hot pressed, or laminated onto both sides of a PFSA sheet to make an MEA or CCM. Figure 2.16 shows how higher lamination pressure flattens the whiskers into the membrane, as would be expected. Figure 2.17 shows a CCM cross section where NSTF is laminated into both sides. NSTF catalyst layer thicknesses are low ($< 0.5\ \mu m$) compared to conventional Pt\C ($< 10\ \mu m$). This dry, rapid manufacturing technique is one of the significant advantages NSTF has over Pt\C. Figure 2.18 shows the flow charts for manufacturing a CCM with either Pt\C or NSTF. The significant cost savings and high volume manufacturing capacity of NSTF based CCMs are explained in *Debe* (2012). Debe argues no other competing technology has the ability to easily adapt to a future where all transport vehicles are PEM fuel cell electric vehicles.

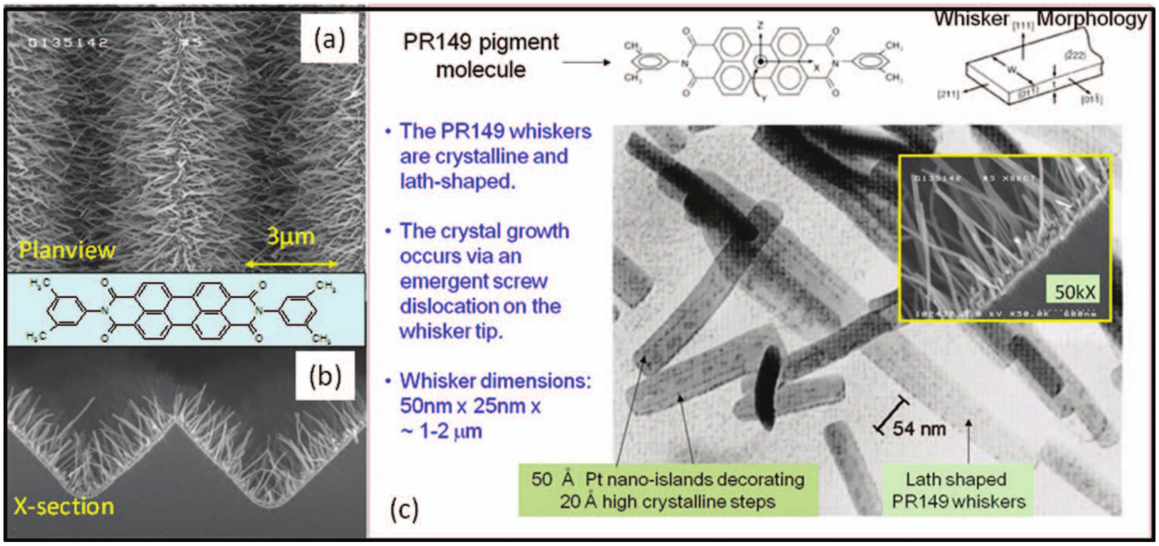


Figure 2.15: The physical features of NSTF: **(a)** top-down view of whiskers on growth substrate **(b)** cross-section view of whiskers on growth substrate **(c)** physical dimensions of whiskers and growth mechanisms. Reprinted with permission from J. Electrochem. Soc. 160, F522-F534 (2013). Copyright 2013, The Electrochemical Society (*Debe*, 2013).

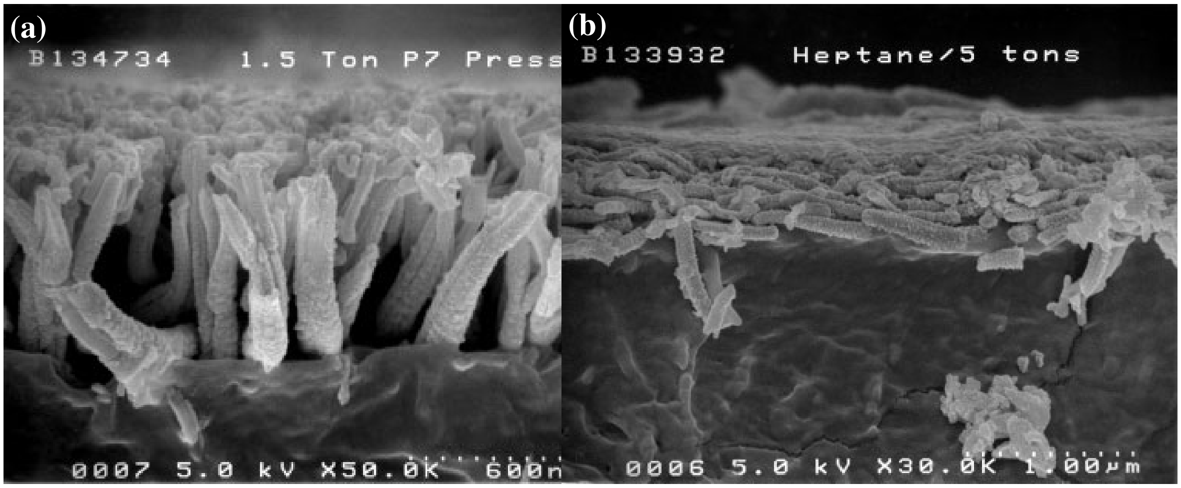


Figure 2.16: Scanning electron microscopy images of sputter coated NSTF whiskers hot pressed into a PFSA membrane showing how whisker orientation with respect to the membrane surface depends on the mass applied to the lamination press: **(a)** 1.5 tons, **(b)** 5 tons. Republished with permission of John Wiley and Sons Inc, from Handbook of Fuel Cells: Fundamentals, Technology, and Applications, M. K. Debe, vol. 3, 2003; permission conveyed through Copyright Clearance Center, Inc. (*Debe*, 2003)

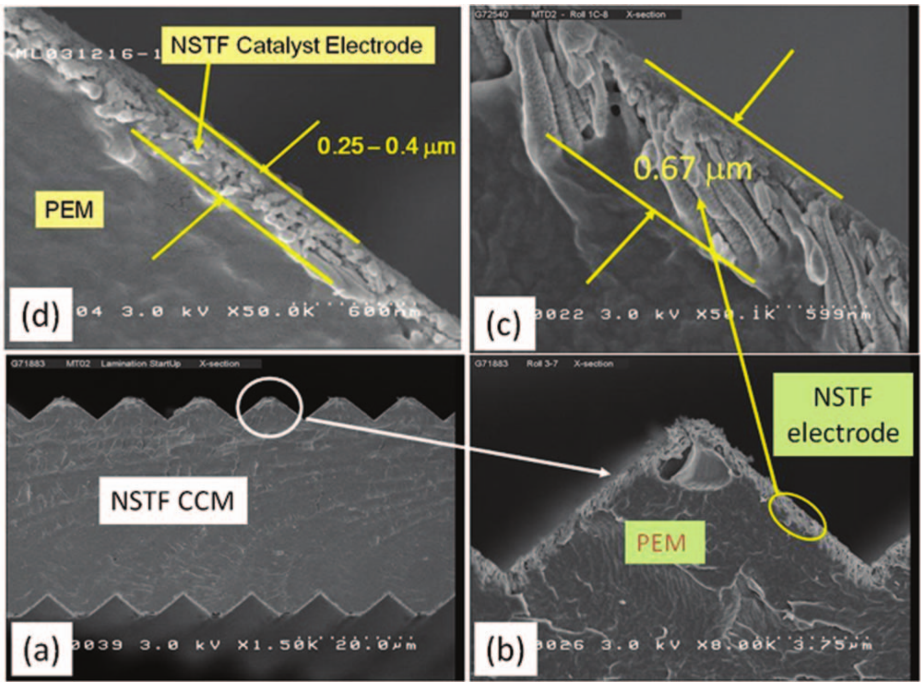


Figure 2.17: Various cross-sections of sputter coated NSTF whiskers laminated into a PFSA membrane to form a CCM. Reprinted with permission from J. Electrochem. Soc. 160, F522-F534 (2013). Copyright 2013, The Electrochemical Society (*Debe*, 2013).

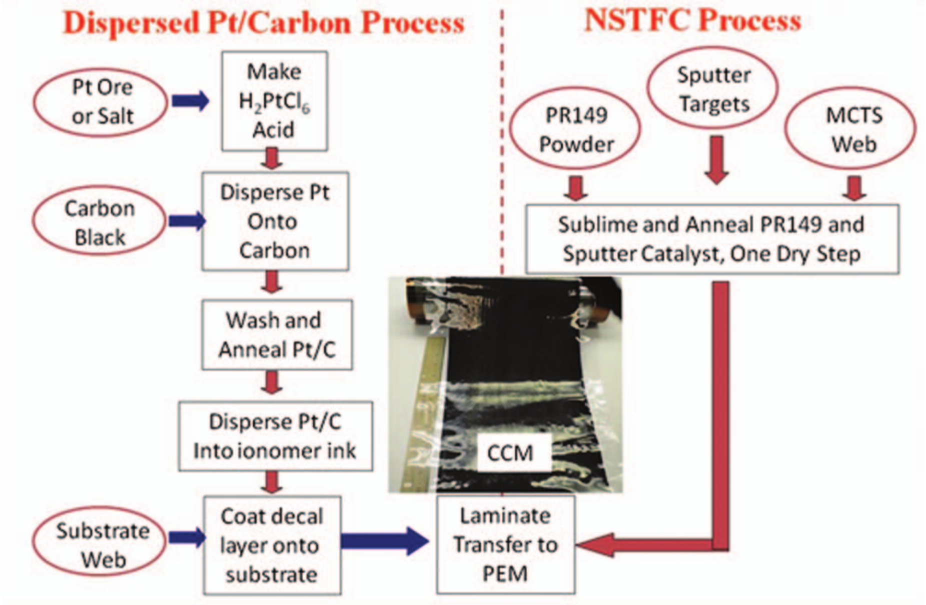


Figure 2.18: The process for manufacturing a CCM with either Pt\C or NSTF. Reprinted with permission from J. Electrochem. Soc. 160, F522-F534 (2013). Copyright 2013, The Electrochemical Society (*Debe*, 2013).

2.2.1 Electrocatalytic Properties of NSTF

3M has invested heavily in NSTF fuel cells because they need less Pt to achieve the same current density. Figures 2.19(b) and (c) show state-of-the-art *I*-*V* curves with near identical performance for Pt\C (panel (b)) with a cathode loading of 0.4 $mg\,cm^{-2}$ and NSTF (panel (c)), with a cathode loading of 0.15 $mg\,cm^{-2}$.

NSTF and Pt supported on NSTF have many other interesting and surprising electrocatalytic properties.

- An ionomer is not needed in the catalyst layer, in contrast to Pt\C.
- Mass specific Pt surface areas (based on H_{UPD} (see *Electrochemical Surface Reactions on Pt* on pg. 18)) are 10 to 25 $m^2\,g^{-1}$ (*Debe*, 2013), which is comparable to a typical high surface area Pt black powder (20 to 28 $m^2\,g^{-1}$ (*Choi et al.*, 2003)) but lower than conventional Pt\C which can range from 50 $m^2\,g^{-1}$ (*Gasteiger et al.*, 2003) to 100 $m^2\,g^{-1}$ (*Yu and Ye*, 2007) when pristine.
- ORR Pt-area-specific activity (geometric current density divided by the surface enhancement factor (Equation 3.3)) is comparable to bulk Pt, which is 5 to 10 times that of Pt\C (*Debe*, 2013).
- NSTF is electrochemically stable up to 2 V_{RHE} (*Debe*, 2003). It does not corrode like carbon.
- Testing by 3M has shown NSTF fuel cells to be much more durable than Pt\C (for example, *Debe et al.* (2006)). They claim this is because of the absence of carbon in the catalyst layer, and the larger radii of curvature of the metal-coated whiskers compared to Pt\C (*Debe*, 2013).

The markedly different properties and behaviour of NSTF from that of Pt\C is intriguing to theoretical electrochemists. *Zenyuk and Litster* (2014) have published a model, the latest of their versions, which seems to successfully model the behaviour of NSTF by making some interesting assumptions: 1) a thin film (20 *nm*) of liquid water on the Pt surface, 2) an alkaline ORR mechanism acting in conjunction with the acidic one, and 3) lifting the electro-neutrality requirement. In other words, according to their model, the interstices of the NSTF whiskers are always flooded (1st assumption), and the ORR mechanism changes along the length of the whisker, with the end farthest from the membrane operating under alkaline conditions (2nd and 3rd assumptions).

2.2.2 The Uncertain Future of NSTF for Fuel Cell Vehicles

The disadvantage for NSTF fuel cells is that the water management is more difficult. Figure 2.19(a) shows a comparison of the water management strategies for both Pt\C and NSTF fuel cells. Even though water is produced at the cathode, 3M recommends moving the water through the membrane against the natural electro-osmotic mass flow, and out the anode. This is because an NSTF cathode is sensitive to flooding. When NSTF was introduced, many researchers viewed it as a breakthrough which would come to dominate the automotive fuel cell industry. However, as manufacturers gained experience testing the new material, the operational difficulties became apparent. NSTF fuel cells have yet to be adopted for use in vehicle fuel cell stacks because of operational problems related to water management. *Gröger et al.* (2015) states poor performance during temperatures below $50°C$ and poor freeze start capability have prevented their commercialization. NSTF fuel cells also suffer from poor performance under dry conditions (*Sinha et al.*, 2011).

Recently an inkjet printing process to deposit Pt\C directly onto the PFSA membrane has shown very promising results (*Breitwieser et al.*, 2015). The performance roughly matches the Pt usage efficiency of NSTF fuel cells. As mentioned in Section 1.2.1 (Fuel Cells vs. Batteries), the margin for improvement is large. It is too early to tell how this new development will play out in the industry. Developments can occur so quickly that the systems are obsolete before they can get to market. For instance, Charlie Freese, executive director of global fuel-cell activities at GM says “It’s not that we couldn’t, we could have one in production, but if we did it would be with an antiquated (propulsion) unit.” (*Amend*, 2016).

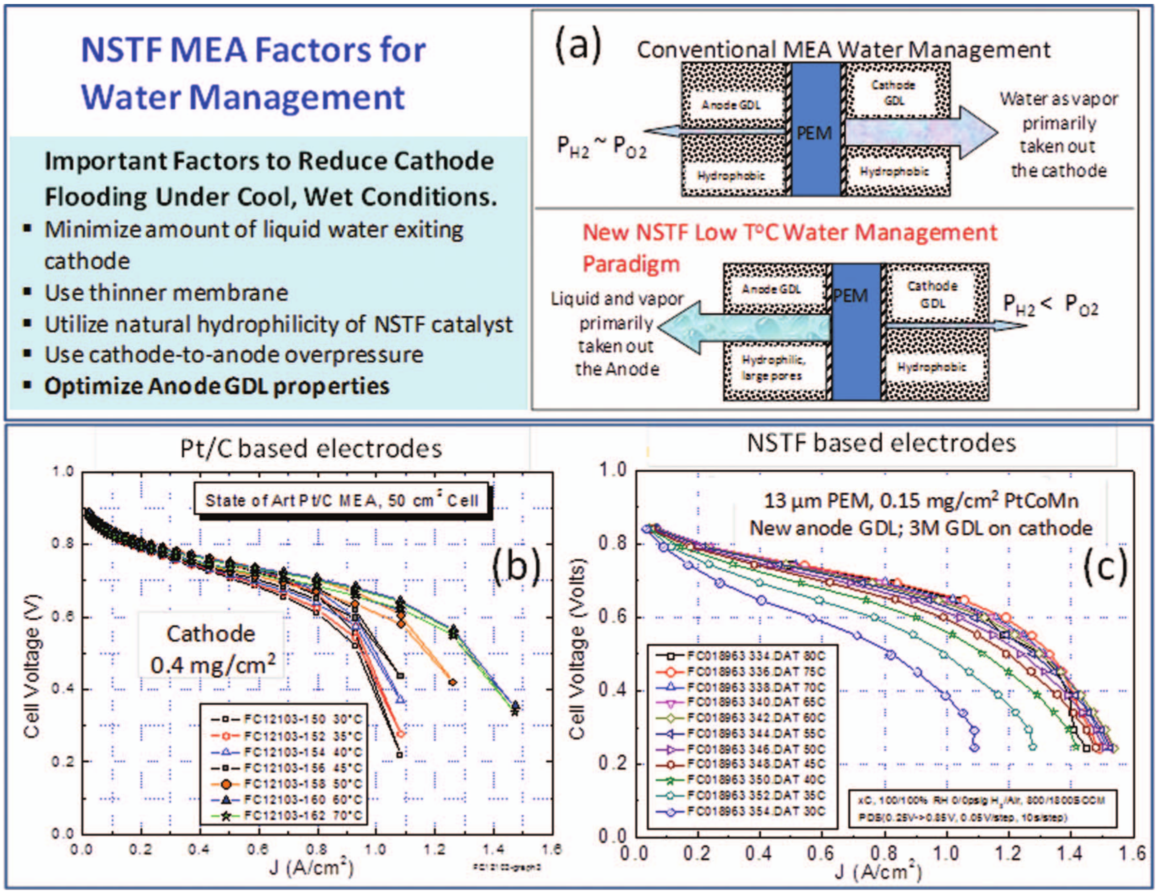


Figure 2.19: Pt\C fuel cells vs. NSTF fuel cells: **(a)** a comparison of the water management strategies and **(b)** *I*-*V* curves for state-of-the art Pt\C and **(c)** NSTF fuel cells. Reprinted with permission from J. Electrochem. Soc. 160, F522-F534 (2013). Copyright 2013, The Electrochemical Society (*Debe*, 2013).

2.2.3 Developing the Materials Solution to the RCDM on NSTF

NSTF, introduced in 2003, was touted not only for its Pt usage superiority, but also for its robustness compared with the current state-of-art Pt\C catalysts. It is somewhat ironic that the materials solution would be implemented with a support that is already inherently resilient. Nevertheless, 3M (and Dalhousie) researchers were the first to propose and receive funding to develop a catalytic solution to the RCDM. Further pragmatism still could question the timing or necessity of such research due to unpublished, and presumably non-existent experience with the real-world performance and durability of NSTF fuel cell stacks in vehicle applications.[1] For instance, one may ponder "is there actually a RCDM problem with NSTF fuel cell stacks, or is their lifespan tolerable as is?" This sentiment is reflected in the USDOE's first review on 3M's program when they said:

> "The philosophy here is obtuse. The question now should be 'what is necessary to assure contemporary fuel cells survive with acceptable durability,' rather than 'what is necessary to make contemporary fuel cells "bullet proof", no matter how they are abused.' It is probably worth thinking along these lines. However, the early markets are being established now, and other developers have solid, durable products." –*Satyapal* (2010)

Therefore, as a preemptive acknowledgement of such criticisms, the research can be justified for two reasons which were already explained in this chapter:

1. Even for NSTF, carbon parts inside the fuel cell, like the micro-porous layer are still vulnerable to damage due to high potentials caused by the RCDM. The micro-porous layer is often treated for hydrophobicity and loss of this property (via high potentials) will deleteriously affect fuel cell performance.
2. Even if the COR is completely replaced with the OER, Pt is vulnerable to changing potentials; the more oxidation and reduction the Pt undergoes, the greater the dissolution. The extent of the surface oxidation of Pt depends on several factors, including potential. A lower potential during SU/SD will lessen the extent of oxidation and so lessen Pt dissolution.

---

[1] Prototype vehicle data is generally not published in the open literature, as the performance and durability data is considered sensitive and confidential. The USDOE's National Fuel Cell Technology Evaluation Centre exists to securely collect, analyze, compare this data while protecting the identity of the participating companies.

The second point was not always appreciated because this project began (*Atanasoski*, 2009) several years before the first publication on the true nature of electrochemical Pt instability (*Topalov et al.*, 2012). Despite the "obtuse philosophy", the research received continued support until 2014, likely due to the uniqueness of the approach, the solid track record of the participating researchers, and the hope that knowledge gained would be transferable to other supports (*Satyapal*, 2010) (though testing of other supports never occurred within the project as USDOE had wished).

As mentioned in Section *Localized Fuel Starvation* (pg. 36), the catalytic solution to the RCDM involves two strategies, which could be implemented independently or simultaneously. Research on the two strategies can be conducted independently because each strategy is confined to one electrode. The only non-3M/Dalhousie affiliated studies for option Ⓐ are those conducted by South Korea's Yonsei University (*Oh et al.*, 2012), and Samsung SDI (*Min et al.*, 2014). More details about these studies are provided in Section 2.4. For option Ⓑ, the only studies are from Argonne National Laboratory (*Genorio et al.*, 2010) and Solvicor (started by Umicore and Solvay, but now owned by Toray) (*Durst et al.*, 2015). The industry has probably gone with a systems engineering strategy, but it seems there is room for more research on the catalytic answer to the RCDM, given the sparsity of the published research (excluding 3M's and Dalhousie's published studies, which are numerous). This PhD project exclusively focused on strategy Ⓐ, i.e. modifying the fuel cell cathode catalyst to enhance its OER activity.

2.3 Materials Properties of Ru and Ir

Enhanced OER activity in the fuel cell cathode should accomplish two things: 1) carbon will be preserved because the oxidative current demand of the RCDM will come from the oxidation of water not carbon, and 2) the potential seen by the cathode during the RCDM will be lower, and this should reduce Pt dissolution by reducing the amount of electrochemical Pt oxide formation. The OER activity of Pt is poor, which is obvious because of the occurrence of the corrosion of carbon (due to the RCDM) in a Pt only fuel cell. Adding a good OER catalyst is the simplest way to enhance the OER activity. So what are the best catalysts for the OER? Furthermore, echoing some questions raised at the very beginning in Section *Project Motivation* (pg. 1), How will these best OER catalyst materials behave on NSTF? Will there be durability issues for the OER catalysts like there is for Pt, and if so what is the nature of the instability? This section explores the answers. The question, "what are the best catalysts for the OER?" ought to be first sufficiently addressed.

2.3.1 Origins of the OER in Acid

Exploration of electrocatalysts for the OER began just before the turn of the twentieth century with the development of industrial electrolyzers A historically noteworthy monograph, rich with details about this burgeoning industry, was recorded by *Hale* (1919). The document shows alkaline electrolyzers[2] were already an industry standard for the large-scale production of hydrogen and oxygen. Hale states that by 1916, some companies had developed nickel-plated electrodes, which remain to this day a common anode material for industrial alkaline electrolyzers The scientific development of OER catalyst materials lagged behind significantly, not surprisingly, because the electrocatalytic processes were not well understood. This understanding culminated in the 1950's with the widespread acceptance of the theories of electrochemical kinetics (*Bockris*, 1991). Scientific research on applied electrocatalysts then experienced a case of tunnel vision, focused exclusively on Pt (*Hadzi Jordanov et al.*, 2004), until a materials innovation from within the chlor-alkali[3] industry gradually became known: the Ru containing anode, which was first patented in 1965 by *Beer* (1980). Increasing knowledge and understanding of these catalyst materials, which produced oxygen as a by-product, probably helped lead to another electrocatalytic first from industry, the PFSA based electrolyzer by General Electric Corporation, invented by *Russell et al.* (1973). Recall that the PFSA membrane is an acidic electrolyte, in which transition metal anodes would quickly corrode. The electrocatalytic materials for this device were kept a trade secret, but suspected to include various combinations of Pt, Ir, Ru and Ta (*Tilak et al.*, 1981). In addition to Beer's material, General Electric's invention could

---

[2] Some of the devices profiled by Hale, particularly the earlier ones, were based on sulphuric acid and electrodes of either carbon or lead. This seems like a bad idea according to present knowledge; carbon and lead are very poor OER catalysts, much worse than nickel in base. However, the higher activation losses of acidic electrolyzers were compensated by their lower ohmic loses due to the much greater ionic conductivity of sulphuric acid. As design improvements (i.e. a closer electrode spacing) reduced ohmic losses, the alkaline electrolyzers performed better than the acidic ones, and became the dominant technology.

[3] The chlor-alkali process produces two commodity chemicals, lye (NaOH) and chlorine gas by passing an electric current through brine. The cathode compartment becomes enriched with lye and Cl_2 evolves on the anode. Prior to Beer's invention, the electrodes were carbon and shrunk with time (like the carbon anodes used for electrowinning aluminum). This is why Beer's catalyst material and its derivatives are commonly known in the literature as "Dimensionally Stable Anodes" (e.g. *Trasatti* (2000)).

have also been inspired by *Damjanovic et al.* (1966), which seems to be the first published demonstration of high OER activity for Ir in acid.

Mixtures of Ir and Ru, have since become the standard catalyst materials for the OER in acidic media. It seems this was first established by *Miles et al.* (1978), and later by numerous studies, many of which are listed in the review by *Park et al.* (2012) and in the introduction of *Cherevko et al.* (2016e). Additional elements, other than Pt, are also predicted by *Pourbaix* (1966) to be stable in the low pH, high potential regions relevant to this study. Pourbaix diagrams for these elements (Rh, W, Pd, Ti, Sn, Ta, and Nb) and some citations on additional elements used for OER-in-acid catalysis are given in Appendix A as starting points for the reader interested in pursuing non-conventional research on the OER in acid. Consideration of these elements is beyond the scope of this project. Therefore Ir and Ru are exclusively chosen for study in this project to implement a materials solution to the problems arising from the RCDM.

2.3.2 Thermodynamic Considerations

2.3.2.1 Pourbaix Diagrams of Ru and Ir

Figures 2.20 and 2.21 show the Pourbaix Diagrams of Ru and Ir, which confirm their stability in acid at water oxidizing potentials. Figure 2.20 shows a large region of corrosion for Ru. Ru forms the volatile and soluble RuO_4 at potentials above 1.383 V_{SHE} (*Pourbaix*, 1966). Ru is the most active element for OER catalysis in acid but keeping the potential below the dissolution limit does not yield practical rates of oxygen evolution. Ir is generally considered to be the second most active element for OER catalysis in acid, and does not suffer from instability. Pourbaix states "iridium appears to be a very noble metal" and "when used as a anode, iridium is not usually attacked, even in the presence of any chlorine liberated by electrolysis." (The corrosion of IrO_2 to ${IrO_4}^{2-}$, shown in 2.21, was considered because Latimer in *Pourbaix* (1966) gave information on the reaction $IrO_2 + 4\,OH^- \longrightarrow {IrO_4}^{2-} + H_2O + 2\,e^-$ at pH=14.)

The Pourbaix Diagram for Ir (Figure 2.21) shows only iridic oxide (IrO_2)[4] and no sesquioxide phase like for Ru. This is because the Gibbs energy of iridium sesquioxide was assumed such that the equilibrium potential for both the iridium sesquioxide and iridium dioxide half reactions are the same. Pourbaix justifies this assumption by stating

---

[4] IrO_2 is a typo in *Pourbaix* (1966), it should show $IrO_2 \cdot 2\,H_2O$ or $Ir(OH)_4$

“$Ir_2O_3 \cdot xH_2O$ (yellow green to blue black) is readily soluble in acids and alkalis, and is easily oxidized to $IrO_2 \cdot 2\,H_2O$ by the common oxidizing agents, including air”. But this contradicts his approach when constructing the diagram for Pt, where he claims the thermodynamic properties of hydrated platinic oxide are known “very approximately” when the amount of hydration is unknown (full quote in *Thermodynamic Considerations of Pt Stability* on pg. 23). Thus the Pourbaix diagram for Ir is a bit misleading, as it gives the perception that electrochemically passivated Ir exists only in the 4+ oxidation state (iridic oxide) when, by extension of Pourbaix’s comments on Pt, it could be thermodynamically stable in the 3+ oxidation state if the state of hydration permits. In reality, Ir^{3+} does exist in anodically grown iridium oxide. The study by *Pfeifer et al.* (2016) is the latest of many studies which provide evidence for the existence of Ir^{3+} in anodically grown Ir oxide. Thus not only are Ir and Ru thermodynamically stable as oxides at potentials lower than oxygen evolution, but they can exist in both the 3+ and 4+ oxidation states.

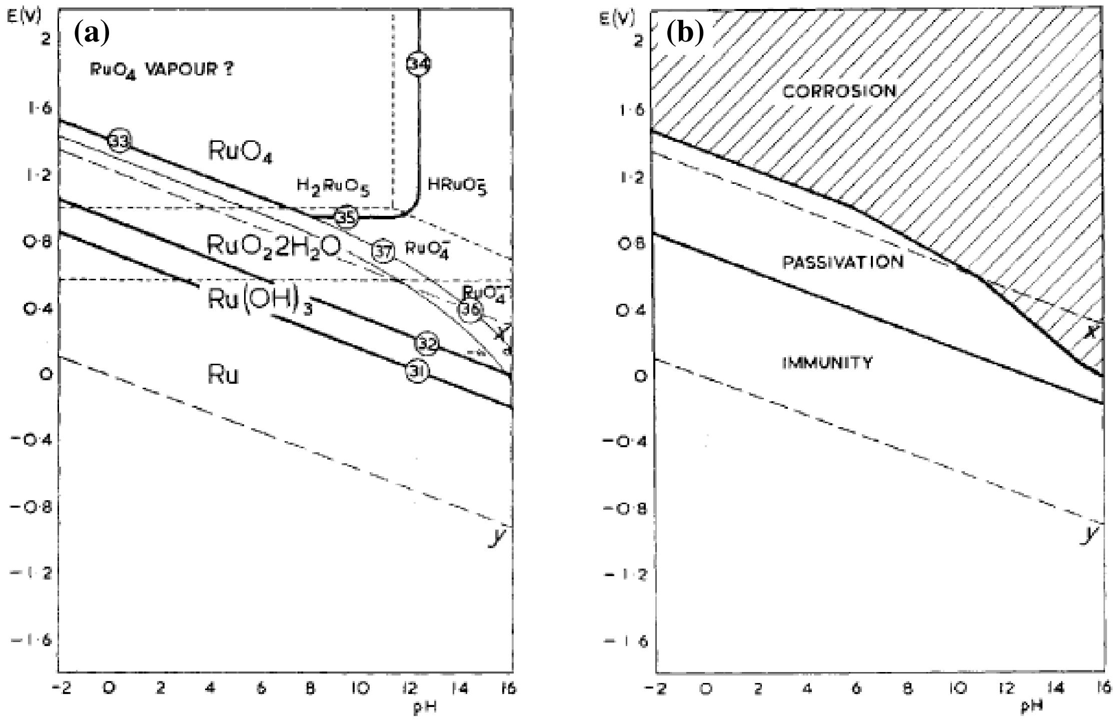


Figure 2.20: Pourbaix diagrams for Ru. Potentials are vs. SHE. Published by Johnson Matthey, reproduced under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (*Pourbaix et al.*, 1959a).

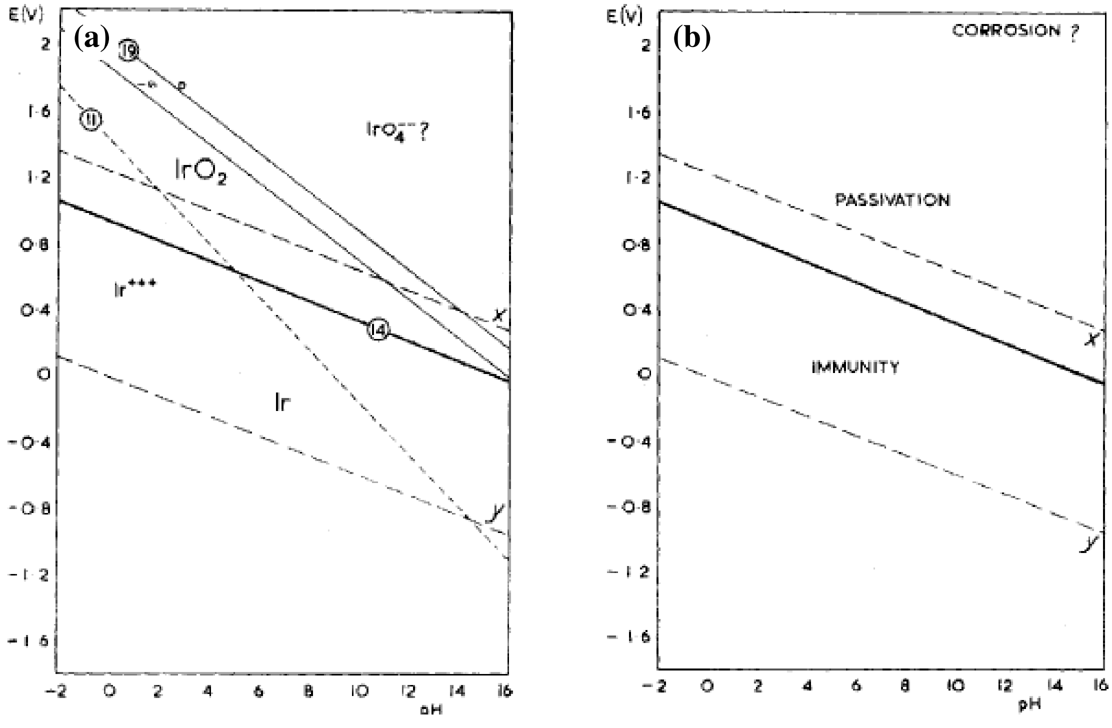


Figure 2.21: Pourbaix diagrams for Ir. Potentials are vs. SHE. Published by Johnson Matthey, reproduced under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (*Pourbaix et al.*, 1959a).

2.3.2.2 Phase Diagrams of Ru, Ir, and Pt

Could Ru and Ir be alloyed to obtain a catalyst with the activity of ruthenium and the stability of Ir? Figure 2.22 shows the Ir-Ru binary phase diagram where Ir and Ru are miscible over most of the binary composition range and a two phase region exists in the middle. Since Pt will also be an essential part of the catalyst material, Figure 2.23 shows a ternary phase diagram for the Pt-Ir-Ru system. Figure 2.24 shows a Pt-Ru binary phase diagram. Both figures show Ru and Pt are miscible over most of the composition range except for a two phase region between 65 and 80 at% Ru. Figure 2.23 also shows Ir and Pt are miscible over the entire composition range. However Figure 2.25 shows a binary phase diagram for Pt-Ir which indicates phase separation occurs over most of the composition range below 900°C. Ir and Pt will likely phase separate while Ru and Pt can form a solid solution below about 60 at% Ru, which is above the upper limit of this project will explore due to loading constraints. It is unknown how anodic oxidation of Ru and Ir (explained in the next section) affects phase separation.

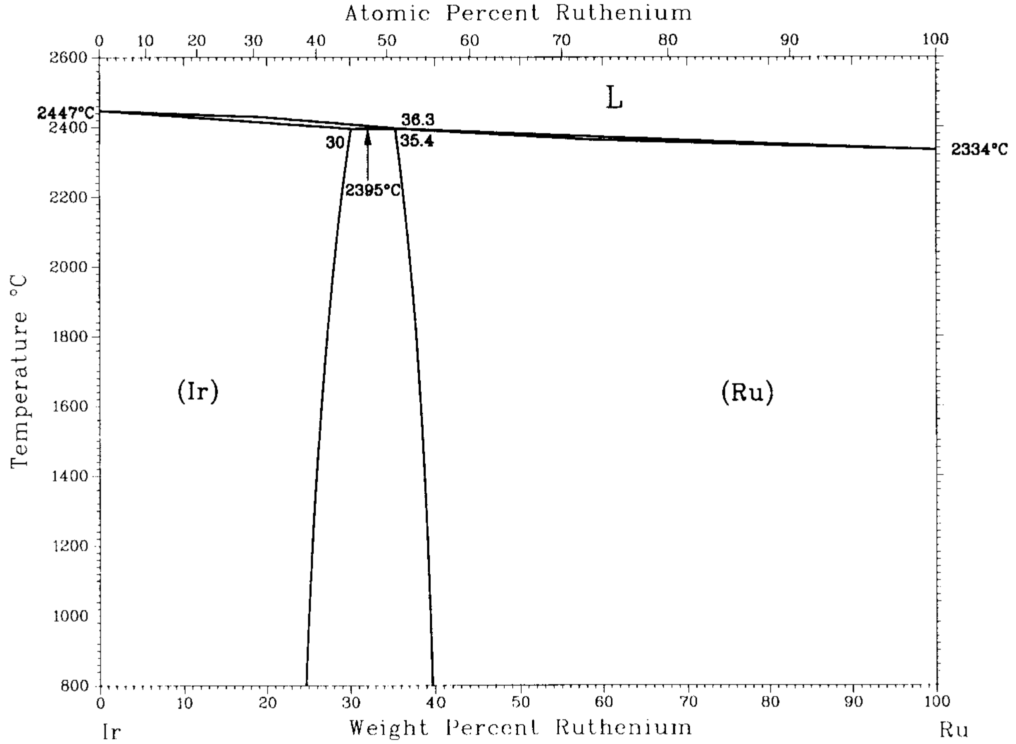


Figure 2.22: Binary phase diagram for the Ir-Ru system. With permission of Springer (*Okamoto*, 1992).

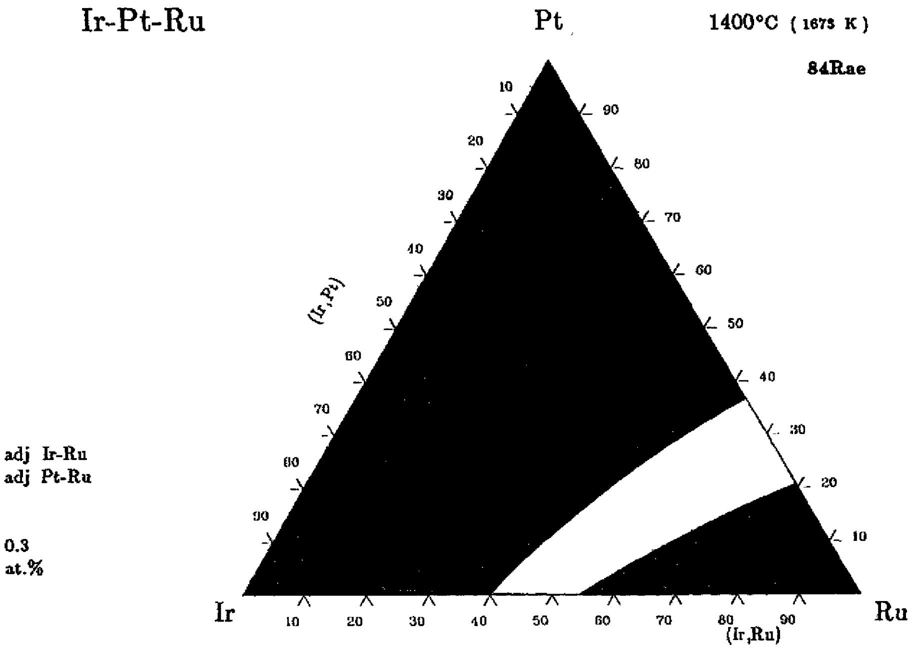


Figure 2.23: Ternary phase diagram for the Pt-Ir-Ru system. Single phase regions are coloured black. Republished with permission of ASM International, from Handbook of Ternary Alloy Phase Diagrams, P. Villars, A. Prince and H Okamoto, vol. 9, edition 1995; permission conveyed through Copyright Clearance Center, Inc. (*Villars et al.*, 1995).

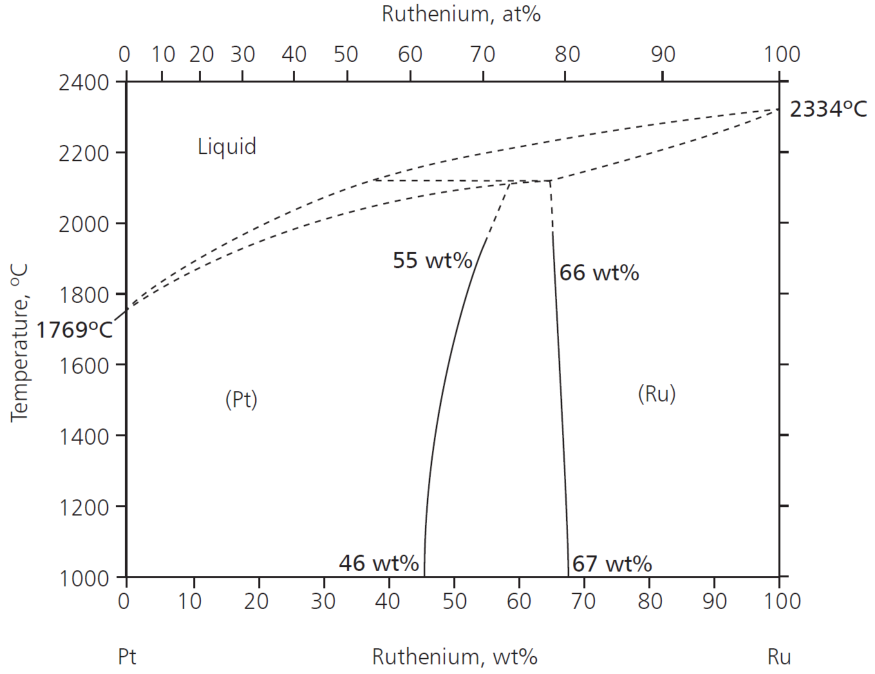


Figure 2.24: Binary phase diagram for the Pt-Ru system. Published by Johnson Matthey, reproduced under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (*Rakhtsaum*, 2013).

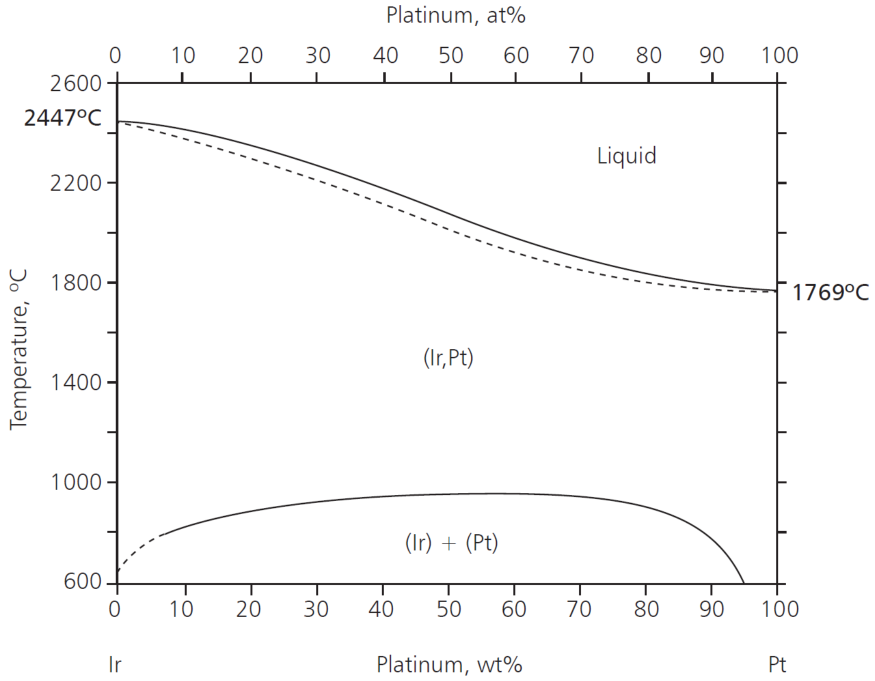


Figure 2.25: Binary phase diagram for the Pt-Ir system. Published by Johnson Matthey, reproduced under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (*Rakhtsaum*, 2013).

2.3.3 A Brief Note on Experience with Ru-Ir Mixtures

It is easy to tell when the Ru stability threshold is crossed as the loss of Ru, seen as OER activity loss, is quite rapid. Figure 2.26 shows this behaviour. Ir is the most active OER catalyst after Ru (also apparent in Figure 2.26) and unlike Ru, is generally regarded as very stable (Section 2.3.5 will describe the nature of Ir stability in detail.) However, Ir is significantly more expensive (almost an order of magnitude) than Ru. The relative costs and activities of Ru and Ir, along with their expected thermodynamic miscibility, present an opportunity to develop an alloy catalyst material with unrivalled stability and activity. *Kötz and Stucki* (1986) were probably the first to attempt and verify this rule-of-mixtures type approach. They showed 20 at% Ir could stabilize Ru. Other studies followed, with varying degrees of success, but mostly confirming the concept to some extent. Figure 2.27, shows an example of how adding (20 at%) of Ir to Ru can improve the stability without losing activity. Balancing activity and stability of Ru-Ir mixtures remains an area of active research. For example *Danilovic et al.* (2014) demonstrated an optimal Ru:Ir ratio of 1:1 if the nanoparticles are pretreated to achieve an Ir enriched surface.

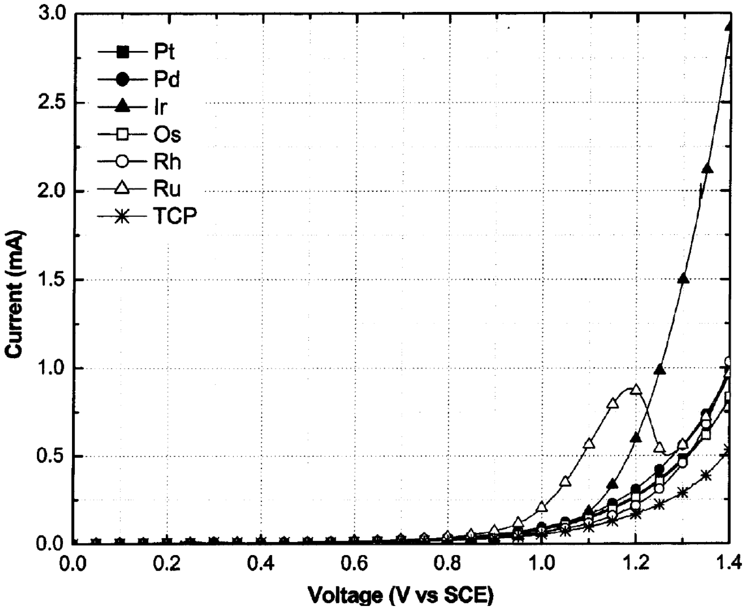


Figure 2.26: OER behaviour of PGM nanoaggregates (20 to 25 *nm*, obtained after calcination/reduction of the PGM salt solutions absorbed in Toray carbon paper) in 0.5 M $NaNO_3$ (pH = 5.6) during a positive going potential scan (5 $mV\ s^{-1}$). Potential is measured vs. the saturated calomel electrode (SCE) ($V_{SHE} = V_{SCE} + 0.241\ V$). Reprinted with permission from Dokoutchaev, A. G. et al. Multicomponent Electrodes for Water Oxidation: From Combinatorial to Individual Electrode Study. Chemistry of Materials 14, 3343-3348 (2002). Copyright (2002) American Chemical Society (*Dokoutchaev et al.*, 2002).

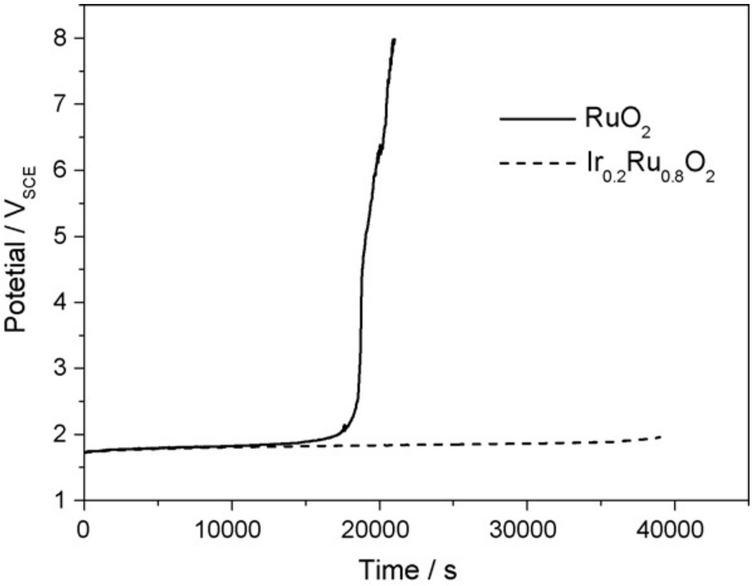


Figure 2.27: Chronopotentiometry experiments of RuO_2 and $Ir_{0.2}Ru_{0.8}O_2$ in 0.5 *M* H_2SO_4. Current density: 50 $mA\,cm^{-2}$. Reprinted from Electrochimica Acta, vol. 54, no. 26, J. Cheng, H. Zhang, G. Chen, and Y. Zhang, Study of $Ir_xRu_{1-x}O_2$ Oxides as Anodic Electrocatalysts for Solid Polymer Electrolyte Water Electrolysis, pp. 6250-6256, Copyright (2009), with permission from Elsevier (*Cheng et al.*, 2009).

2.3.4 Electrochemical Oxides of Ir and Ru

Ru and Ir catalyse the OER as oxides, and are frequently synthesized as oxides (note the legend in Figure 2.27 lists oxides). If they are not synthesized as oxides prior to OER catalysis, the surface of the metallic phase becomes anodically oxidized by reaction with water. For instance the anodic oxidation of metallic Ru proceeds according to the reaction:

$$\text{Ru}^{0} \text{ to } \text{Ru}^{3+}: \qquad 2\,\text{Ru} + 3\,\text{H}_2\text{O} \longrightarrow \text{Ru}_2\text{O}_3 + 6\,\text{H}^+ + 6\,\text{e}^- \tag{2.1}$$

and can oxidize further according to the reaction:

$$\text{Ru}^{3+} \text{ to } \text{Ru}^{4+}: \qquad \text{Ru}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\,\text{RuO}_2 + 2\,\text{H}^+ + 2\,\text{e}^- \tag{2.2}$$

The next anodic oxidation reaction does not continue to build oxide layer, but destroys it producing the volatile ruthenium tetraoxide:

$$\text{Ru}^{4+} \text{ to } \text{Ru}^{8+}: \qquad \text{RuO}_2 + 2\,\text{H}_2\text{O} \longrightarrow \text{RuO}_4 + 4\,\text{H}^+ + 4\,\text{e}^- \tag{2.3}$$

and RuO_4 is a mildly acidic according to:

$$\text{RuO}_4 + 2\,\text{H}_2\text{O} \longrightarrow \text{H}_2\text{RuO}_5 \longrightarrow \text{HRuO}_5{}^- + \text{H}^+ \tag{2.4}$$

The anodic oxidation of Ir is completely analogous to Reactions 2.1 and 2.2. The next anodic oxidation step for Ir is not analogous to Reaction 2.3, but is suspected to be:

$$\text{Ir}^{4+} \text{ to } \text{Ir}^{6+}: \qquad \text{IrO}_2 + \text{H}_2\text{O} \longrightarrow \text{IrO}_3 + 2\,\text{H}^+ + 2\,\text{e}^- \tag{2.5}$$

More on IrO_3 is provided in Section 2.3.5.

The thermodynamic oxidation of Ru and Ir to the +3 or +4 oxidation state (reaction 2.1 or 2.2) takes place at potentials lower than the thermodynamic oxidation of water (i.e. the OER). Figure 2.28 shows all the relevant thermodynamic potentials for Ru and Ir on one scale.

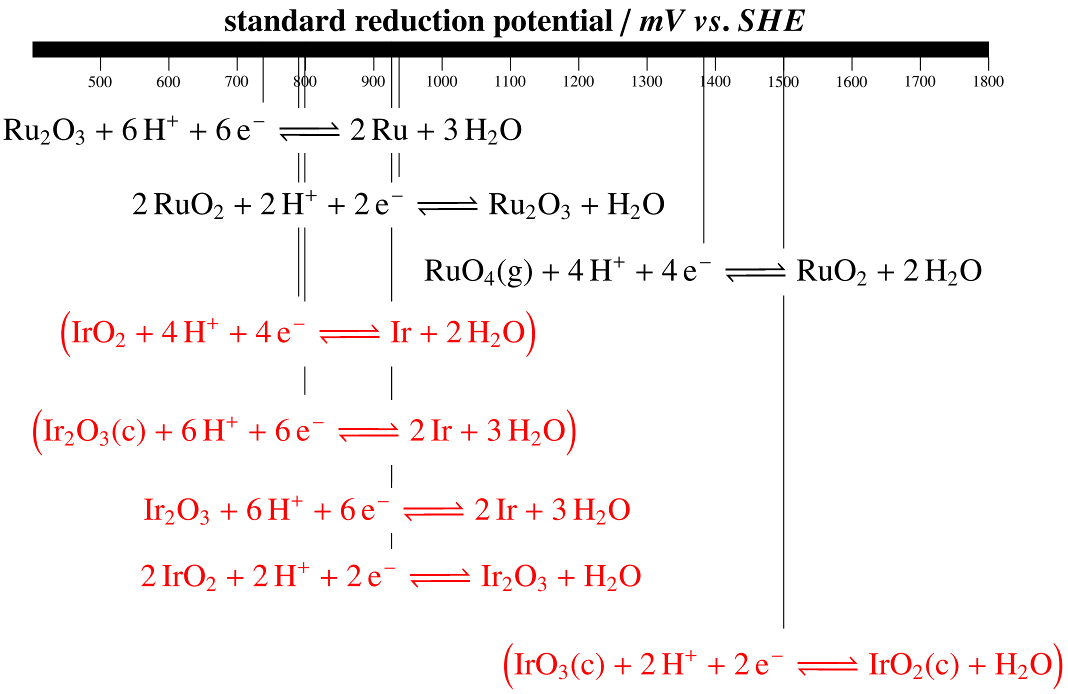


Figure 2.28: The standard reduction potentials[5] of acidic electrochemical half reactions with water for Ru and Ir. Oxides are hydrated unless indicated as crystalline with (c). RuO_4 is volatile so is indicated as gaseous (g). Large parenthesis indicate the potential is "estimated" according to *Bratsch* (1989). Other potentials are taken from *Pourbaix* (1966).

The ability of Ru and Ir to exist in both the 3+ and 4+ oxidation states gives Ir and Ru an electrochemical property known as pseudocapacitance[6]. Shifting of equilibrium potential with the extent of hydration would also play a role in broadening the potential range over which the redox reaction occurs, which would better simulate a true capacitor. The electrochemically formed oxides of Pt are always electrochemically reducible back to the metallic phase, which is not the case for Ir (*Buckley and Burke*, 1975) and Ru (*Hadzi-Jordanov et al.*, 1978).

---

[5] Note that Figure 2.21 shows the potential vs. RHE and SHE are equivalent under acidic conditions (pH <6) for reactions 2.1 through 2.3 (including analogous Ir reactions).

[6] The prefix 'pseudo' is used to distinguish the phenomena from electrical double-layer capacitance. Metals other than Ru and Ir also display this behaviour, e.g. W, Co, (*Conway et al.*, 1997) and Mn (*Subramanian et al.*, 2005).

2.3.4.1 Noteworthy Review Literature on Ru and Ir Electrodes

The electrochemical formation and pseudocapacitive behaviour of anodically grown Ir and Ru oxide is complicated. The behaviour of preoxidized Ir and Ru is also not simple. Research on Ru and/or Ir electrocatalyst materials started in the late 1960's with the goal of understanding Beer's Ru anode invention which revolutionized the chlor-alkali industry. Summarizing the research conducted during the 70's and 80's is challenging, because 1) the jargon is inconsistent, 2) the explanations are highly speculative; few hypotheses were confirmed conclusively according to the rigour expected by present scientific enquiry, 3) there were many contradictory results and disagreements between research groups. For example the nature of the OER mechanism discussed in *Electrochemical Kinetics for Hydrogen Fuel Cells and Electrolyzers* on pg. 15, continues to be a topic of debate. In addition to these challenges, most of the Ir and Ru materials subject to research in this era were thermally prepared oxides; the Ir and Ru catalysts materials herein are synthesized in the metallic phase via magnetron sputtering. Therefore a comprehensive summary of work on the OER catalysed by Ir and/or Ru in acid is beyond the scope of this report.

Nevertheless, as starting points for the aspiring OER-in-acid researcher, the important review publications are listed. A two volume monograph titled "Electrodes of Conductive Metallic Oxides" contains chapters which summarize much of the early (1970's) work on Ir and Ru; these chapters are *Burke* (1980), *Trasatti and Lodi* (1980), *Nidola* (1981), and *Trasatti and Lodi* (1981). A six volume series titled "The Anodic Behaviour of Metals and Semiconductors" also contains chapters by *Gabe* (1981) and *Belanger and Vijh* (1977) which summarize early work on Ru and Ir. Additional important reviews on early literature are "Properties and applications of RuO_2-based electrodes" by *Trasatti and O'Grady* (1981) and "Electrochemistry of Hydrous Oxide Films" by *Burke and Lyons* (1986). Much of this early work focused on fundamental physical properties like crystallography, band structure, and conductivity, as well as electrochemical properties like how the thermal synthesis parameters affected pseudocapacitive charge characteristics, chlorine evolution activity, and oxygen evolution activity (particularly the Tafel slope). Reviews on work completed post 1980's are difficult to find, though *Fabbri et al.* (2014) provides a concise presentation of the hypotheses proposed, and *Cherevko et al.* (2016e) cites a substantial number of studies from this period in his introduction.

It is nevertheless prudent to plainly state the most basic nature of these materials; electrochemically produced oxides of Ru and Ir are pseudocapacitive, amorphous, hydrated, and have a porous quality. The acceptance of these qualities are widespread throughout the literature but their origins are difficult to ascertain. For instance, regarding the hydrated nature, *Pourbaix* (1966) favoured using thermodynamic values for hydrated substances, and some early studies used the word "probably" with respect to the hydrated nature of Ir (*Buckley and Burke*, 1975) and Ru (*Burke and Mulcahy*, 1976). Regarding the pseudocapacitive, amorphous, and porous qualities of anodically grown Ir and Ru oxide electrodes, the review by *Burke and Lyons* (1986) is probably the best source of studies which show, or speculate on these qualities for Ru and Ir. A glimpse into the complexity of the Ir/Ru electrode is presented in the following section.

2.3.4.2 The Anodic Oxidation of Ru and Ir Supported on NSTF and Flat Glassy Carbon

Rather than delve into the literature to explain what happens when Ru and Ir become anodically oxidized, this section shows original data collected at the start of this project.[7]

As previously stated (pg. 59), metallic Ru or Ir are irreversibly electrochemically oxidized. The progress of these changes can be monitored if the upper potential starts below the thermodynamic oxidation potential and is gradually increased. Figures 2.29 through 2.32 show this process for Ru and Ir thin film on flat glassy carbon and on NSTF. (Figure 2.32 (Ir on flat glassy carbon) did not have the upper potential gradually increased). Several questions drove the planning of experiments shown in this section.

1) Can the loss of Ru or Ir metallic phase and gain of Ru or Ir oxide phase be assessed with electrochemical data?

2) When does the metallic Ru or Ir begin transformation into an anodic oxide? (i.e. How far away form the equilibrium potentials in Figure 2.28 does the transition begin?)

3) When is the metallic phase of Ru or Ir completely converted to the oxide phase?

---

[7] The data was never considered for publication because it contains unattractive aspects, such as current outside the measurement range, unknown loadings, and inconsistent testing protocols. Furthermore, the electrochemical testing protocols used could have been refined to better highlight the salient features of the conversion from the metallic phase into the anodic oxide film, because some of the changes which differentiate the development stages are minute. The tests were not repeated with more ideal parameters because the nature of the pseudo capacitive properties of Ir and Ru was not the focus of this research project. Nevertheless, the data is useful and shown here because it comprehensively shows the differences between Ir and Ru and between a flat film and NSTF.

4) Drawing from the behaviour of Ru in Figure 2.27, at what upper potential does Ru OER current peak?

5) Is the OER required for Ru or Ir anodic oxidation?

6) Can the amorphous, hydrated, and porous nature of anodically oxidized Ru or Ir be discerned from electrochemical data only?

The testing protocol for each experiment is shown as a potential vs. time graph split left-to-right, top-to-bottom over panels A, B, and C. Panels D and E show selected CVs which are cross-referenced to the testing protocol (panels A, B and C) by colour. Panel D shows the CVs when the material is mostly metallic, and panel E shows the CVs when the material is mostly oxide. Panel F shows an attempt to track various species with well defined points on the CV (this is an attempt to answer to question **1**)). Labelled CVs in panels A, B, C and F CVs that demarcate key transition points in the anodic oxide transformation are based on maxima and minima of these quantitative phase/species indicators in panel F. These phases/species are H_{UPD}, reversible oxide and irreversible oxide. The H_{UPD} species quantifier is the H_{UPD} desorption region (0 to ~ 0.2 V_{RHE}) maximum current minus the double-layer region[8] ($\sim$0.2 to $\sim$0.4 V_{RHE}) minimum current. A distinction will be made between the two types of electrochemical Ru or Ir oxide (reversible and irreversible) in the following sub-sections. Three CV labels (and colours) are common to all Figures (2.29 through 2.32). One of these key transition points is a yellow CV with different labels for Ru ("Min. cap. in non-H_{UPD} region", (where cap. = capacitance)) and Ir ("Start of irrev. oxide growth" (where irrev. = irreversible)). This yellow CV could be thought of like a mid-way point between the metal and oxide phase, and so is always shown in both panel D and E. Two additional CV labels are used for Ru.

The basic form of the testing protocol for the Ru samples was alternating CVs and holds. The upper potential gradually increased from 0.76 to ~ 1.7 V_{RHE} to observe the expected instability after ~ 1.383 V_{RHE} (i.e. to answer question **4**)). Ir does not have an expected instability threshold (the conversion to IrO_3 is not well documented and not observed with electrochemical data only, see Section 2.3.5), so a different type of protocol was developed. The upper limit of all CVs (Ru and Ir) was capped at 1.2 V_{RHE}.

---

[8] Throughout this report, the phrase "double-layer region" should be taken to mean the potential range between the H_{UPD} desorption/adsorption and the reversible oxide formation/reduction. For Pt, the current in this range is due to double-layer charging. For Ir and Ru, the current in the "double-layer region" contains Faradaic contributions because there is some overlap between H_{UPD} desorption/adsorption and reversible oxide formation/reduction.

What drove the design of the testing protocol for Ir? Two things about Ir on flat glassy carbon and on NSTF were known from prior unpublished work: 1) significant pseudocapacitance growth on Ir occurs in conjunction with the OER, and 2) the potential at which noticeable OER current starts, the onset potential, was known. Therefore, the question arose: is O_2 evolution necessary for Ir pseudocapacitance growth? (i.e. question **5**)). The upper hold potentials in Figures 2.31 and 2.32 were chosen to be just before the OER onset potential (the anodic hold current was always $< 0.005\ mA\ cm^{-2}$). Figure 2.31 (Ir on NSTF) panels A, B and C show the potential holds were always at 1.35 V_{RHE} and Figure 2.32 (Ir on glassy carbon) panels A, B and C show that the potential holds were always at 1.4 V_{RHE}.

Before the questions on the conversion of metals to oxides are specifically answered, two other phenomena, observable in Figures 2.29 through 2.32 are addressed in the two following sections: *Electrochemical Cleaning* and *Reversible Oxides*. One should be familiar with the knowledge and terminology associated with the Pt CV in Figure 1.8 (pg. 19) before proceeding with this section.

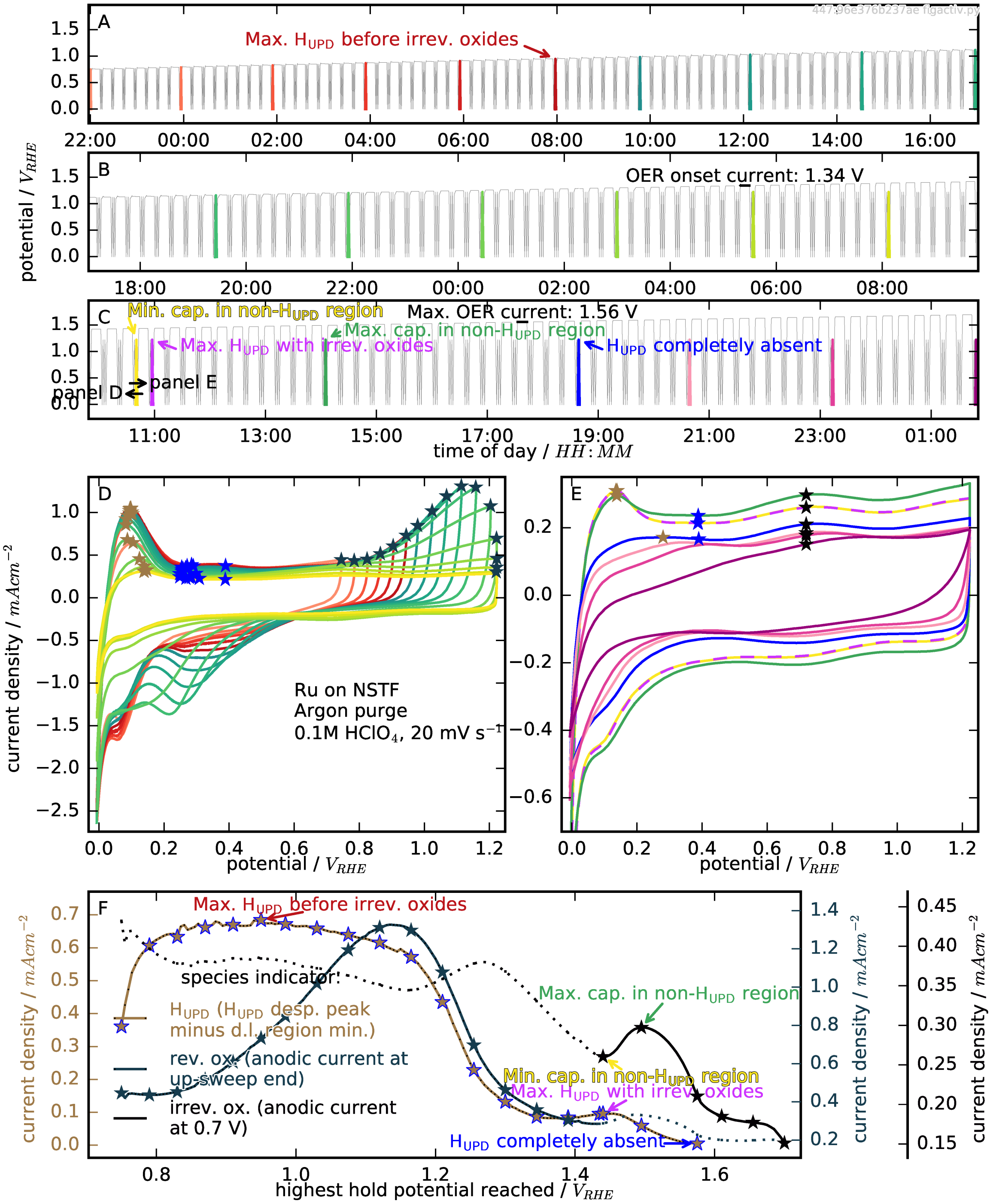


Figure 2.29: The anodic oxidation of Ru sputtered (see Section 3.2.3) on NSTF grown by 3M on pyrolytically coated compressed graphite (see Sections 3.2.1 and 3.2.2). Potential was measured vs. a mercury/mercurous sulfate electrode (MSE) then converted to RHE ($V_{RHE} = V_{MSE} + 0.638\ V$). Abbreviations: cap.= capacitance, rev.= reversible, irrev.= irreversible, desp.= desorption, d.l.= double-layer.

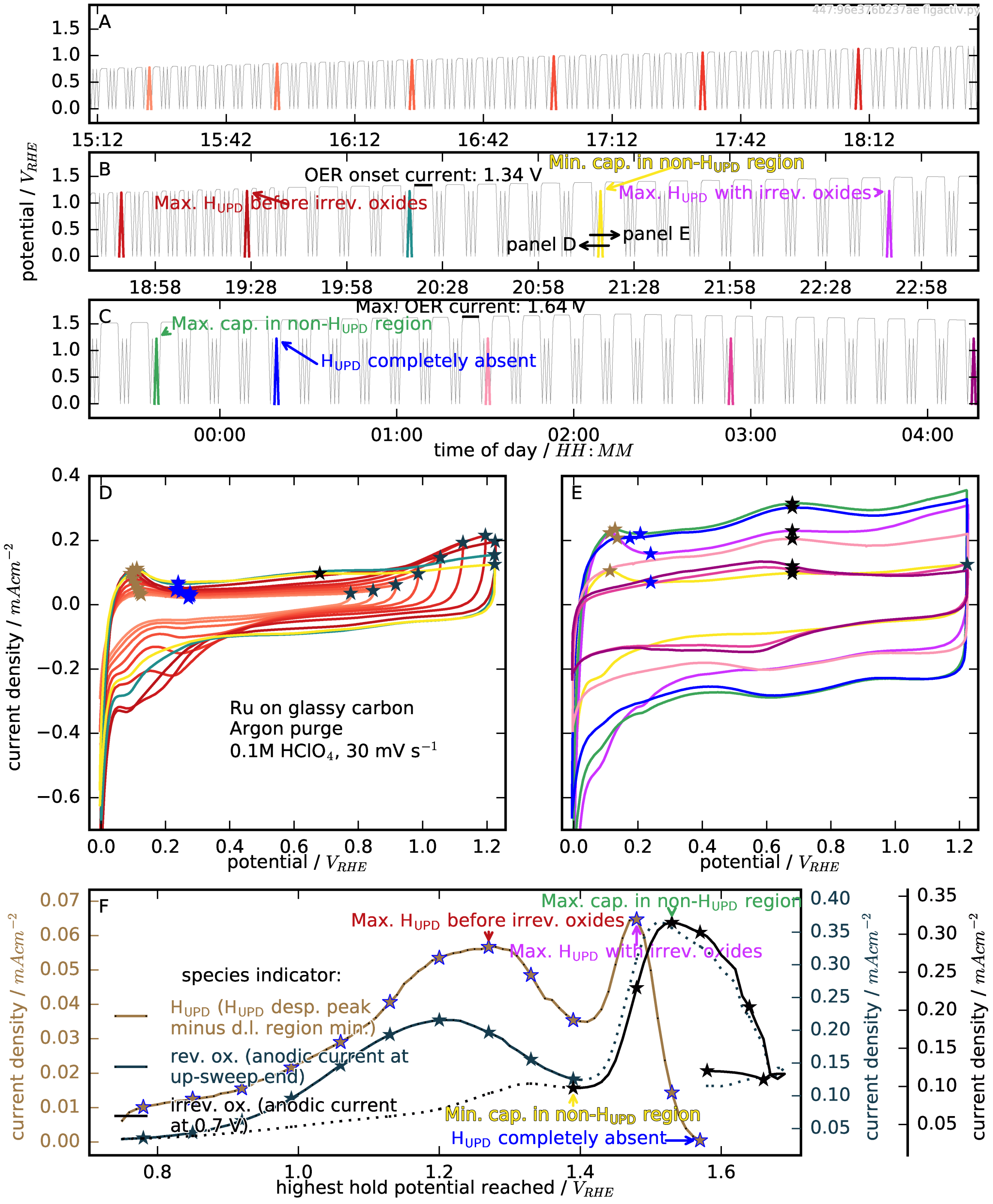


Figure 2.30: The anodic oxidation of Ru sputtered (see Section 3.2.3) on flat glassy carbon (final polish with 5 micron alumina suspension). Potential was measured vs. MSE then converted to RHE ($V_{RHE} = V_{MSE} + 0.638\ V$). Abbreviations: cap.= capacitance, rev.= reversible, irrev.= irreversible, desp.= desorption, d.l.= double-layer.

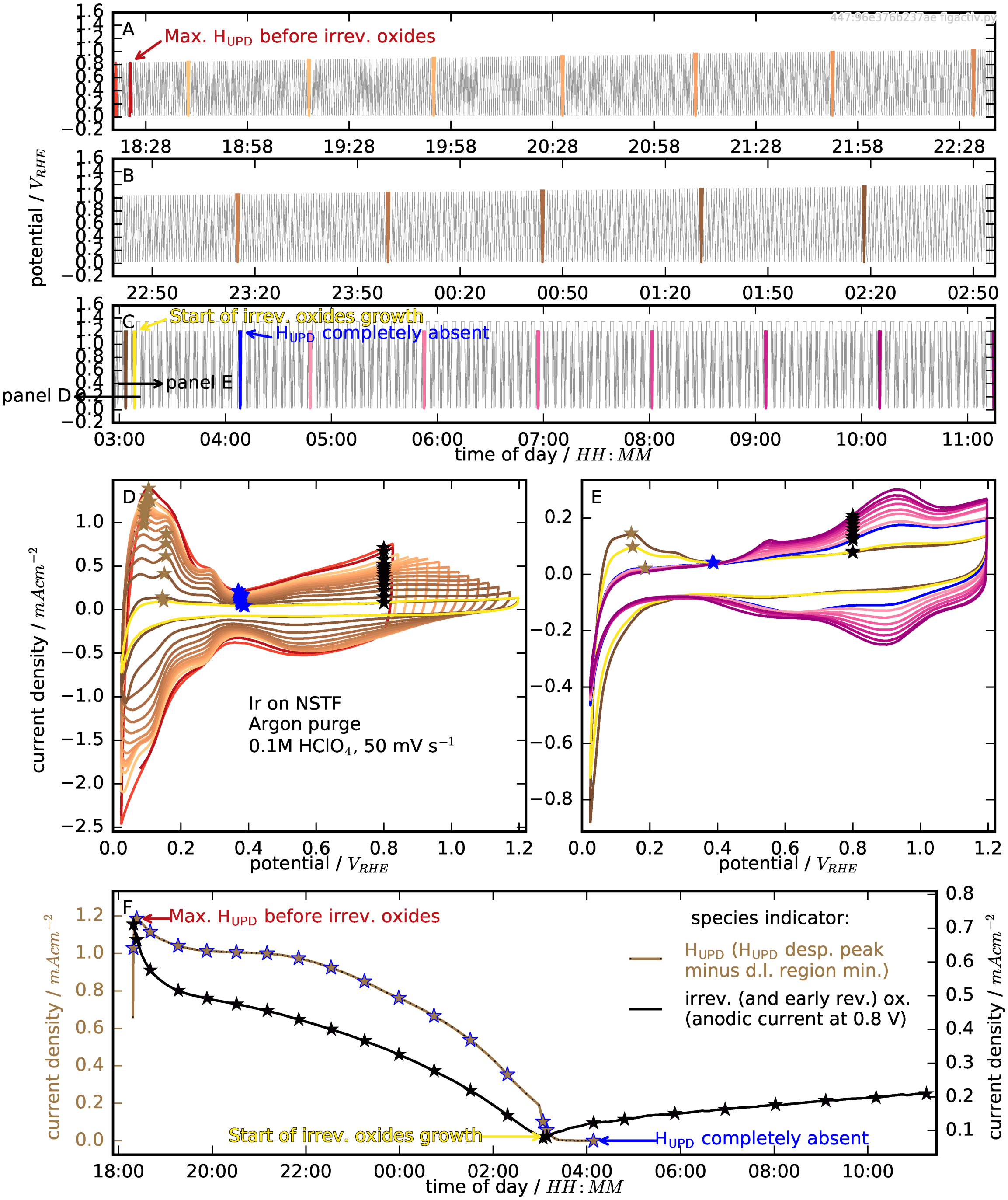


Figure 2.31: The anodic oxidation without OER of Ir sputtered (see Section 3.2.3) on NSTF grown by 3M on on pyrolytically coated compressed graphite (see Sections 3.2.1 and 3.2.2). Potential was measured vs. MSE and converted in real time to RHE via electronics hardware (see Section 3.1.5). Abbreviations: cap.= capacitance, rev.= reversible, irrev.= irreversible, desp.= desorption, d.l.= double-layer.

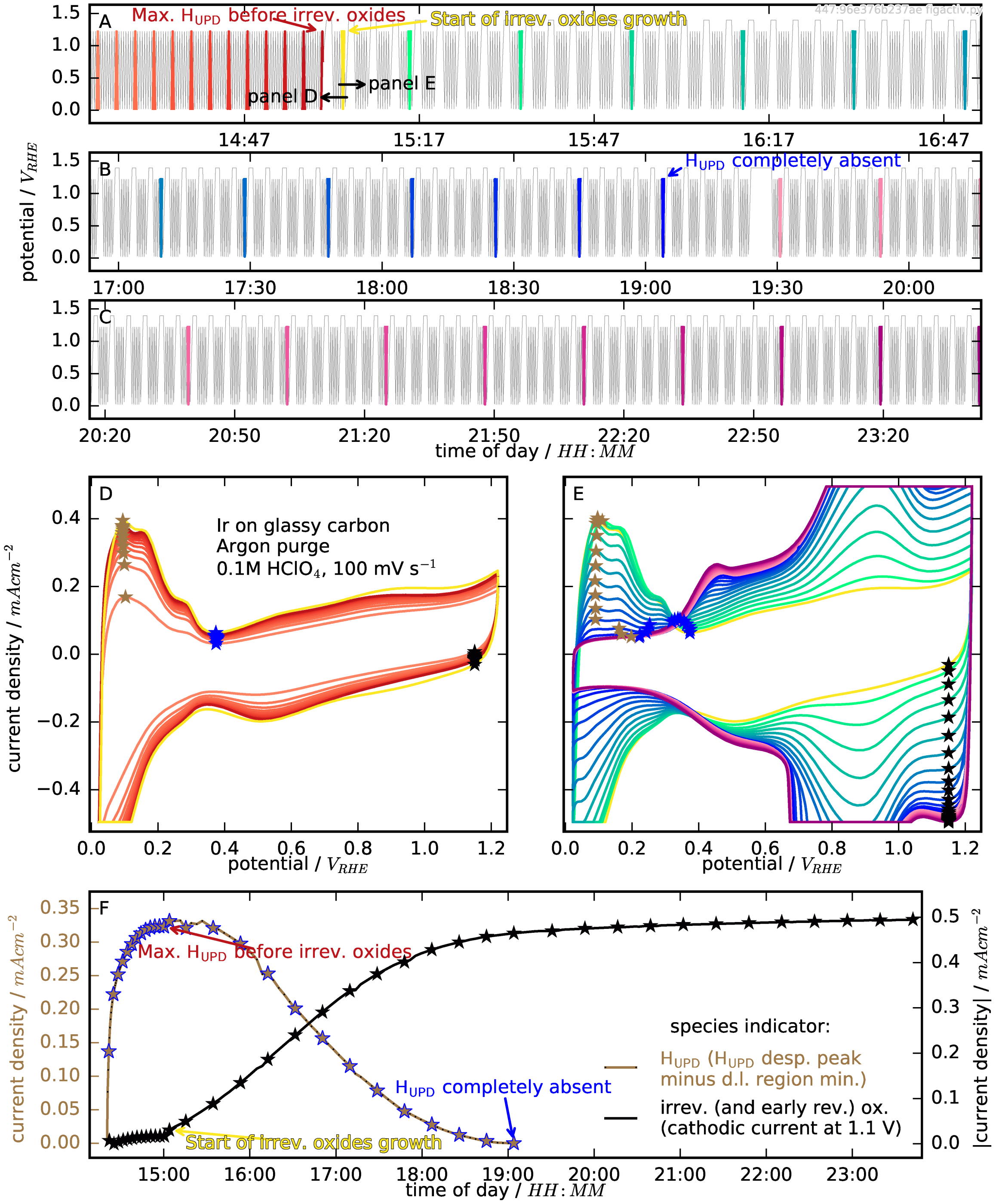


Figure 2.32: The anodic oxidation without OER of Ir sputtered (see Section 3.2.3) on flat glassy carbon (final polish with 5 micron alumina suspension). Potential was measured vs. MSE and converted in real time to RHE via electronics hardware (see Section 3.1.5). Abbreviations: cap.= capacitance, rev.= reversible, irrev.= irreversible, desp.= desorption, d.l.= double-layer.

Electrochemical Cleaning

It is widely accepted the voltammetric waves in the lower potential region (0 to 0.4 V_{RHE}) of PGMs correspond to H_{UPD} desorption (positive/anodic current) and adsorption (negative/cathodic current); for example, *Woods* (1974) studied the H_{UPD} features of Pt, Ir and Rh. Therefore an H_{UPD} desorption charge on Ru or Ir should correspond directly to the metallic surface area as for Pt. Since H_{UPD} is directly adsorbed on (and desorped off) metal atoms, contaminants which adsorb to PGMs may inhibit this surface reaction and thus decrease the charge/area of the CV features associated with this reaction (*Solla-Gullón et al.*, 2000). PGM adsorbing contaminants like volatile organic molecules, NO_x, SO_x, H_2S, CO and NH_3 may be present in ambient air. Electrochemical cleaning removes these substances through desorption or electrochemical oxidation with a rapidly alternating potential. Often, CVs with a rapid sweep rate of 500 $mV\ s^{-1}$ are used. The most familiar use of electrochemical cleaning is for Pt, where the peaks become sharper with each consecutive CV cycle, culminating in a stable CV shape. The cleaning CVs are generally not shown in published CVs of Pt or Pt-alloy materials. For more details on electrochemical cleaning of Pt, see *Solla-Gullón et al.* (2000). The following are remarks about the electrochemical cleaning observed for each of the figures:

- Figure 2.32 (Ir on flat glassy carbon): panel D (0 to 0.4 V_{RHE}, anodic/positive current) shows the H_{UPD} desorption wave grows with time and stabilizes at ~83 CV cycles (14:53 panel A/F). This is good evidence of electrochemical cleaning. However, Pt does not take this long to reach a stable CV. Why does the cleaning process take much longer for a flat film of metallic Ir than it would for Pt? This question has no obvious answer in the literature. Perhaps it is simply the nature of Ir, that it does not catalyse the oxidation of organics well, or perhaps the sample was exposed to some air particularly laden with difficult to oxidize organic compounds.
- Figure 2.31 (Ir on NSTF): Panel F shows the H_{UPD} species indicator is reached very quickly (within eight cycles), after which the CV shape uniformly shrinks for many cycles (light to dark copper colour, most of panel A and B). This was quite mysterious upon initial analysis. An explanation is offered on pg. 76.
- Figure 2.29 (Ru on NSTF): panel D shows a couple of cleaning CVs. These are mostly hidden behind all the other CVs, but the effect can be see in panel F: the H_{UPD} species indicator takes ~ 10 CV sets to reach a relatively stable value

(~0.65 $mA\,cm^{-2}$).

- Figure 2.30 (Ru on flat glassy carbon) does not show definitive electrochemical cleaning behaviour.

Figures 2.29 though 2.32 show features which appear similar to platinum's oxidation reduction behaviour. These features are discussed before addressing the questions on the anodic oxide conversion process, because they appear while the electrode is metallic, i.e. in conjunction with the H_{UPD} peaks.

Reversible Oxides

In addition to the H_{UPD} adsorption and desorption waves, Ru and Ir can display CV features highly reminiscent of reversible[9] oxide formation and reduction displayed by Pt. The widely accepted understanding for Pt, goes as follows: as the potential is swept up from the double-layer region toward more positive potentials, 2-D phases of adsorbed hydroxide groups (from an electrochemical reaction with water) form on the metallic surface. As the potential increases, the hydroxide groups are electrochemically reduced to adsorbed oxygen atoms. In each step, protons are added to the electrolyte and electrons to the electrode. Further complexity is added to the Pt oxidation process by place-exchange (discussed in *The Nature of Electrochemical Pt Dissolution* on pg. 27) which enables the formation of an oxide phase beyond the thickness of a monolayer, i.e. the 2-D phase. The process has been well characterized with electrochemical data along with other techniques, and summarized in the review by *Conway* (1995). A similar process probably happens on Ir and Ru. For example, a distinction between thin (monolayer) oxygen species and thicker oxide layers has also been presumedfor Ir (*Peuckert* (1985) and *Woods* (1979)) and Ru (*Hadzi-Jordanov et al.*, 1978) based on electrochemical data only. Therefore, it can assumed that the presence of a metallic phase can be inferred from both H_{UPD} CV features, and CV features that correspond to the formation (and reduction) of the reversible oxide. Both are electrochemical reactions which form a 2-D phase on a metallic surface.

---

[9] The words reversible and irreversible can have different meanings within the field of electrochemistry. Sometimes even within the same context, their usage can be inconsistent For example, a reversible oxide in this report is taken to mean an electrochemically formed oxide which can be electrochemically reduced back to metal. This usage is consistent with reports by L. D. Burke in his reports on Ru and Ir. In studies on Pt by B.E. Conway, the meanings are different. The reversible oxide is taken to mean that portion of the electrochemically formed oxide which shows no hysteresis in reduction after formation, and that portion which does show hysteresis is called an irreversible oxide.

The reversible oxide on Ru is tracked in panel F with the positive/anodic current at the end of each up-sweep. The reversible oxide is not tracked for Ir because on Ir, the reversible oxide peaks grow into the irreversible oxide peaks, with no prior diminishing, as for Ru. The following observations are on the voltammogram features that correspond to the reversible oxide.

1. Figure 2.29 (Ru on NSTF): panel D (0.75 to 0.82 V_{RHE}, anodic/positive current) shows the oxide formation peaks are initially absent or very small. The peaks reach a maximum when the upper CV potential reaches 1.14 V_{RHE} (panel D/F).
2. Figure 2.30 (Ru on flat glassy carbon): panel D, 0.7 to ~0.9 V_{RHE}, anodic/negative current shows the formation peaks are initially absent or very small. The peaks reach a maximum when the upper CV potential reaches 1.2 V_{RHE} (panel D/F).
    - Ru in general: panel D shows a double-layer region is impossible to discern, in stark contrast to Pt. The D panels, 0.1 to 0.4 V_{RHE}, cathodic/negative current show there is strong overlap of the oxide reduction peak with the H_{UPD} adsorption peak. This was also observed by *Hadzi-Jordanov et al.* (1978)).
3. Figure 2.31 (Ir on NSTF): See general comments below.
4. Figure 2.32 (Ir on flat glassy carbon): See general comments below.
    - Ir in general: The D panels show the oxide waves (0.4 to 1.2 V_{RHE}, positive current) and their corresponding reduction peaks (0.4 to 0.8 V_{RHE}, negative current) are more similar to Pt then Ru, but there is still some overlap with the H_{UPD} regions. For this reason, the double-layer region (~0.35 to 0.45 V_{RHE}) is less clear than for Pt (see Figure 1.8, 0.37 to 0.55 V_{RHE}) and does not reflect the true double-layer current.

The Conversion to Anodic Oxide

The six questions on the conversion of metals to oxides listed on pg. 61 are now specifically answered, using Figures 2.29 through 2.32.

1) *Can the loss of Ru or Ir metallic phase and gain of Ru or Ir oxide phase be assessed with electrochemical data?* In general yes, and the answer is the F panels. Oxides will be addressed first.

- **Oxide Gain:** Two types of oxide can be electrochemically quantified, one of which, the 2-D reversible oxide, is actually an indicator of the underlying metallic phase. The gain of the other type of oxide, the irreversible type, can be estimated with CV data for both Ru and Ir.

  - **Ru:** panel F shows the irreversible oxide was estimated with the positive/anodic current at 0.7 V_{RHE}. This potential was chosen because, by visual assessment, its current was most closely in proportion to the area bound by the entire CV (excluding the H_{UPD} waves).
  - **Ir:** panel F shows the irreversible oxide for Ir on NSTF was estimated with the positive/anodic current at 0.8 V_{RHE}. The current at any potential > 0.45 V_{RHE} could have been used. For Ir on flat glassy carbon, the irreversible oxide was estimated with the negative/cathodic current at 1.1 V_{RHE}, because the current for most other potentials within the irreversible oxide range (> 0.45 V_{RHE}) surpasses the limits of measurement.

- **Metallic Loss:** The metallic phase loss (due to irreversible oxidation) can be estimated with an H_{UPD} or reversible oxide wave.
  - **Reversible Oxide:** The gain and loss of the reversible oxide can be estimated for Ru only. The gain and loss of reversible oxide for Ir cannot be tracked because the reversible oxide peaks grow into the irreversible peaks. The Ru F panels show the reversible oxide was estimated with the positive/anodic current at the end of the up-sweep. The cathodic/negative reversible oxide reduction wave cannot be used because it overlaps with the H_{UPD} adsorption wave. The Ru F panels show two maxima and one minimum. The data after the minimum (dotted line) is not indicative of reversible oxide because of influence from the irreversible oxide. The increase in the reversible oxide species indicator (i.e. before the first maximum) should not be interpreted as an increase in metallic phase.
  - **H_{UPD}:** The H_{UPD} species can be quantified with the difference between an H_{UPD} wave peak current and the corresponding anodic or cathodic minimum current in the double-layer region. This was easier than determining a wave area/charge. For Ru, the H_{UPD} $\underline{\text{de}}$sorption wave must be used to assess metallic phase loss because of the aforementioned H_{UPD} $\underline{\text{ad}}$sorption wave overlap with the reversible oxide reduction wave.

2) *When does the metallic Ru or Ir begin transformation into an anodic oxide? (i.e. How* *far away form the equilibrium potentials in Figure 2.28 does the transition begin?)* It is safe to assume the transformation begins at the first sign of decrease of metallic surface area.

- **Ru** The F panels show the first maximum (or beginning of decrease) of the $\mathrm{H_{UPD}}$ species indicator and reversible oxide species indicator are at different upper hold potentials. Furthermore, F panels show the order of maxima are switched for the two types of Ru. What species indicator is best for predicting when the metallic phase truly starts decreasing? Probably the reversible oxide indicator, because the double-layer region minimum does not represent the true double-layer current, and this is because oxide reactions (reversible and irreversible) occur over the entire CV potential range. This is probably the source of the odd behaviour seen in the $\mathrm{H_{UPD}}$ indicator, like two maxima for both samples, and a very slow initial increase to the first maximum for the flat film sample. Furthermore, the reversible oxide maxima (1.14 V_{RHE} for NSTF and 1.2 V_{RHE} flat film on glassy carbon) are closer together than the maxima for the $\mathrm{H_{UPD}}$ indicators. These potentials are well above the equilibrium potential for the first anodic oxidation of Ru (0.738 V_{RHE}).
- **Ir** There is no reversible oxide indicator, so the beginning of metallic phase loss should be estimated with the $\mathrm{H_{UPD}}$ indicator, but this is not possible for both Ir samples. For the Ir flat film, the $\mathrm{H_{UPD}}$ reaches its maximum after the first 1.4 V_{RHE} hold. However, the irreversible oxide indicator also jumps up after this potential hold. Therefore the exact beginning of metallic phase loss is difficult to discern using only electrochemical data. For Ir on NSTF, the $\mathrm{H_{UPD}}$ indicator starts to shrink after ~4 CVs. This may be loss of metallic Ir, but not because of conversion to irreversible oxide (details in the next Section), therefore the irreversible oxide indicator must be used to determine when the transformation to anodic oxide begins, which is after the first two 1.35 V_{RHE} holds. It is impossible to tell how 'far away' from the equilibrium potential the conversion starts because of the Ir testing protocol.

3) *When is the metallic phase of Ru or Ir completely converted to the oxide phase?* The completion of the conversion from metal to irreversible oxide can be easily discerned by the disappearance of the $\mathrm{H_{UPD}}$ wave.

- The point at which this occurs, is the CV labelled "$\mathrm{H_{UPD}}$ completely absent" in all Ru and Ir Figures. This point was algorithmically determined when either the H_{UPD} desorption maximum, became less than the double-layer region minimum, or in the case of overlapping potential ranges, when the potential of the double-layer region minimum became less than the potential of the H_{UPD} desorption maximum. Table 2.1 shows the potential ranges for searching for the these values.

Table 2.1: Potential ranges (in V_{RHE}) for searching for the H_{UPD} desorption maximum and the double-layer region minimum.

	NSTF		Flat Film	
	H_{UPD} region	double-layer region	H_{UPD} region	double-layer region
Ru	0.02 to 0.35	0.19 to 0.39	0.02 to 0.17	0.17 to 0.6
Ir	0 to 0.19	0.185 to 0.5	0 to 0.20	0.22 to 0.4

- **Ru** It is interesting to note the H_{UPD} desorption wave lasts many CV cycles after there are no traces of reversible oxide waves, and even after the Ru has started to corrode (after the green CV label "Max. cap. in non-H_{UPD} region"). Perhaps the H_{UPD} can form on metallic Ru covered by an irreversible oxide, and the reversible oxide reaction can only happen on metallic Ru in contact with the electrolyte.
- **Ir** It should be noted that using the H_{UPD} wave shrinkage to track the conversion of the Ir metallic phase to oxide is possible only because the amount of Ir is practically finite. Experiments with bulk Ir show no change in H_{UPD} features with the growth of pseudocapacitance (*Buckley and Burke* (1975) and *Peuckert* (1985)).

4) *Drawing from the behaviour of Ru in Figure 2.27, at what upper potential does Ru OER current peak?* These potentials are labelled in the C panels of the Ru Figures.

- The potential at which the OER current reaches a maximum for Ru on NSTF is 1.56 V_{RHE} and for the flat Ru film, is 1.64 V_{RHE}. However, the CVs show the Ru loss starts earlier than this. The irreversible oxide reaches a maximum (the green CV and label "Max. cap. in non-H_{UPD} region") at 1.495 V_{RHE} for the NSTF sample and 1.53 V_{RHE} for the flat film sample. It is safe to assume that this maximum is caused by Ru corrosion at subsequently higher hold potentials. For both samples, the equilibrium potential for Ru corrosion (1.383 V_{RHE}) is passed even before the anodic oxide pseudocapacitance (irreversible oxide indicator) starts to grow (the yellow CV labelled "Min. cap. in non-H_{UPD} region", occurring at 1.39 V_{RHE} for flat film, and 1.44 V_{RHE} for NSTF). More careful experiments would be required to ascertain the practicable tipping point potential for Ru stability.

5) *Is the OER required for Ru or Ir anodic oxidation?* Presumably yes for Ru, definitely no for Ir.

- **Ru** The protocols were not designed to answer this question, but in each Ru Figure's panel B, the potential at which OER current begins is noted as 1.34 V_{RHE} (labelled "OER onset current"). This is a subjective threshold that was determined by visual assessment of the chronoamperometry data for each potential hold. Nevertheless, it points to the fact that the OER starts while there is still some reversible oxide activity. It would be interesting have question #**5**) answered, i.e. find out if some irreversible oxidation could be started if the alternating cycle-hold protocol was prolonged with the upper potential kept below 1.34 V_{RHE}.
- **Ir** The test protocols were designed to answer this question, and indeed, it has been shown than the OER is not required for irreversible oxidation and pseudocapacitance growth.

6) *Can the amorphous, hydrated, and porous nature of anodically oxidized Ru or Ir be discerned from electrochemical data only?* No.

- For Ir, the pseudocapacitance continues to increase after the electrochemical evidence for the presence of a metallic phase (the H_{UPD} peaks) disappears. This is particularly noticeable for the NSTF sample. There are two possible explanations for this: Either the material becomes more porous, which could increase the number of Ir sites that participate in the oxidation/reduction reaction, or some metallic Ir, which cannot be observed electrochemically, remains. Regarding the latter, if the resistance of electrical pathway to the metallic Ir is significantly higher than normal, the adsorption/desorption of H_{UPD} could be stopped. It is conceivable this happens on NSTF supported Ir because there is always more material deposited on the tip of the NSTF whisker. Figure 2.33 shows a TEM image on an NSTF whisker coated with Pt, and a schematic showing the location of the hypothetical remaining metallic Ir which cannot be observed via the H_{UPD} reactions.

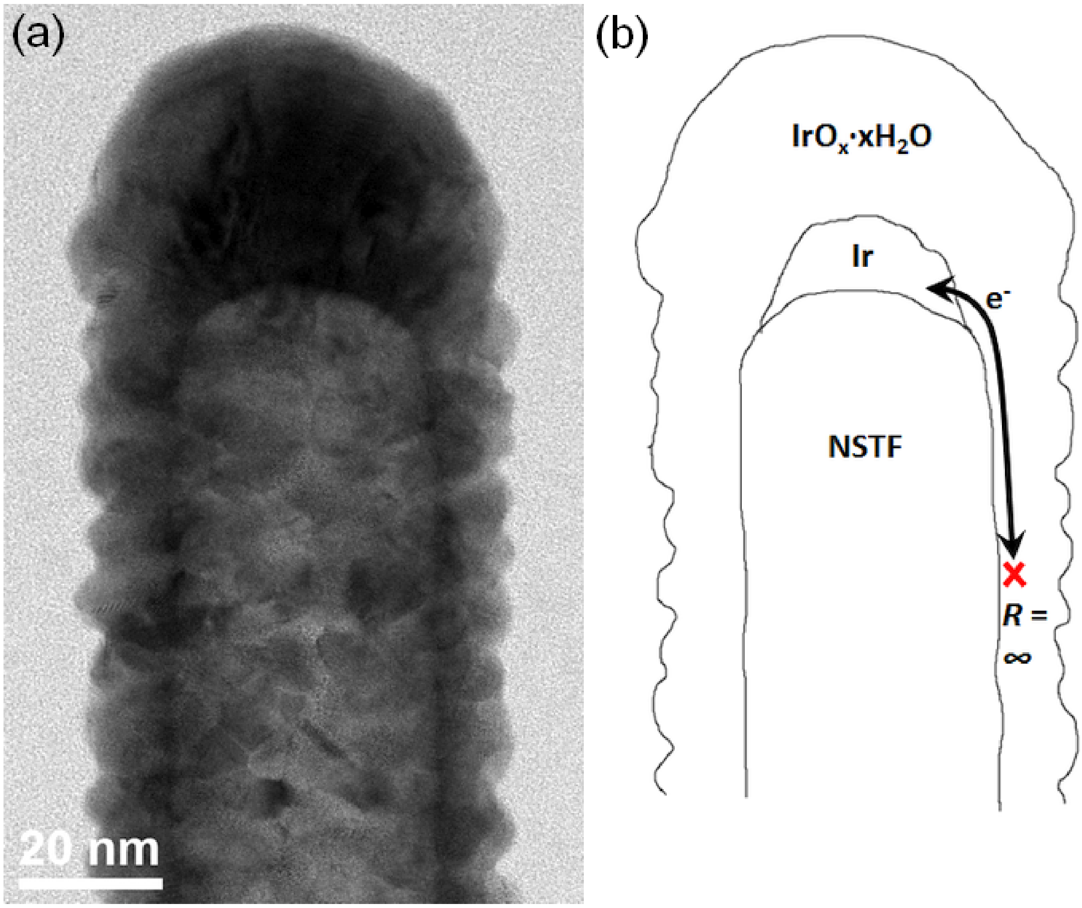


Figure 2.33: **(a)**: A TEM image from *Cullen et al.* (2014) of a single NSTF whisker sputter coated with 85 $\mu g\, cm^{-2}$ of Pt. **(b)**: A hypothetical schematic, draw to the scale of the whisker in panel (a), of an Ir coated NSTF whisker with some unconverted metallic Ir remaining. The panel (b) schematic is offered as a possible explanation for the continued growth in pseudocapacitance despite the disappearance of the H_{UPD} peaks (seen in Figure 2.31E). Recall, NSTF is an organic material and not an electric conductor.

The H_{UPD} Shrinkage of Ir on NSTF

Up to this point, explanations have been provided for the development of the CVs in Figures 2.29 through 2.32 with one major omission: the shrinkage of the CVs in Figure 2.31D (Ir on NSTF). The shrinking behaviour of Ir on NSTF was very mysterious. It was thought perhaps with cycling, Ir crystallites on the NSTF were converted to an amorphous phase with less activity for H_{UPD} or reversible oxide reactions. Based on the literature reviewed at the time of these experiments (~2010 to 2012) Ir corrosion was not even considered as an explanation, as Ir has a reputation for excellent physical and chemical stability in the field of materials engineering. Based on very recent knowledge from the ICP-MS flow cell technique (*Cherevko et al.*, 2014), the mysterious shrinking behaviour of Ir on NSTF is probably due to Ir dissolution, or more specifically, "cathodic" dissolution, explained in the Section 2.3.5.

Summary

The anodic oxidation of Ru or Ir results in the conversion of the metallic phase to an oxide phase though electrochemical half reaction with water. This oxide phase, called an anodic oxide, or irreversible oxide in this report is hydrated, amorphous, and cannot be electrochemically reduced back to a metal (in contrast to a thickened Pt anodic oxide, which can always be electrochemically reduced back to Pt metal with sufficiently low potential). This oxide phase provides additional capacitance over and above the electrolyte capacitance from the electric double-layer, and the capacitance provided by surface reactions involving the adsorption and desorption of a monolayer of some chemical species from the electrolyte (i.e. the H_{UPD} and reversible oxides). This additional capacitance, called pseudocapacitance, arises from the facile switching between oxidation states +3 and +4; The pseudocapacitance growth is probably encouraged by potential cycling, though this hypothesis was not directly tested by the experiments presented in this section.

For all the respects discussed in the preceding paragraph, Ru and Ir behave the same, but there are some specific differences. Table 2.2 shows a summary of the differences between Ir and Ru.

Table 2.2: The differences between Ir and Ru regarding the development of reversible and irreversible oxides.

observable characteristic in CV	**Ru**	**Ir**
extent of hysteresis of reversible oxides	there is overlap between the reduction of reversible oxide and H_{UPD} adsorption (Ru has more hysteresis than Pt, and more than Ir)	no clear double-layer region as with Pt, small overlap between reversible oxide and H_{UPD} adsorption (hysteresis is less than Ru, more than Pt)
pseudocapacitance features	almost featureless pseudocapacitance, broad peaks in middle (0.6 V_{RHE}) and end (1.2 V_{RHE}) of CV	pseudocapacitance shows clearly discernible peaks
potential range of pseudocapacitance	increased capacitance over entire water stability range	no increased capacitance in H_{UPD} region
concurrence of reversible and irreversible oxides	reversible oxide starts to disappear when upper potential reaches $\sim 1.2\ V$ and seems to completely disappear before irreversible oxide growth begins	fate of reversible oxide unclear from electrochemical data, but the waves seem to morph into irreversible oxide waves, suggesting both types of oxides can co-exist

It is hoped that this rather lengthy section has provided the reader with a appreciation of the complexity of Ir and Ru electrodes. The most important takeaway message is that these materials are dynamic, always changing, even under steady state conditions, making them difficult to consistently characterize across disparate research efforts. Though not explicitly demonstrated in this Section, the OER activity of an anodically oxidized Ru/Ir electrode is highly dependant on its electrochemical history. Similarly, if the electrodes are synthesized as oxides, the OER properties are also highly dependant on the synthesis parameters (this was the conclusion of much of the early literature listed in the Section *Noteworthy Review Literature on Ru and Ir Electrodes*, pg. 60). Being precious metals, Ru and Ir are always prepared on some kind of catalyst support or substrate, which also has a significant influence on OER properties. Optimizing the factors that affect stability (Ir to Ru ratio) and activity (synthesis parameters, electrochemical pretreatment, and substrate) could be considered an art, perhaps reminiscent of the early days of metallurgy. Should a hydrogen economy ever be realized, and water electrolysis play an important role in hydrogen production, research on these materials will certainly intensify.

2.3.5 Stability of Ir and Ru

Iridium is arguably the most corrosion resistant of all the noble metals, inert to the dissolving action of molten metals and aqua regia, (*Hunt*, 1987) except the finely divided state (i.e. Ir “black”) which is soluble in hot concentrated aqua regia (*Pourbaix*, 1966). Iridium dioxide, even in the finely divided state, is insoluble in acids (including aqua regia) and bases. Only hydrated IrO_2 (prepared by boiling alkali metal iridochloride with lye in air) is soluble in acid (hydrochloric, nitric, and sulphuric) and slightly soluble in alkalis (*Pourbaix*, 1966). Is the electrochemical stability of Ir congruent with its reputation for physical and chemical resilience? Not quite... *Rand and Woods* (1974) were probably the first to report electrochemical Ir dissolution from a Ir electrode cycled between 0.06 to 1.54 V_{RHE}. *Buckley and Burke* (1976) were probably the first to report the dissolution of Ir for prolonged (0 to 200 *min*) holds between 1.85 to 1.95 V_{SHE}. Interestingly, each these early studies unknowingly triggered only one of the two mechanisms of Ir dissolution; the dynamic mechanism is probably exclusively active in *Rand and Woods* (1974), and the anodic mechanism is almost certainly the only mechanism at work in *Buckley and Burke* (1976). These two mechanisms have, like for Pt, been clarified only very recently by researchers working under Karl Mayrhofer’s electrocatalysis group at the Max Planck Institute for Iron Research using their ICP-MS flow cell method (*Klemm et al.*, 2011).

2.3.5.1 Anodic Dissolution of Ir and Ru

The suspected culprit of anodic Ir dissolution is IrO_3 formation, but it is difficult to find rigorous evidence which proves this compound is electrochemically formed, and leads to Ir migration to the electrolyte. *Kötz et al.* (1984a) proposed an OER mechanism which includes an Ir dissolution reaction:

$$IrO_3 + H_2O \longrightarrow {IrO_4}^{2-} + 2\,H^+ \tag{2.6}$$

Kötz et al. (1984a) credits this to *Burke* (1980), but there is nothing in *Burke* (1980) even suggestive of such a reaction. Regarding IrO_3, this compound does exist as a gas at high ($> 800°C$) temperatures due to equilibria between Ir, IrO_2 and O_2 (*Cordfunke and Meyer*, 1962). Also, Figure 2.28 (pg. 59) shows crystalline IrO_3 as an electrochemical oxidation product of crystalline IrO_2, with a estimated standard reduction potential of 1.5 V_{SHE}

(*Bratsch*, 1989). Regarding IrO_4^{2-}, the existence of this ion is confirmed by *Pourbaix* (1966) who states: "on fusion with alkaline oxidizing substances (hydrated IrO_2) forms iridate IrO_4^{--}". However, there seems to be no evidence of IrO_4^{2-} existing in acidic solution, casting some doubt on the mechanism of *Kötz et al.* (1984a) (Reaction 2.6).

Figure 2.34B shows the mechanism of *Kötz et al.* (1984a) from which Reaction 2.6 is obtained. It corresponds nicely to a more believable OER mechanism for Ru (*Kötz et al.* (1983), Figure 2.34A), which links oxygen evolution to the well known Ru anodic corrosion reaction. Both mechanisms require the evolution of O_2 be preceded by the formation of an unstable oxide. *Kötz et al.* (1984b) provide experimental support for the Ru OER dissolution mechanism with data on dissolved Ru amounts, in proportion with OER rate. *Kötz et al.* (1984a) do not provide experimental evidence of concurrent Ir dissolution and oxygen evolution, but showed X-ray photoelectron spectroscopy (XPS) evidence for Ir^{6+} existence during the OER, and cite *Wöhler and Witzmann* (1908) regarding the instability of IrO_3. *Wöhler and Witzmann* (1908) "reported that by fusing iridium with sodium per-oxide, a compound of approximate composition IrO_3 could be obtained, and that this liberates oxygen on treatment with sulphuric acid solution."—*Buckley and Burke* (1976)

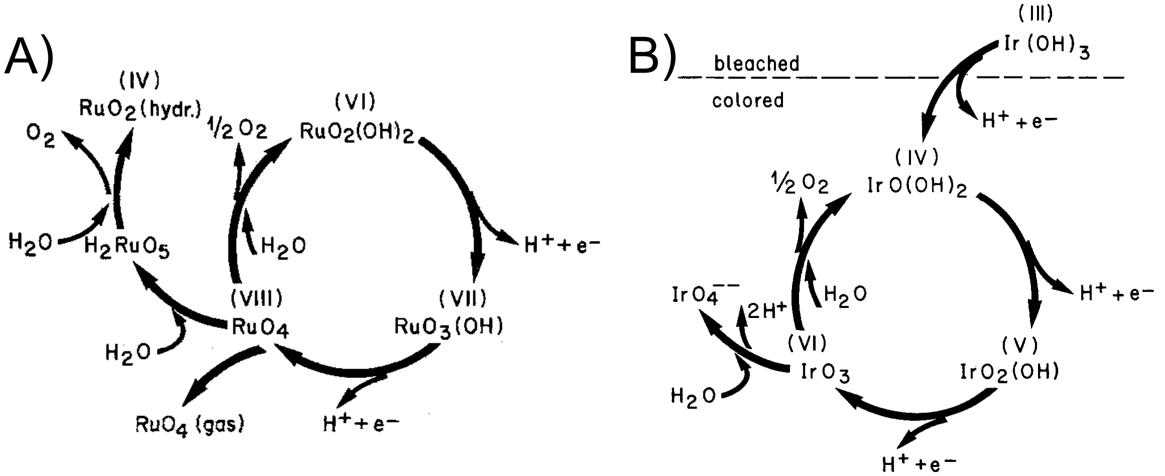


Figure 2.34: Mechanisms for oxygen evolution and corrosion on **A)** Ru/RuO_x and **B)** Ir/IrO_x electrodes. **A)**: Reprinted with permission from J. Electrochem. Soc. 130, 825-829 (1983). Copyright 1983, The Electrochemical Society (*Kötz et al.*, 1983). **B)**: Reprinted with permission from J. Electrochem. Soc. 131, 72-77 (1984). Copyright 1984, The Electrochemical Society (*Kötz et al.*, 1984a).

Despite the questionable Ir corrosion mechanism, the mechanisms in Figure 2.34 agree with the latest data on Ru and Ir dissolution, which show a good correspondence between corrosion and oxygen evolution. *Cherevko et al.* (2016e) essentially confirms the hypothesis that anodic dissolution of Ru or Ir necessarily occurs along with the OER. Figure 2.35 shows increasing metal dissolution rates with potential up-sweep current for Ru, Ir, RuO_2, and IrO_2. Though not obviously apparent in Figure 2.35, there is a strong similarity between the onset potentials of OER current and metal dissolution for Ru, Ir, RuO_2 and IrO_2 in acid (see Table 1 in *Cherevko et al.* (2016e)), providing further evidence for a concurrent OER corrosion mechanism. Figure 2.35 also shows the dissolution from metallic Ru and Ir are about two orders of magnitude greater than that from their respective oxides. *Cherevko et al.* (2016e) does not suggest an explanation for Ru, but states that for Ir, it may be due to poor passivation of the electrochemically formed oxide; anodic Ir oxide formed without cycling is only one to two monolayers thick (*Peuckert*, 1984).

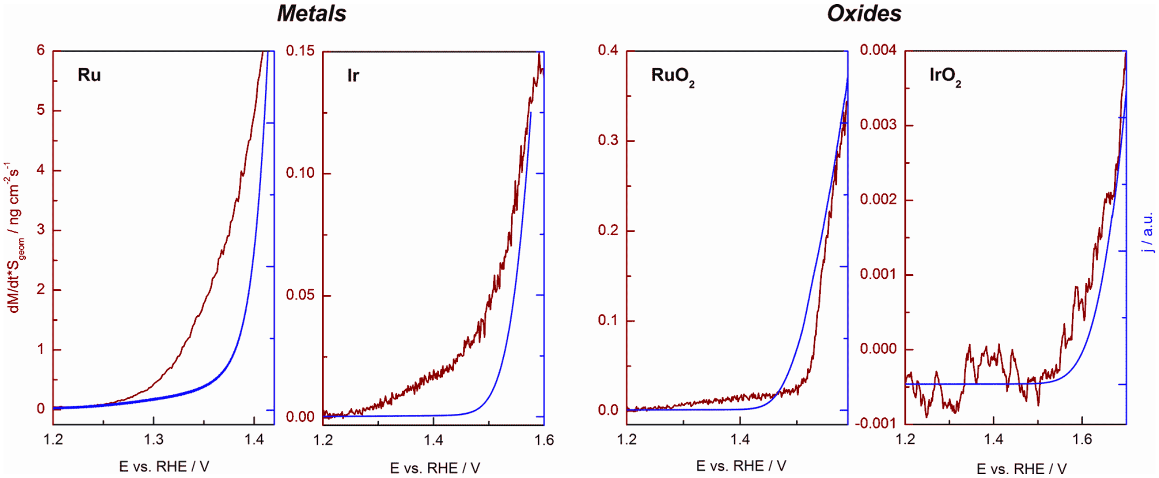


Figure 2.35: Anodic ramp (blue curve and left axis) and dissolution (red curve and right axis) data for Ru, Ir, RuO_2 and IrO_2. Current density axes scales have a maximum of 5 $mA\,cm^{-2}$ Scan rate: 1 $mV\,s^{-1}$. Electrolyte: 0.1 M H_2SO_4. Sample synthesis: sputter deposition (Ar, 0.67 Pa, 250 W AC) $Ir(O_2)$: 225 nm $Ru(O_2)$: 300 nm, oxide preparation: metal annealed at 600°C for 5 h in air. All films on 20 nm Ti adhesion layer, on 1.5 μm thermal SiO_2 on single crystal silicon wafer. Reprinted from Catalysis Today, 262, Cherevko, S. et al., Oxygen and Hydrogen Evolution Reactions on Ru, RuO_2, Ir, and IrO_2 Thin Film Electrodes in Acidic and Alkaline Electrolytes: A Comparative Study on Activity and Stability, pg. 170-180, Copyright (2016) with permission from Elsevier. (*Cherevko et al.*, 2016e)

2.3.5.2 A Brief Note on the Emergence of New Knowledge Relevant to this Project

As previously mentioned, (pg. 48) the dynamic nature of electrochemical Pt instability was not known when this project began. Neither was the knowledge presented in the next two sections, which is analogous to the dynamic Pt dissolution mechanism. The experimental work presented in this thesis was planned and carried out before this collection of very relevant and surprising knowledge was published. Had this knowledge been known at the outset, experiments may have been planned differently. These sections are included because they are very relevant for those interested in carrying on the work of this thesis project.

2.3.5.3 Cathodic (Dynamic) Dissolution of Ir

Cherevko et al. (2014) revealed a new Ir dissolution process, believed to be similar to the dynamic dissolution proposed for Pt explained in *The Nature of Electrochemical Pt Dissolution* (pg. 27). Figure 2.36 shows simple potential and dissolution profiles for Ru, Ir and Pt. Ir looks similar to Pt but with two important differences: 1) the Ir cathodic dissolution peak occurs much later. This corroborates with the larger hysteresis in the Ir reversible oxide formation/reduction peaks (discussed in *Reversible Oxides*, point 3 pg. 70). Figure 2.36 shows the anodic dissolution peaks (the smaller ones) for Ir and Pt look the same but different mechanisms are at work. The anodic dissolution for Ir is part of the oxygen evolution process, while the for Pt, the anodic dissolution is due to the dynamic process shown in Figure 2.6 (pg. 31). A review of Figure 2.4 (pg. 28) will confirm the anodic dissolution of Pt does not correspond with the OER. Unfortunately, the jargon ‘anodic dissolution’, initiated by Mayrhofer’s group members, is used for both Pt and Ir and does not indicate which mechanism is at work.

The nature of Ir electrochemical dissolution actually has many intricacies, explained in two papers devoted to metallic Ir (*Cherevko et al.*, 2016a), and anodically grown Ir oxide (*Cherevko et al.*, 2016b). For example, Figure 2.37 shows the interplay between anodic and cathodic dissolution as metallic Ir is subjected to square waves with increasing upper potentials. Figure 2.38 shows how the total Ir lost during the oxidizing cycles is highly dependent on the upper potential limit. Figure 2.39 shows how dissolution from anodically oxidized Ir during a constant current changes with the extent of anodic oxidation. These are all important pieces of knowledge when considering the catalyst synthesis and recommended operating parameters for an Ir based electrolyzer It is hoped more important knowledge on the nature of Ir dissolution will come forth as the research with this powerful technique continues. For instance, what is the influence of various pre-oxidizing methods (i.e. thermal, reactive sputtering, etc.) on dissolution behaviour? What is the relationship between anodically oxidized Ir stoichiometry and activity? The nature of the dissolved species is another big knowledge gap waiting to be filled, though not by the ICP-MS flow-cell technique.

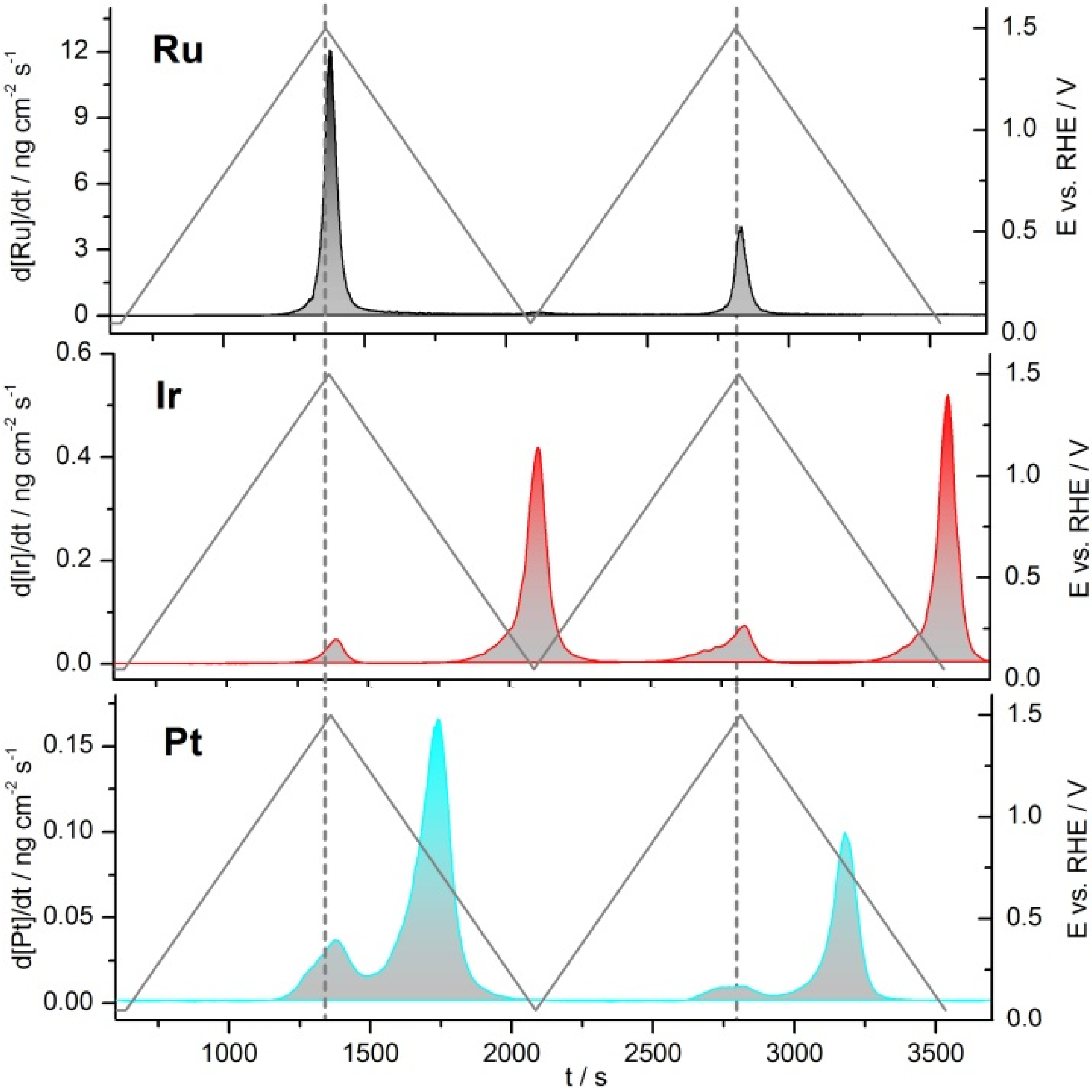


Figure 2.36: Dissolution of polycrystalline Ru, Ir and Pt caused by potential sweeps between 0.05 and 1.5 V_{RHE}. Electrolyte: 0.1 M H_2SO_4 purges with Ar, sweep rate: 2 $mV\ s^{-1}$. Reprinted from ChemCatChem, 6, S. Cherevko, A. R. Zeradjanin, A. A. Topalov, N. Kulyk, I. Katsounaros, and K. J. J. Mayrhofer, Dissolution of Noble Metals During Oxygen Evolution in Acidic Media, pg. 2219-2223, Copyright (2014) with permission from Elsevier (*Cherevko et al.*, 2014).

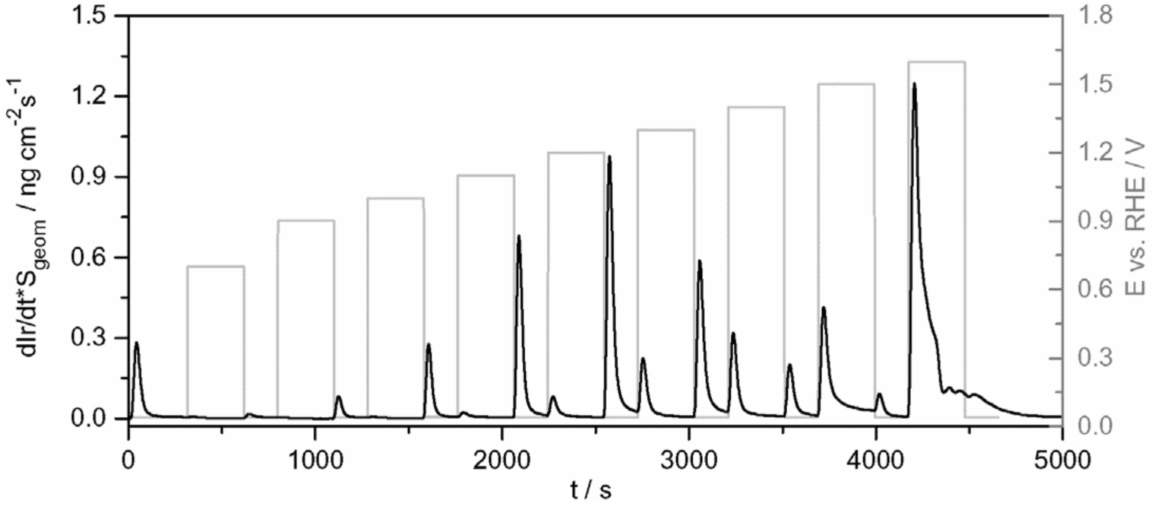


Figure 2.37: Dissolution response of metallic Ir subjected to potential hold cycles returning to 0.04 V_{RHE} each cycle and with upper potential increasing from 0.7 to 1.6 V_{RHE}. Anodic dissolution occurs on potential up-step; cathodic dissolution occurs on potential down-step. (Electrolyte: 0.1 M H_2SO_4, Ar saturated). Reprinted from Catalysis Today, 773, Cherevko, S., Geiger, S., Kasian, O., Mingers, A. & Mayrhofer, K. J. J., Oxygen Evolution Activity and Stability of Iridium in Acidic Media. Part 1. - Metallic iridium, pg. 69-78, Copyright (2016) with permission from Elsevier (*Cherevko et al.*, 2016a).

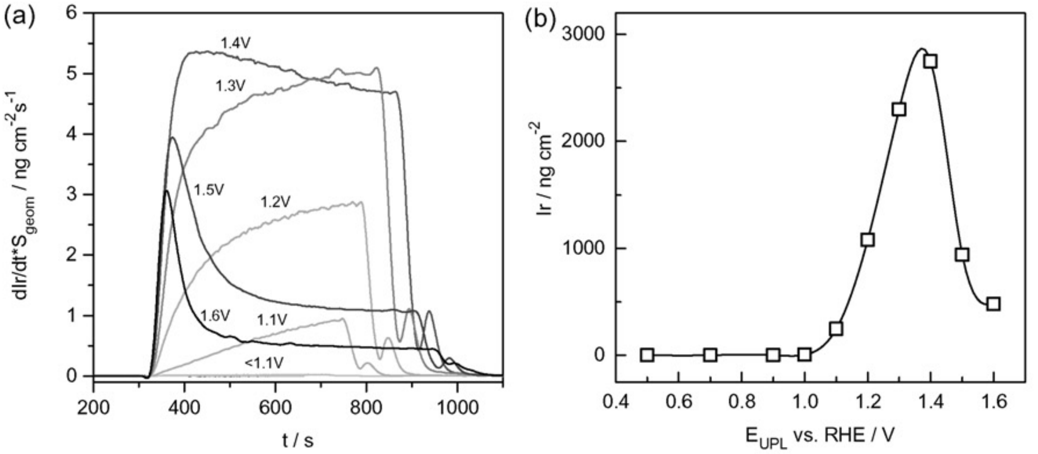


Figure 2.38: **(a)**: Dissolution rate with time during 100 potential cycles (for the purpose of anodically oxidizing metallic Ir) with different upper potential limits. Potential cycles were sawtooth, lower potential limit was 0.04 V_{RHE}, sweep rate: 500 $mV\ s^{-1}$, electrolyte: 0.1 M H_2SO_4). **(b)**: Total dissolution amounts for the different upper potential limits. Reprinted from Catalysis Today, 774, Cherevko, S., Geiger, S., Kasian, O., Mingers, A. & Mayrhofer, K. J. J., Oxygen Evolution Activity and Stability of Iridium in Acidic Media. Part 2. - Electrochemically Grown Hydrous Iridium Oxide, pg. 102-110, Copyright (2016) with permission from Elsevier (*Cherevko et al.*, 2016b).

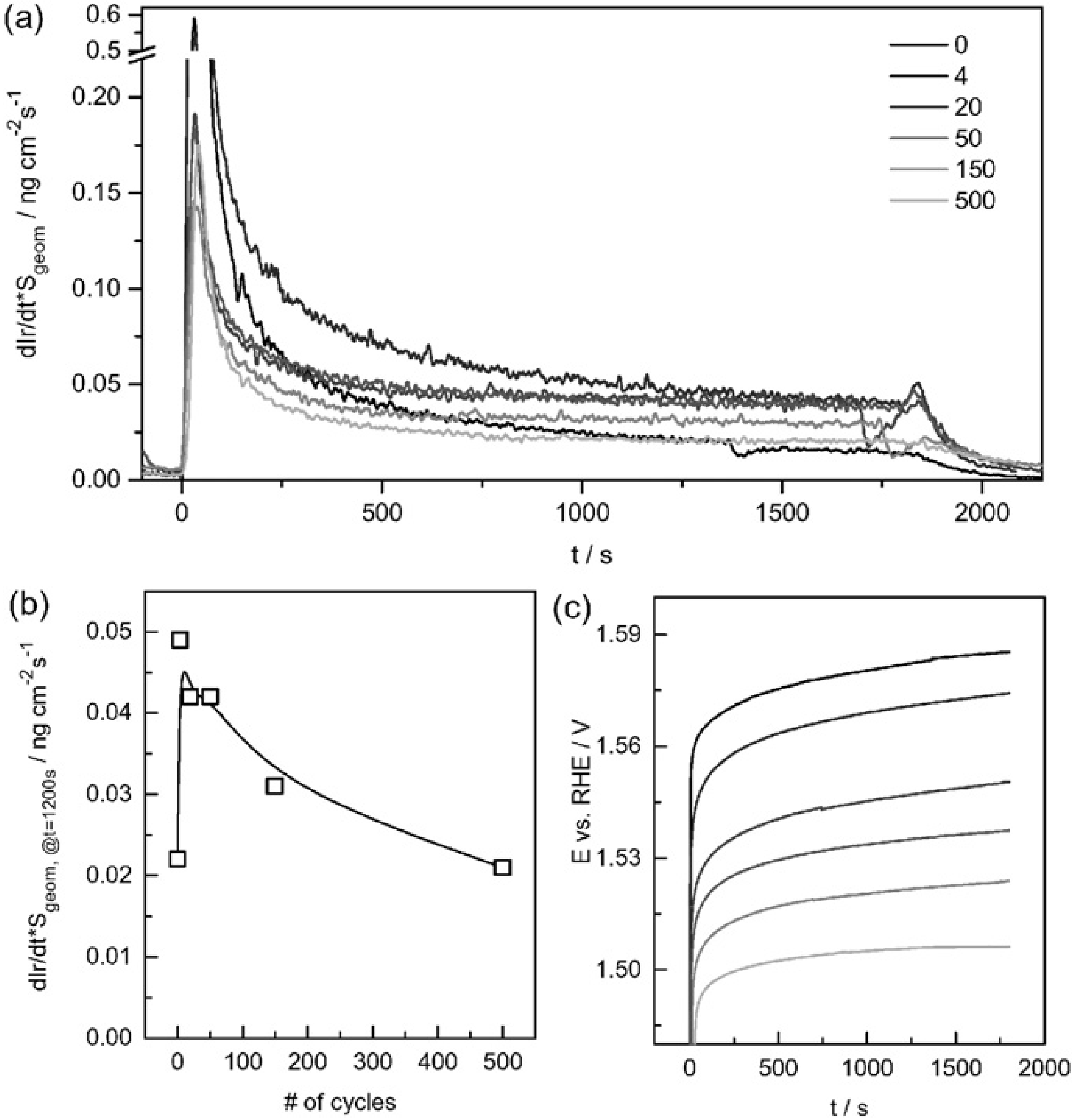


Figure 2.39: **(a)** Dissolution response of a 0.5 $mA\,cm^{-2}$ hold for metallic Ir samples previously anodically oxidized to various extents with a differing number of potential cycles, indicated in the legend. (Potential cycles were sawtooth, between 0.04 and 1.5 V_{RHE}, 500 $mV\,s^{-1}$, electrolyte: 0.1 M H_2SO_4). **(b)** The Ir dissolution rate at 1200 *sec* plotted against previous oxidation cycles. **(c)** Potential response of a 0.5 $mA\,cm^{-2}$ hold for the different oxidation cycles. Reprinted from Catalysis Today, 774, Cherevko, S., Geiger, S., Kasian, O., Mingers, A. & Mayrhofer, K. J. J., Oxygen Evolution Activity and Stability of Iridium in Acidic Media. Part 2. - Electrochemically Grown Hydrous Iridium Oxide, pg. 102-110, Copyright (2016) with permission from Elsevier (*Cherevko et al.*, 2016b).

2.3.5.4 Cathodic (Dynamic) Dissolution of Ru

Figure 2.36 shows that Ru displays a large anodic dissolution amount, in agreement with Figure 2.35. However, there is more to the Ru story, which is hinted at by the very small Ru dissolution signal at 2100 *sec* in Figure 2.36. Figure 2.40 shows Ru dissolution from Ru metal, RuO_2, and RuO_2 nanoparticles can behave similarly to Ir, if the upper potential does not exceed 1.3 V_{RHE}.

This figure is provided here merely as proof of ruthenium's dynamic/cathodic dissolution[10] behaviour but is rich with new insights into the stability of various types of Ru materials. A complete discussion is left to the original author's (*Hodnik et al.*, 2015) report.

---

[10] *Hodnik et al.* (2015) use the phrase "transient dissolution" instead of "cathodic dissolution" (started by *Topalov et al.* (2012)), which is probably a better description of the mechanism.

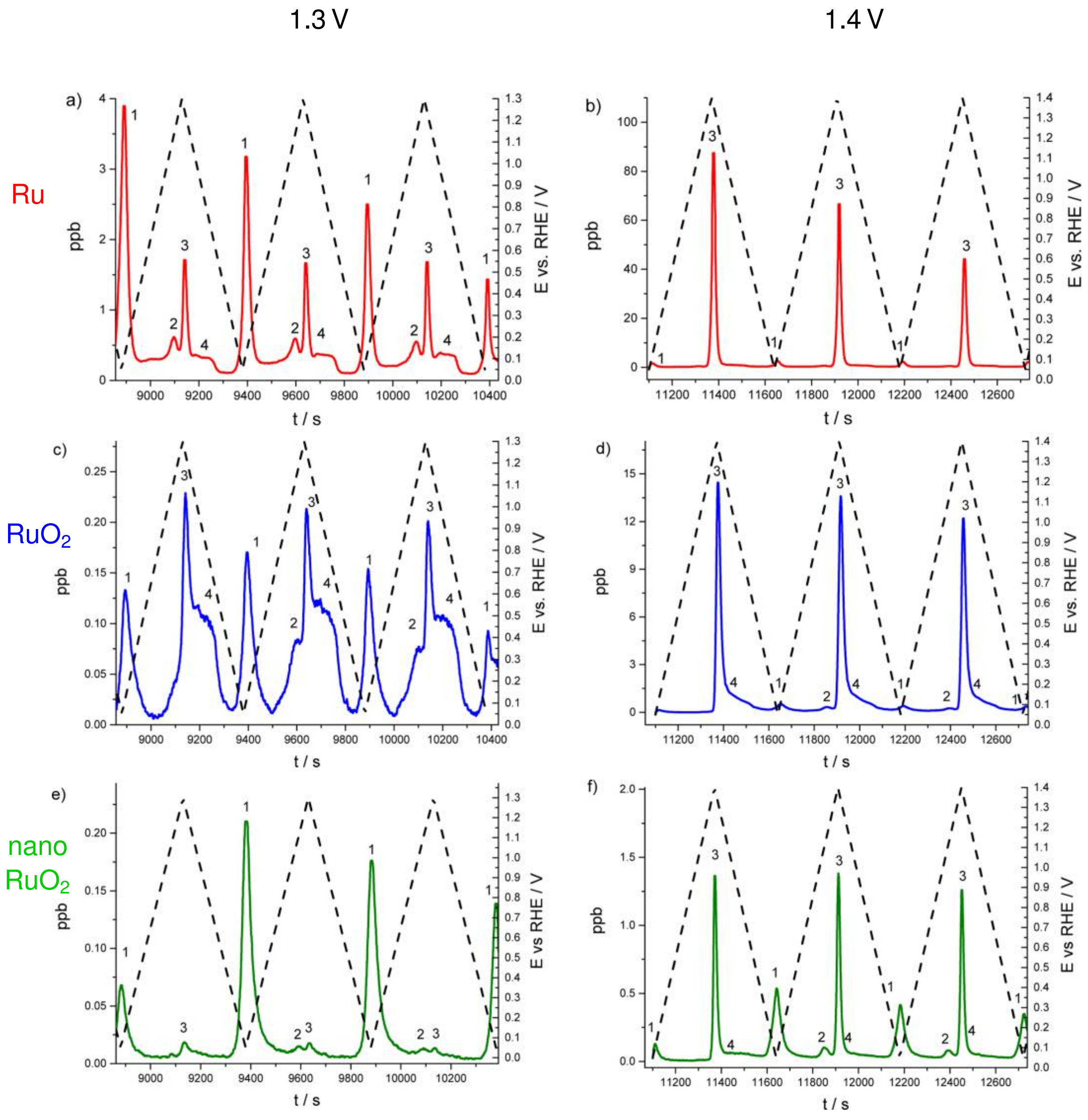


Figure 2.40: Variation of Ru concentration in a flow (263 $\mu L\,min^{-1}$) of 0.1 M HClO$_4$ due to potential sweeps (dashed lines, sweep rate: 5 $mV\,s^{-1}$) with upper potential limits of 1.3 V_{RHE} on the left column (**a)**, **c)**, **e)**) and 1.4 V_{RHE} on the right column (**b)**, **d)**, **f)**) for metallic Ru (Red lines), RuO$_2$ (blue lines), and RuO$_2$ nanoparticles (green lines). Reprinted with permission from Hodnik, N. et al. New Insights into Corrosion of Ruthenium and Ruthenium Oxide Nanoparticles in Acidic Media. J. Phys. Chem. C 119, 10140-10147 (2015). Copyright (2015) American Chemical Society (*Hodnik et al.*, 2015).

2.3.5.5 Justifying a Dynamic Dissolution Mechanism for Ir and Ru

The cathodic dissolution behaviour of Ir and Ru appears to be similar to that for Pt, only with a larger hysteresis. But is the cathodic dissolution mechanism for Ir and Ru similar to the mechanism ascribed to Pt? Remember, the Pt mechanism depends on an electrochemical reduction of Pt oxide to metallic Pt. Up to now, the formation of anodic oxide Ir and Ru had been described as irreversible once the potential goes above ∼1.2 V_{RHE}, i.e. the Ir and Ru oxide is unreducible by electrochemical action. How then can the cathodic dissolution behaviour for Ru and Ir be reconciled with the most probable mechanism? For Cherevko, the answer lies in a conceptual model for the Ir oxide layer first proposed *Burke and O'Sullivan* (1981), and later expounded by *Pickup and Birss* (1987), *Trasatti et al.* (1994) and *Godwin et al.* (2014). Figure 2.41 shows this model is composed of a compact anhydrous oxide sandwiched between the metal and the hydrated oxide. It should be stated that based on state-of-art knowledge, (*Steegstra et al.* (2013), *Minguzzi et al.* (2014), *Minguzzi et al.* (2015) and *Pfeifer et al.* (2016)) Ir^{+6} does not predominate in the hydrated film as shown in Figure 2.41. It is surmised that only the hydrated oxide is formed irreversibly, while the anhydrous oxide layer, only several atomic monolayers thick, is electrochemically reducible back to the metallic form. This allows for the mechanism described in Figure 2.6 to function on Ru or Ir. The corroded metal ions must, of course, migrate through the hydrated layer, proposed to be of a sol-gel type structure, to be carried away by the electrolyte.

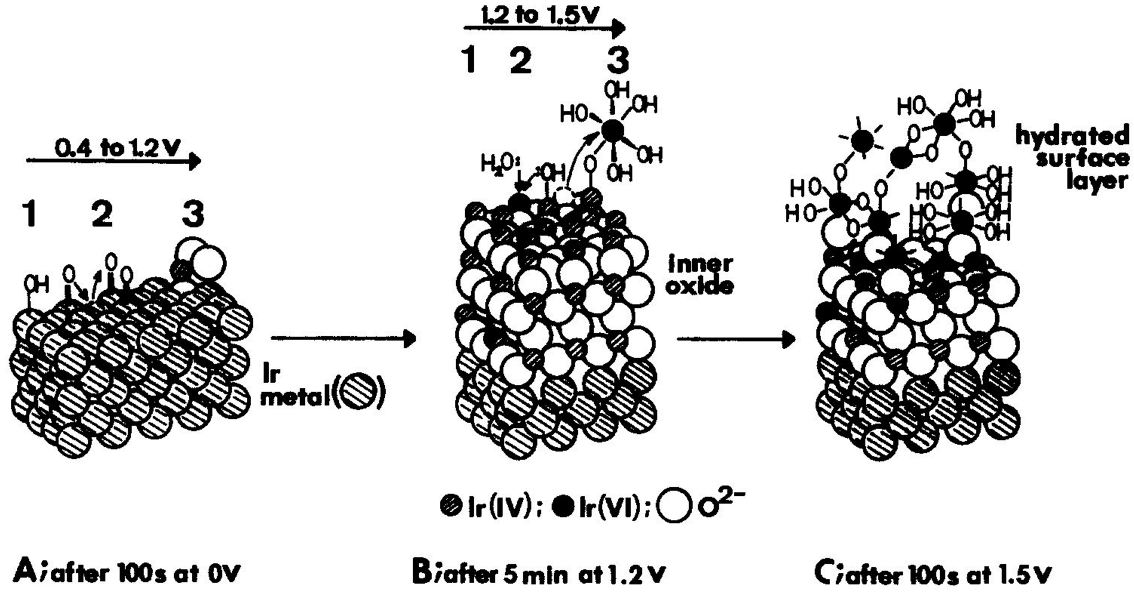


Figure 2.41: A conceptual anodic IrO_2 film formation model. Reprinted from Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 220, Pickup, P. G. & Birss, V. I., A Model for Anodic Hydrous Oxide Growth at Iridium, pg. 83-100, Copyright (1987) with permission from Elsevier (*Pickup and Birss*, 1987). [11]

2.4 Project Uniqueness

As mentioned in Section *Developing the Materials Solution to the RCDM on NSTF* (pg. 48), apart from 3M/Dalhousie studies, there are only two other published studies on mitigating the damaging effects of the RCDM through the addition of OER catalysts to the cathode (option Ⓐ): *Oh et al.* (2012) and *Min et al.* (2014).

Oh et al. (2012) studied the effect of two types of IrO_2 powder mixed with a Pt\C catalyst. The stress test was simply a constant voltage of 1.6 *V* applied to a fuel cell for 30 minutes with H_2 in the fuel cell anode and N_2 in the fuel cell cathode. (During the stress test, the fuel cell anode was actually a cathode and the fuel cell cathode was actually an anode.) This type of stress test stands in contrast to the alternating potentials used for this project and most other fuel cell catalyst degradation tests in the literature (see Section 3.3). As explained previously in *The Nature of Electrochemical Pt Dissolution* (pg. 27), a changing potential causes more Pt dissolution than a static potential so *Oh et al.'s* (2012) stress test was comparatively mild. The degradation of the carbon was assessed via on-line mass

---

[11] Based on state-of-art knowledge (*Steegstra et al.* (2013), *Minguzzi et al.* (2014), *Minguzzi et al.* (2015) and *Pfeifer et al.* (2016)), Ir^{+6} (Ir(VI)) does not predominate in the hydrated film at 1.5 $V_{(RHE)}$ as illustrated.

spectrometry measurements of CO_2. Pt loss was not directly assessed other than through changes in the *I*-*V* curve and CV. *Oh et al.* (2012) found the conventional IrO_2 powder was effective at preventing significant *I*-*V* loss when the loading was 0.016 $mg_{IrO_2}\,cm^{-2}$. Their improved high surface area powder was similarly effective at 0.008 $mg_{IrO_2}\,cm^{-2}$. (Pt loading for their study was 0.4 $mg_{Pt}\,cm^{-2}$.)

Min et al. (2014) studied the effect of various combinations of Ru and Ir mixed with Pt\C. Their stress test alternated the voltage of the fuel cell between 0.9 and 1.4 V, and the voltage was held at each peak (1.4 V) until 5 $mC\,cm^{-2}$ had passed. First, they found the best compromise between OER activity and stability (Ru is more active but less stable than Ir, see Section 2.3.4) was an Ir to Ru ratio of 1:1. Then, using this optimized OER catalyst, they found a cathode catalyst containing 2.5 wt% of OER catalyst maintained an *I*-*V* curve close to the initial after 5000 SU/SD potential cycles. Comparatively, there was a larger degradation in performance for the Pt\C (Pt only) catalyst. *Min et al.* (2014) was published simply as a conference abstract, so some of the details are not complete.

This thesis project stands apart from the studies by *Oh et al.* (2012) and *Min et al.* (2014) because the catalyst materials are supported on NSTF, not Pt\C, and the RDE is used to test the catalyst materials, not a fuel cell. The RDE was initially selected to characterize catalyst activity and durability because it could enable rapid screening of many compositions (discussed further in Section 3.1.4). However, using the RDE to characterize the durability of NSTF supported catalysts brought an unintended consequence; ORR activity decline under simulated RCDM was due only to Pt loss. The effect of carbon corrosion, which would have a significant impact in fuel cell studies, was excluded. It is also difficult to compare the results of this project to *Oh et al.* (2012) and *Min et al.* (2014) because the stress tests are different. As will be shown in Section 3.3.2, the lower potential for the stress test used for this project was 0.65 V_{RHE}. This is much more aggressive toward the Pt than the lower voltage of 0.9 V (explained in Section *The Nature of Electrochemical Pt Dissolution*, pg. 27) used by *Min et al.* (2014). Thus in a certain sense, all the results of this project are unique contributions to the field.

Chapter 3

Experimental Techniques and Methods

As stated throughout Chapters 1 and 2, the aim of this project is to make NSTF-supported Pt fuel cell cathode catalysts more durable by adding Ir and Ru. Only the rotating disk electrode (RDE) was used to experimentally determine catalysts activities and durability. About 400 glassy carbon electrode substrates suitable for use with an RDE were prepared by cutting glassy carbon rods. These rod sections, or ‘disks’, were sent to 3M for one of their flat ends to be coated with NSTF. Catalyst materials Pt, Ir, and Ru were deposited on to the NSTF coated disks with a magnetron sputtering machine. Several RDE stations were then used to test all samples synthesized for this project. More details on the sample preparation is provided in Section 3.2.

Regarding durability, Chapters 1 and 2 do not cover details about tests for fuel cell durability; only the catalyst degradation mechanisms from operational (Section 2.1.3) and materials (Sections 2.1.1 and 2.3.5) perspectives are discussed. Therefore, in addition to describing sample measurement and synthesis, this chapter includes a third section on designing a measurement protocol to assess durability. Experimental and analytical methods specific to Chapter 4 and 5 are provided in the respective chapters.

3.1 The Rotating Disk Electrode Technique for the ORR

Obtaining kinetic information, or activity, is the primary aim of fuel cell catalyst research. How then, does one measure the activity of a catalyst material? This is not a straightforward measurement, because phenomena other than electrochemical kinetics almost always influence electrochemical data; recall from Figure 1.5, a fuel cell *I*-*V* curve is influenced by reaction kinetics, electrical resistance, and mass transport phenomena. Therefore, raw fuel cell data cannot simply be fitted with the Tafel equation (Eq. 1.11, pg. 13) to obtain the two kinetic parameters. How then, does one tease out the kinetic information from such an *I*-*V* curve? Or perhaps a more basic question is, how is a fuel cell *I*-*V* curve useful for studying catalysis measured in the first place?

The PEM fuel cell is actually special among fuel cells because the anode reaction (HOR on Pt) incurs virtually no kinetic losses in acid (*Sheng et al.*, 2010). Therefore, to measure a PEM fuel cell *I*-*V* curve useful for extracting ORR activity on the cathode, one could simply apply a variable load to the cell, and measure the resulting voltage and current for various resistances. However, this low-tech method would not work for obtaining kinetic information for an alkaline fuel cell, for instance, due to significant kinetic losses on both electrodes. For *I*-*V* data to be useful in obtaining a catalyst's activity parameters, it must be influenced by only one catalytic reaction. The proper way of studying electro-catalysis, is to characterize one electrode apart from the other, and this is done with a potentiostat.

3.1.1 The Potentiostat

A potentiostat is a circuit of operational amplifiers. This invention by *Hickling* (1942), revolutionized the field of electrochemistry because it enabled the study of a single electrode. The three electrodes are called the working, counter (or auxiliary), and reference electrode. The working electrode is the sample under study. The potential of the working electrode (i.e. voltage between the working and reference electrode) is controlled by the op-amp circuit while the electrical current passes between the working and counter electrode.

The data produced by the potentiostat is current, potential and time. Either the potential is held constant, or it is changed with time, a technique called voltammetry. Most potentiostats can also operate under a 'galvanostat mode' in which the potential is measured with time as the current is held constant.

The *I*-*V* relationship for just one electrode[1] still contains influences from kinetics, resistance, and mass transport phenomena. To obtain data which will reveal catalytic activity, the influence of mass transport and ohmic phenomena should be first minimized with experimental techniques, then eliminated with mathematical corrections. Section 3.1.3 is about this numerical correction process. The next section shows how the influence of mass transport is experimentally minimized with convection.

---

[1] Since the data is for only one electrode, it should, strictly speaking, be called an *I*-*E* (current potential) relationship, but the *I*-*V* terminology is kept.

3.1.2 Rotating Disk Electrode Background and Theory

The rotating disk electrode (RDE) was developed by Russian researchers[2] to introduce convection to electrochemical experiments. Figure 3.1 shows a schematic of an RDE shaft, the part that spins. The part labelled electrode isolator, also called the shield, mantle or shroud, exists to approximate a plane surface of infinite extent. The shroud, usually made of some type of durable plastic such as Teflon or polyether ether ketone, is attached to the end of a longer rod which extends up out of the electrolyte and is attached to a rotator. Electrical connectivity is made with some sort of brush contacting the rod. When the electrode shaft is rotated, electrolyte is drawn up toward the centre of the electrode, and convected outward along the radius. Figure 3.1 also shows the electrolyte streamlines during rotation.

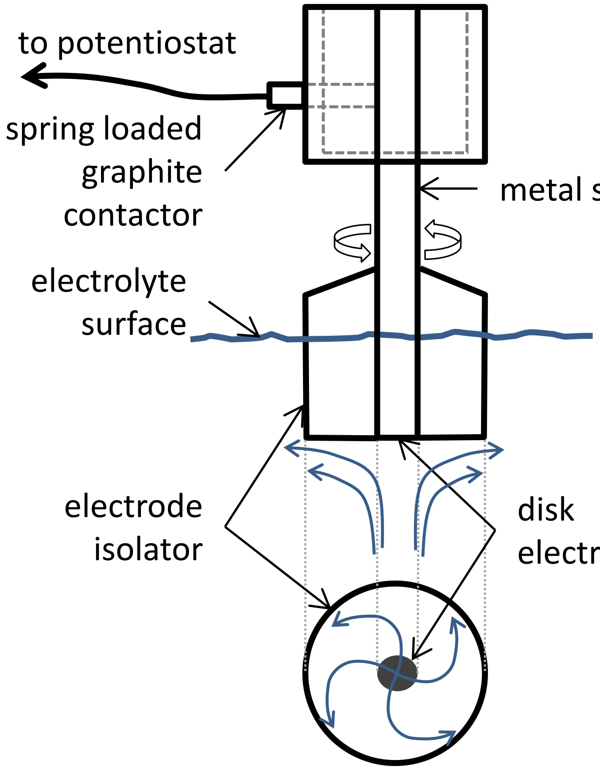


Figure 3.1: Schematic of a RDE shaft. The basic parts of the rotating electrode are labelled and the electrolyte streamlines are drawn in blue (lighter shade).

The RDE is one of several hydrodynamic electrode methods (see *Brett and Brett*

---

[2] The first publications describing the technique, which are in Russian, are cited by *Opekar and Beran* (1976) under Levich (1942) (who described the theory) and Siver and Kabanov (1948) who ran the first RDE experiments)

(1993a) for more) which convect electrolyte across a working electrode surface. Prior to the hydrodynamic methods, all electrochemical experiments were carried out in quiescent electrolytes. The *I-V* data, or the potential/current vs. time data, collected from quiescent experiments can be analyzed to obtain kinetic parameters using equations derived from Fick's Second Law and electrochemical kinetics.[3] However, perfect quiescence is very difficult to achieve due to thermal gradients.

A hydrodynamic technique is also better for studying the ORR because gases can be introduced via sparging, which results in quicker saturation and purging of previously dissolved gases. Forced convection also means Fick's First Law can be used (along with the Butler-Volmer equation) to derive expressions which account for mass transport effects. The equation that results for the rotating disk electrode was first described by *Koutecký and Levich* (1958), and is surprisingly simple:

$$\text{The Koutecký-Levich Equation:} \qquad \frac{1}{i_{fara}} = \frac{1}{i_d} + \frac{1}{i_k} \qquad \text{or:} \qquad i_k = \frac{i_d i_{fara}}{i_d - i_{fara}} \tag{3.1}$$

where i_{fara} is the Faradaic current density, (i.e. no capacitive and surface reaction current, explained in the next section), i_d is the diffusion limited current density for a given rotation rate, and i_k is the kinetic current density (the parameter of interest). i_d can be determined theoretically based on viscosity and rotation rate but the equation is not presented here because the experimental value of i_d was used in the data processing.

The theoretical treatment which results in both the equation for i_d and the Koutecký-Levich equation can be found in *Levich's* (1962) seminal book: "Physicochemical hydrodynamics". Sections 5.7 to 5.9 of *Brett and Brett* (1993b) and also *Treimer et al.* (2002) provide derivations.

This section described an experimental technique designed to minimize mass transfer effects (the RDE) and a numerical correction (Equation 3.1) which go hand-in-hand. Other mathematical corrections are described in the next section. Some caveats about using the RDE rather than a fuel cell to determine ORR activity are mentioned in the section following the next (3.1.4). Details about the RDE hardware are given in Section 3.1.5.

---

[3] Electrochemical Methods by *Bard and Faulkner* (2000) provides these expressions and their derivations For potential step experiments see equation 5.2.11 and 5.5.27. For potential sweep experiments, see equation 6.3.12. Chapter 8 on galvanostat techniques, provides other expressions concerning kinetics.

3.1.3 Analyzing ORR Data Measured with the RDE

As described in the previous section, the current should be corrected for mass transport effects with the Koutecký-Levich equation. The i_{fara} for this relation comes from another correction which removes capacitive and surface reaction current to yield the Faradaic current. In this report, this is referred to as the background subtraction (i.e., a subtraction of background current due to non-ORR processes). The potential of the raw data can be corrected for ohmic drop, and this must be done before the background subtraction. There can be a fourth numerical adjustment, previously discussed in Section *Electrochemical Kinetics: Theoretical Background* (pg. 14), which normalizes the current to the catalytically available Pt surface area. This could be done at any stage, but is normally done as the final step. The combination and use of these corrections by the fuel cell community essentially come from *Schmidt et al.* (1998), who was the first to use the RDE to characterize the ORR activity of a Pt\C fuel cell catalyst. A book chapter by the same author (*Schmidt and Gasteiger*, 2003) is an excellent resource for researchers who use the RDE to characterize fuel cell catalysts. Section 10 of the User Manual for the Pine Modulated Speed Rotator is also very useful.

Therefore, in order of application, the corrections are: 1) Ohmic drop subtraction 2) background subtraction 3) mass transport correction, and optionally 4) surface area normalization. The ohmic drop correction was only applied in Chapter 5.

3.1.3.1 A Note on Different Methods for Chapters 4 and 5

As mentioned in Section *Structure of this Thesis* (pg. 21), Chapter 4 describes a preliminary work to develop methodology for the USDOE/3M durability project, and Chapter 5 is the second, more polished study, which improves upon the data processing methods and presentation. As such, there were many differences in how ORR data was processed between Chapters 4 and 5. Details regarding all the differences will be given in the respective Chapters.

3.1.3.2 Background Subtraction

Two cyclic voltammograms (CVs) are performed, one with the electrolyte saturated with an inert gas (Argon) to remove all traces of O_2, and the second with the electrolyte saturated with O_2. The current of the CV in Ar, which is due only to double-layer charging and current from surface reactions (H_{UPD} absorption/desorption and oxide formation/reduction), must be subtracted from the current of the CV in O_2 to obtain the Faradaic ORR current. The equation is:

$$i_{fara(ORR)} = -(i_{O_2} - i_{Ar}) \tag{3.2}$$

where $i_{fara(ORR)}$ is the current density due only to the ORR, i_{O_2} is the current density in oxygen saturated electrolyte, and i_{Ar} is the current density in Argon saturated electrolyte; note i_{O_2} and i_{Ar} may be corrected for ohmic drop. The negative immediately after the equals sign is not necessary, but is there to make the cathodic current positive in preparation for Tafel model processing (a logarithm operation cannot be performed on a negative number).

Only one sweep of the CV is selected for i_{O_2} and i_{Ar}; an up-sweep (positive going) because the ORR current is higher during the up-sweep due to less Pt oxide coverage. The sweep selected is always the last full up-sweep, which for this project, is usually the fourth full up-sweep. The selection of only one sweep creates two numerical processing problems: 1) the CV data must be accurately separated into separate sweeps (which is not so simple when noise is present in the potential data), and 2) the subtraction requires currents for equivalent potentials. Regarding this last point, the problem can be solved with interpolation, but this requires monotonic (constantly increasing or decreasing) potential data, and this was never the case due to measurement noise. Solving these problems are explained in the sections named *Sweep Cusp Determination* and *Sweep Monotonicity* in Chapters 4 and 5.

3.1.3.3 Experimental Diffusion Limited Current

The experimental diffusion limited current (i_d) must be determined for the Koutecký-Levich equation. For all subsequent chapters, the diffusion limited current was obtained by averaging the currents from the last full up-sweep and last full down-sweep between 0.18 and 0.29 V_{RHE}. Sometimes the Pine potentiostat would malfunction and not measure current lower than $-0.5\ mA$ ($-2.35\ mA\,cm^{-2}$ for $\varnothing\,5.2\ mm$ disk electrode), or sometimes carbon corrosion (explained in Section 4.6) would have too great an influence. Therefore, if experimental diffusion limited current was greater than $-3.5\ mA\,cm^{-2}$ (rotation speed was 900 rpm), the nearest diffusion limited current (from within the same experiment) was used.

3.1.3.4 Normalization to Catalytic Surface Area

Active catalytic surface area was estimated by dividing the charge (the integrated area under the H_{UPD} desorption curve of the CV in Ar saturated electrolyte divided by the sweep rate) by the widely accepted $210\,\mu C\,cm^{-2}$ for polycrystalline Pt to obtain the ECSA. More details about this technique were explained in *Electrochemical Surface Reactions on Pt* (pg. 18). The ECSA is further divided by the planar surface area to obtain the surface enhancement factor (SEF), which is a convenient ratio which relates the atomic Pt surface area to the geometric surface area of the disk electrode. All these simple relations are summarized below:

$$SEF = \frac{ECSA}{SA_{geo.}} = \frac{\frac{Q_{H_{UPD,des}}}{210\ \mu C\,cm^{-2}}}{0.212\ cm^2} \qquad \text{therefore} \qquad i_k^{Pt} = \frac{i_k}{SEF} \tag{3.3}$$

where i_k^{Pt} is the Pt specific kinetic current density, $Q_{H_{UPD,des}}$ is the H_{UPD} desorption charge, and A_{geo} is the geometric (sometimes called planar) surface area of the electrode. All the glassy carbon electrode disks used in Chapters 4 and 5 measured 5.2 *mm* in diameter, so the geometric surface area is 0.212 cm^2. A typical SEF for a planar, mirror polished, polycrystalline Pt electrode is about 1.5. When current is surface area corrected, it simply means the geometric current density (given in units $mA\,cm^{-2}$ throughout this report) was divided by the SEF, yielding the platinum specific current density (units: $mA\,cm_{Pt}^{-2}$).

3.1.3.5 The ORR Performance Metric

As discussed in the last paragraph of *Electrochemical Kinetics for Hydrogen Fuel Cells and Electrolyzers* (pg. 18), in lieu of the exchange current density (i_o), activity is given as “current at a specified potential (or vice-versa)”. Sometimes, though rarely, activity is given as an “onset potential” (*Gewirth and Thorum*, 2010) which is the potential when appreciable current, not always defined, starts. Citing a “half-wave” potential (*Snyder et al.*, 2010) which is the potential at half the diffusion limited current, is also common in fuel cell literature. Normally ORR activity is reported as background and mass transfer corrected current at 0.9 V_{RHE} (*Gasteiger et al.*, 2005). How did this convention begin and why was 0.9 V_{RHE} chosen? A direct answer to both questions is difficult to find in the literature, but it probably had to do with the effect of mass transport (i.e. minimizing the error due to the mass transport correction) and errors due to the background subtraction.again, PP generously came up with some replacement text to make it more formal and more clear.

Since the study by *Schmidt et al.* (1998), the Koutecký-Levich equation has been widely used in research on high surface (e.g. Pt\C) Pt based oxygen reduction catalysts. However, it comes not without a caveat: errors in i_k significantly intensify with higher i_{fara}. *Gasteiger et al.* (2005) noted this, and *Vidal-Iglesias et al.* (2012) wrote a paper devoted to the matter which can be summarized with the following quote:

> "Vidal-Iglesias et al. carried out a detailed mathematical analysis that projected ×3 magnification of error in i_k at ${}^{i}/_{i_d} = 0.5$ for an arbitrary experimental error in the measured raw current. It is thus advisable to report the measured ORR activity at potentials corresponding to the range $0.1 < {}^{i}/_{i_d} < 0.5$."[4] –*Shinozaki et al.* (2015c)

The convention of reporting ORR activity as background and mass transfer corrected current at 0.9 V_{RHE} is supposed to serve as a standard for comparison between different studies. (*Gasteiger et al.*, 2005). However as catalysts improved, the current at 0.9 V_{RHE} moved into the range where intensified errors from the Koutecký-Levich correction became a concern. Because of this concern, NSTF supported catalysts were probably the first group of catalyst materials to break with convention and report the ORR current at a higher potential (1.0 V_{RHE} in *Liu et al.* (2010), 0.95 V_{RHE} in *van der Vliet et al.* (2012)) as the ORR performance metric for RDE studies. Other state-of-the-art (non-NSTF) catalyst materials followed suit (0.95 V_{RHE} in *Chen et al.* (2014)).

3.1.4 ORR Activity: RDE vs. Fuel Cell

It is worthwhile to point out that this project is about fuel cell catalysis, but fuel cells were not used in any experimental work. After the Pt\C ink breakthrough (*Wilson and Gottesfeld*, 1992) it took some time for the RDE technique to be applied to Pt\C materials (*Schmidt et al.*, 1998). What motivated this new approach to researching Pt\C cathode catalyst materials? The following reasons have already been given in this chapter:

1. A three electrode potentiostat is the proper way to study a single catalytic reaction.
2. The RDE is a forced convection system, which enables the use of Fick's first law to better model mass transfer effects.

---

[4] i in the quoted text is the same as i_{fara} in the Koutecký-Levich equation (Equation 3.1)

Despite these reasons, fuel cells can be, and regularly are, used to accurately characterize the ORR activity of a catalyst. This is because, regarding point 1.: the HOR on the fuel cell anode has no kinetic loss, so a potentiostat is not required, and regarding points 2.: the transport in the gas phase is extremely fast compared to the liquid phase, so there is virtually no mass transport polarization in a fuel cell at high potentials ($> 0.8\ V_{RHE}$). To illustrate the ability of the fuel cell to accurately characterize ORR activity, Figure 3.2 shows very good quantitative agreement between mass activity of a Pt\C catalyst in a fuel cell and in an RDE.

Therefore it seems the only clear reason for the RDE[5] is one not mentioned yet: testing a catalyst with the RDE requires less work/time than with the fuel cell. This is, in-short why the Dahn Lab was contracted by 3M for fuel cell catalyst research; the Dahn Lab's expertise with the RDE and combinatorial materials synthesis should enable *rapid screening* of many different catalysts (i.e. made from different Pt alloys, with different sputtering conditions, loadings etc). This expertise did enable rapid screening for the earlier contracts, but not so much for the durability contract; no one anticipated the complications that would arise from long term (several days) experiments and repeated high ($> 1.2\ V_{RHE}$) potentials.

Other than the work/time savings, those who espouse the RDE technique regularly justify it by saying "trends of activity and durability in RDE studies can be used to predict trends in Proton Exchange Membrane Fuel Cells" (*Kocha et al.*, 2013). While this is easy for most researchers to accept, there has been no comprehensive study demonstrating this claim. One of the biggest criticisms of using the RDE for ORR catalysis research is that the potential range of data from the RDE ($\sim$0.8 to 1.0 V_{RHE}) does not correspond to that of an operating fuel cell ($\sim$0.5 to 0.7 V_{RHE}). Ideally, one would like to believe differences between catalysts at RDE potentials necessarily correspond to the same performance (activity) differences at fuel cell potentials. However, *Zalitis et al.* (2013) have shown some interesting data from their novel floating electrode technique[6] which casts some doubt on this hypothesis. Nonetheless, the RDE has had considerable momentum in fuel cell catalyst research community and is widely viewed as the best way to determine the intrinsic ORR

---

[5] Another advantage is the RDE can enable the determination of the extent of H_2O_2 formation as side-product of the ORR.

[6] *Kucernak and Toyoda* (2008) developed a three electrode method which uses a floating working electrode as an alternative to the RDE for studying the kinetics of gas electrodes. *Zalitis et al.* (2013) (same group) improved the method to enable the study of ultra low ($\geq 0.16\ \mu g\, cm^{-2}$) loaded Pt\C and claim the ORR on their electrode was "not mass transport limited at current densities in PEFC relevant potentials (0.6 to 0.8 $V\, vs\, RHE$)"

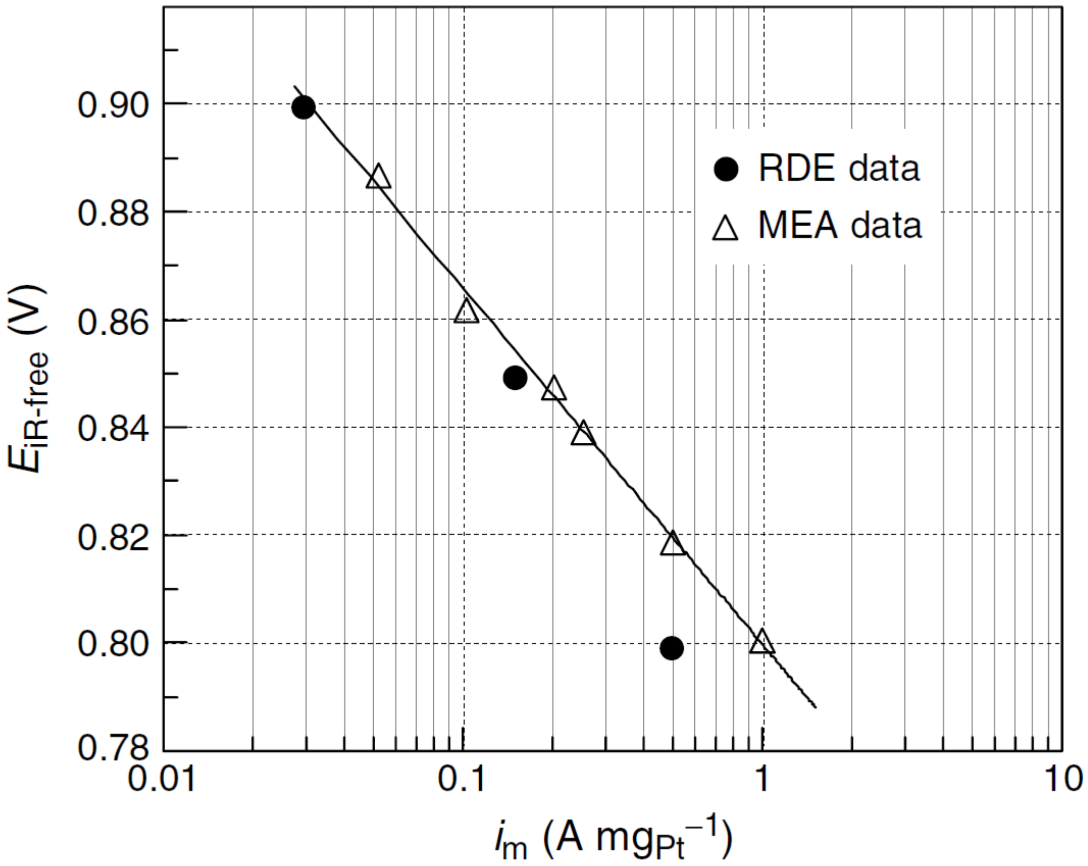


Figure 3.2: A mass activity Tafel plot of a 47 wt% Pt\C (Vulcan XC72) catalyst tested in an RDE and a fuel cell. RDE: 0.1 $HClO_4$, 60°C, 1600 rpm, 14 $\mu g_{Pt}\, cm^{-2}$, 0.283 cm^{-2} disk electrode. No corrections applied, instead electrolyte was kept O_2 saturated and currents were recorded after 10 minutes after a potential step from 1.0 V_{RHE}. Fuel Cell: fully humidified H_2\O_2 (stoichiometric flows of 2.0\9.5) at $120kPa_{abs}$ at 60°C, Nafion 112, 0.4 $mg_{Pt}\, cm^{-2}$. *iR*-free voltages were measured after holding 10 minutes at each current density, corrected for H_2 crossover current of 0.9 $mA\, cm^{-2}$. Republished with permission of John Wiley and Sons Inc, from Handbook of Fuel Cells: Fundamentals, Technology, Applications, Gasteiger, H. A., Gu, W., Makharia, R., Mathias, M. F. & Sompalli, B. Volume 3, 2003; permission conveyed through Copyright Clearance Center, Inc. (*Gasteiger et al.*, 2003).

activity for a given catalyst material.

It is prudent to mention here that despite the expectation to measure the intrinsic activity, the RDE still has a poor reputation: it is considered as being “plagued with intricacies” by *Kocha et al.* (2013). Considerable effort had been devoted to refining the technique for the fuel cell community. Any researcher preparing to use the RDE for fuel cell catalysts research should become familiar with studies by *Shinozaki et al.* (2015a), *Shinozaki et al.* (2015b), *Shinozaki et al.* (2015c), *Garsany et al.* (2011), *Garsany et al.* (2010), the USDOE merit review presentation by *Kocha* (2014), and the recorded USDOE webinar by *Kocha et al.* (2013). Unfortunately, most of the data for this project was collected before these were published, but good RDE practise was passed down from previous PhD projects (*Liu* (2011) and *Bonakdarpour* (2007)) .

3.1.5 Dahn Lab RDE Instrumentation

This section contains specific details about the RDE hardware used in this project. Most of the equipment and methods were ‘inherited’ from prior fuel cell projects in the Dahn Lab.

3.1.5.1 Pine Equipment

The following three paragraphs describe hardware manufactured by Pine Instrument Company, or duplicates of the Pine hardware made by Dahn Lab machinist Simon Trussler.

Potentiostat

An AFCBP1 bipotentiostat[7], controlled with PineChem 2.8.0H software (which was automated with keyboard and mouse control programmed in Visual Basic 6.0) equipped with a Pine filter board (AB01CBPF) with default jumper settings. The filter board significantly reduced the electrical noise in the potentiostat signal. The AFCBP1 was controlled and read with a computer via a National Instruments PCI-MIO-16XE-10 A/D (16-bit) card.

---

[7] The ‘bi’ signifies there are two working electrodes on this potentiostat, along with the one counter and one reference electrode. The second working electrode was never used for this project, but is very useful for ORR research because it can detect the production of H_2O_2, an ORR by product detrimental to PFSA membranes.

Rotator and Shaft

A Pine MSR rotator, and an AFE6MB shaft was used. The rotator was calibrated with a strobe light by Dahn Lab members after shipment according to instructions in the manual. The rotation speed was controlled with a precision 0 to 5 *V* source (Keithley 213), which was controlled by a computer.

RDE Tip Assembly and Mounting Jig

An E6TQ ChangeDisk tip was used to test different electrode samples. Use of this tip is very common in RDE research. Figure 3.3a), b) & c) shows the parts of this tip. The preparation of glassy carbon disks for this tip is explained in Sections 3.2.1 and 3.2.2. Disk samples were mounted in the ChangeDisk tip with a tool designed by *Liu et al.* (2010) to ensure the catalyst surface remained pristine. Only the disk surface edge contacts the tool. In the final step of the tip is pushed down to into the tool to ensure the disk surface and ends of the u-cup and the tip are flush. Figure 3.4 shows the tool. Figure 3.5 shows how the tool was operated.

3.1.5.2 Electrolyte, Glassware and Electrodes (non-Pine Equipment)

The following paragraphs describe the electrolyte, or materials that come into contact with the electrolyte. Any material that contacts the electrolyte may be a source of contamination, thus all the parts described in this section (and the RDE tip) were meticulously cleaned. The cleaning procedures can be found in Appendix B and C of *Bonakdarpour* (2007).

Electrolyte

The electrolyte was 0.1 M $HClO_4$ prepared from doubly distilled 70 *wt%* stock solution (GFS Chemical Inc.) and pure (18.2 $M\Omega$) water from Barnstead NANOpure DIamond RO (D12651) and UV (D11911) water filtration systems. $HClO_4$ is used widely in fuel cell ORR catalysts research, because the anions of the alternative acids (H_2SO_4, H_3PO_4, HCl) strongly adsorb on Pt surfaces and hinder the ORR on Pt; this is well documented by many studies, for example see *El Kadiri et al.* (1991). In addition, some authors (*Paulus et al.* (2001) and *Gasteiger et al.* (2005)) argue the non-absorbing perchlorate anion more closely mimics the conditions of a PEM fuel cell, because the anions in the PFSA membrane are

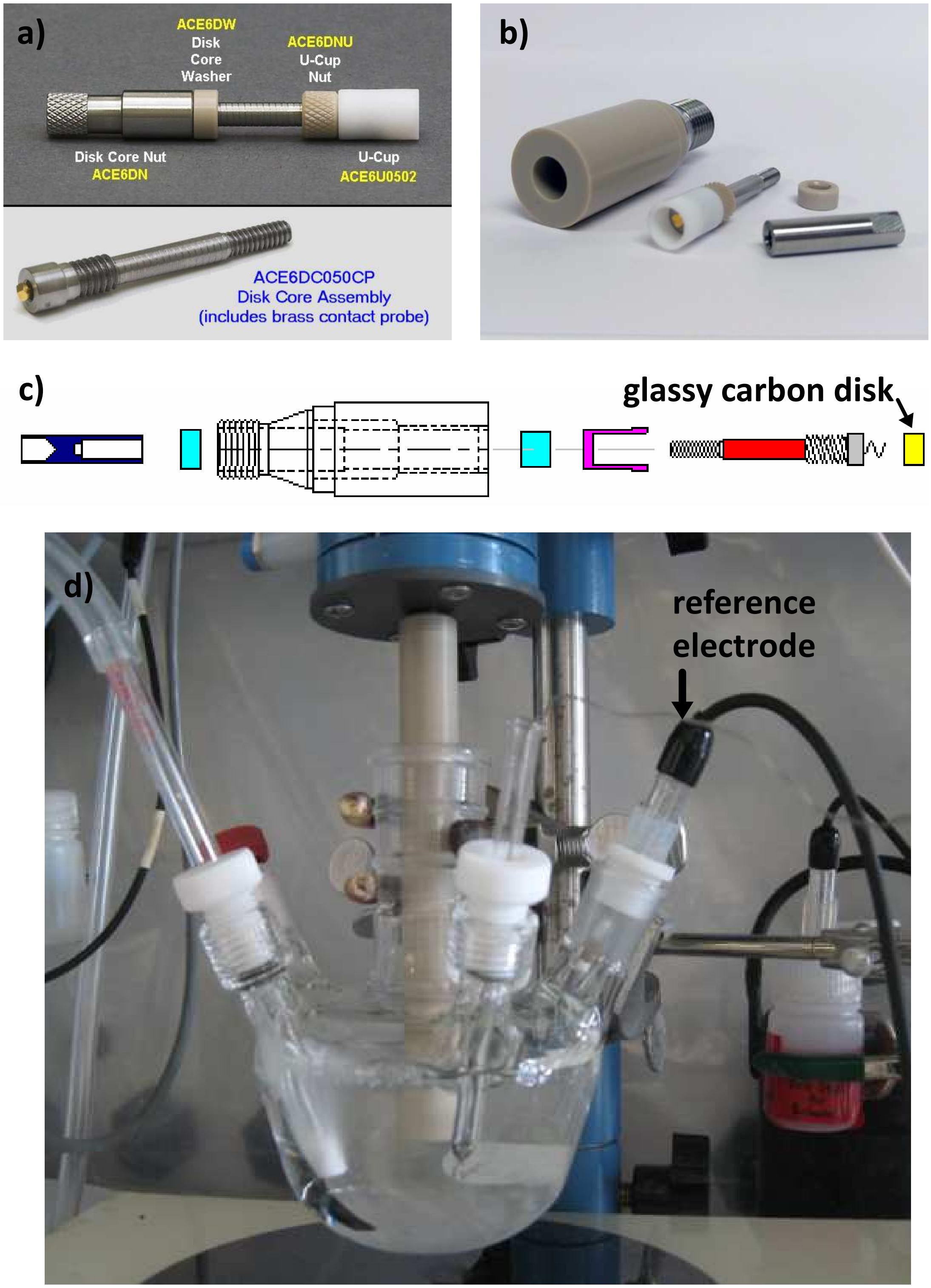


Figure 3.3: **a)** and **b)**: All parts that make up the Pine E6TQ ChangeDisk RDE Tip (*Pine Research Instrumentation*, 2016). **c)**: Assembly schematic of the E6TQ ChangeDisk RDE Tip (*Pine Research Instrumentation*, 2005). **d)**: Photo of an operating RDE flask with electrodes and gas diffuser.

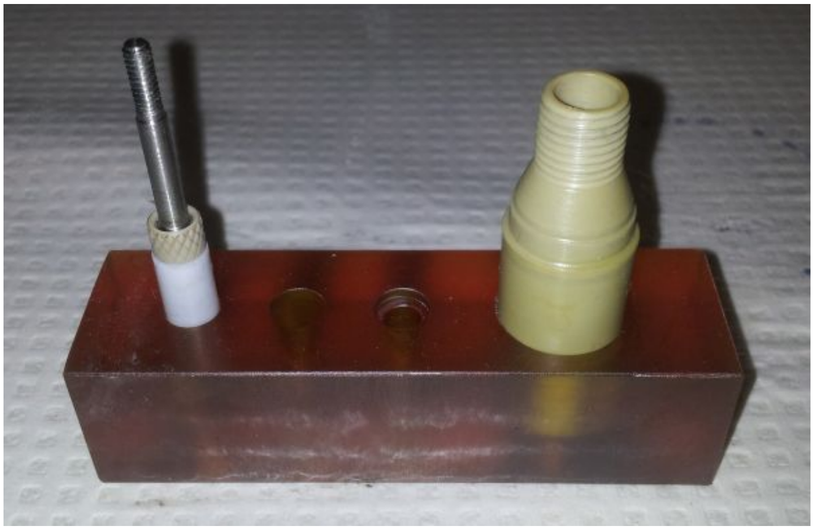


Figure 3.4: A tool designed in-house to help assembly the RDE tip while ensuring the catalyst surface remains pristine.

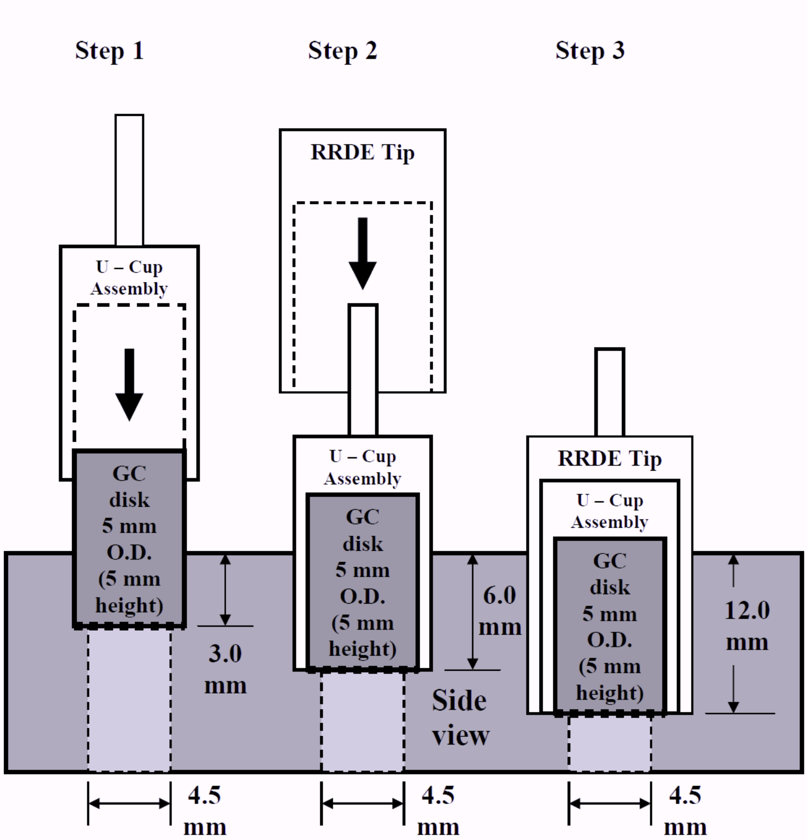


Figure 3.5: The method of using the tool shown in Figure 3.4 to assemble the RDE tip. Reprinted with permission from J. Electrochem. Soc. 157, B207 (2010). Copyright 2010, The Electrochemical Society (*Liu et al.*, 2010).

immobilized and thus are also non-adsorbing. Cleanliness is very important when making electrochemical measurements. All parts that came into contact with the electrolyte (i.e. parts described in the following subsections) were meticulously cleaned.

Glassware

A single compartment five-hole flask (#6961-64 from ACE Glass) contained the electrolyte, electrodes, and gas sparger, which was a 2 *μm* fritted tube (#9435-10 from ACE Glass). Figure 3.3d) shows an operating five-hole flask with the gas sparger bubbling and all the electrodes in place.

Counter Electrode

Pt wire counter electrodes were made by the Dalhousie Chemistry Department glass blower.

Reference Electrode

A mercury/mercurous sulfate electrode (MSE) reference electrode made by Koslow Scientific (5100A, glass, ⌀ 9 *mm*) was used because it does not contain Cl^-, which strongly binds to Pt (*Stamenkovic et al.*, 2001). Potentials are reported vs. the RHE, which is very common in the fuel cell literature. Instead of converting the potential numerically post-experiment, an ‘in-situ’ conversion from MSE to RHE was done with a precision voltage source. This is explained in the next section.

3.1.5.3 Reference Electrode Calibration with a Voltage Source

The potential of a reference electrode changes as the electrode is used, therefore periodic calibration is required. Initially, a calibration was done by measuring the MSE potential at which the HER\HOR on a rotating polycrystalline Pt electrode yielded zero current. However, the RDE experiments in this project were long (2 to 4 days) compared to typical RDE ORR experiments (hours) because of the durability testing protocols (described in Section 3.3). Calibration before and after the long test revealed several *mV*’s drift in the MSE potential. This is not surprising, as the MSE electrodes were filled with 3.5 M H_2SO_4. The slow leakage of H_2SO_4 through the reference electrode frit would yield a slow change in reference potential. Figure 3.6 shows the change in MSE potential (versus the RHE) with H_2SO_4 concentration.

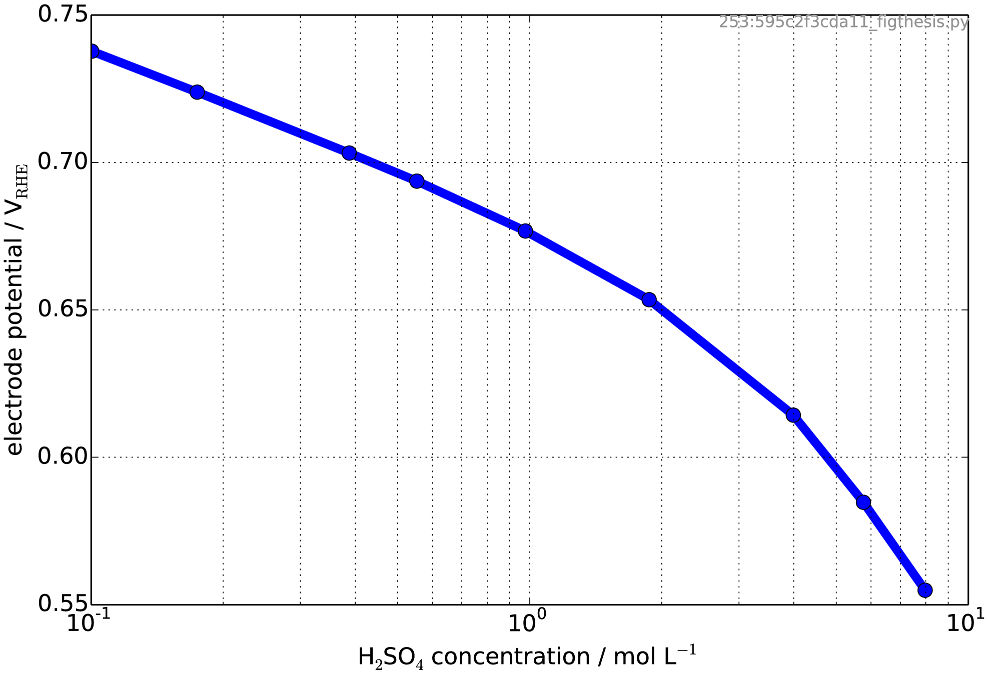


Figure 3.6: Change in MSE potential vs. RHE with H_2SO_4 concentration. Data from *Beck et al.* (1960).

This drift was a problem, because it meant potentials written in the PineChem set-up files needed to be changed with each experiment. The problem was solved by inserting a computer controlled voltage source (Keithley 213) between the working and counter electrode. The reference electrode calibration procedure entailed purging the electrolyte with hydrogen for ten minutes, then running a 0 *V* hold on the working electrode. The voltage source was then adjusted so the hydrogen oxidation or evolution current measured by the potentiostat was as close to zero as the Keithley 213 would allow (resolution of 0.1 mV). Shifting the potential with hardware meant the potentials in the setup files did not have to be changed for every reference electrode calibration. All experiments could conveniently be written vs. the RHE.

A pure Pt working electrode would be ideal for calibrating the reference electrode. However, the calibration before each experiment was performed with the sample to be tested, because Pt is the dominant element, and the exchange current densities of the HOR on either Ir or Ru are very close to Pt (*Cardarelli*, 2008). When no Pt was present on the sample (e.g. the Figures in Section *Electrochemical Oxides of Ir and Ru*, pg. 58), the reference electrode was calibrated using a polycrystalline Pt electrode made by Pine.

3.1.5.4 Current Source

Galvanostatic holds were required for the durability testing protocol, which is explained in Section 3.3 The Pine AFCBP1 bipotentiostat was capable of operating in a galvanostat mode, but the PineChem software did not have access to this, so a Keithley 2400 series source measure unit was used for the parts of the protocol which required constant current holds. A computer controlled switch was designed and built to switch the connectivity to the electrodes between the potentiostat and the Keithley source measure unit.

3.1.5.5 Other Experimental Information

- The temperature of the electrolyte was always at ambient, i.e. ~25°C.
- All gases (Ar, O_2 and H_2) were of grade “Ultra High Purity” supplied by Praxair.
- Gases were sparged for ten minutes before electrochemical measurement to saturate electrolyte and remove the previously dissolved gas.
- The rotator speed was 900 *rpm* at all times. The applicability of the Koutecký-Levich equation was previously tested in the Dahn Lab by *Bonakdarpour et al.* (2006).

3.1.5.6 Summary of the Dahn Lab RDE Stations

The Dahn Lab has developed several combinatorial techniques which are capable of measuring or synthesizing large numbers of samples at once. For instance, catalyst samples (for both RDE and fuel cell) are synthesized with a sputtering machine, modified in-house to be able to synthesize many different compositions in one sputtering run (*Dahn et al.*, 2002). After attempting combinatorial measurement techniques for fuel cell and RDE samples, and none working sufficiently well, five RDE stations were assembled to handle the volume of samples which resulted from the combinatorial sputtering machine. A computer controlled, solenoid gas switch was designed and built in-house to control gas flow to each of the stations. Figure 3.7 shows all the components for the RDE stations. Figure 3.8 shows a photo of all five stations in (and on top of) an old glove box.

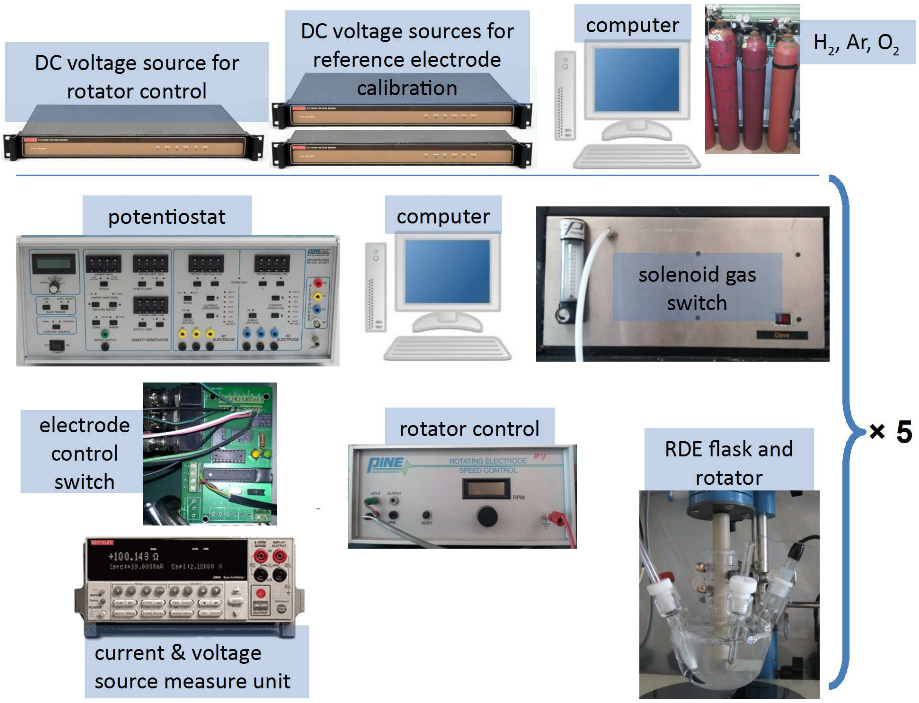


Figure 3.7: All the equipment that made the entire Dahn Lab RDE experimental set-up.

Figure 3.8: Photo of the five RDE stations. (Not all the equipment labelled in Figure 3.7 is shown.)

3.2 Sample Synthesis

RDE catalyst samples were synthesized in three main steps. First the glassy carbon disks were cut and polished, then they were coated with NSTF by 3M, then the disks were coated with catalyst material (i.e. Pt, Ir, and/or Ru) in a sputtering machine (at the Dahn Lab). The adhesion and stability of the NSTF on glassy carbon under RDE conditions had been previously demonstrated in the Dahn Lab by *Liu et al.* (2010).

3.2.1 Disk Preparation

The Pine RDE hardware (Figures 3.3a), b), and c)) requires cylindrical carbon inserts (disks) about 5*mm* high and 5*mm* in diameter to function as the catalyst substrate (or current collector). The height dimension is flexible due to a spring loaded contact pin (seen in the lower half of Figure 3.3a)). The diameter of the disk and inner diameter of the u-cup must exactly match. Therefore the u-cup wall thickness determines the size of disk that can be used in the RDE tip. Pine sells carbon disks and u-cups but the Dahn Lab elected to make its own due to significant cost savings.

Glassy carbon is a good material for a current collector because it is non-metallic, inert (corrosion resistant) and non-porous, but it is difficult to work and machine to exact tolerances due to its brittleness. For these reasons the Dahn Lab switched to disks made of compressed graphite (grade AXF-5Q, Poco Graphite Inc. now owned by Entegris) for some time, but due to concerns about data quality, switched back to glassy carbon for this project.[8] It should be noted that glassy carbon did not fix the data quality problem (see Section 4.6). Therefore it is conceivable that pyrolytically coated graphite could be used for future work.

Many u-cups were made for the Poco Graphite disks which were 5.2 *mm* in diameter. Therefore the new glassy carbon disks also had to be ⌀5.2 *mm* to make use of all the u-cups made for the Poco Graphite disks. Disks were cut from glassy carbon rods manufactured by Hochtemperatur-Werkstoffe GmbH (Gemeindewald 41, 86672 Thierhaupten, Germany). The rods were machined by HTW on a centerless grinder to ensure a diameter of 5.2 ±

---

[8] When the durability project first began, compressed graphite rods (grade AXF-5Q by Poco Graphite Inc., now owned by Entegris) were used. Disks were cut from the graphite rods by Dahn Lab staff, and sent back to Poco Graphite to be ‘pyrolytically coated’, which involves coating the disks with an organic resin, then calcination to convert the resin into a glassy carbon-type material.

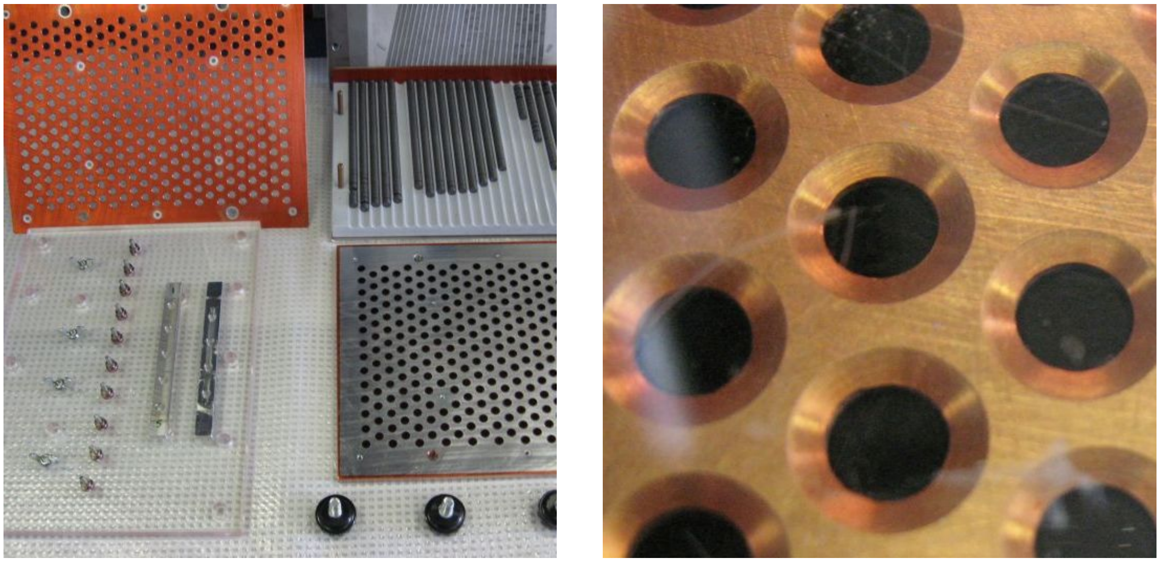
$0.001mm$. The rods were cut on a low-speed saw with a diamond coated blade (shown in Figure 3.9(b)). A specialized rig to secure the rod during cutting was designed and made by Dahn Lab Machinist Simon Trussler. Finishing the cut was done very carefully; if the arm holding the rod was allowed to fall at cut completion, the fracture would extend up the side if the rod, which would compromise the u-cup seal around the disk. Therefore, the long cutting process could not be left unattended. The disks retained a small 'burr' from the cutting which was removed by securing the disk in a drill press and very slowly lowering the rotating disk onto sandpaper. The drill press was also used to make the planar surface exactly perpendicular to the disc cylinder walls. This was done by hanging a weight on the one of the three drill press handles while moving coarse grit sandpaper under the disc (still secured in the chuck). The disks were then sanded and polished in steps ending with mirror finish (0.05 μ alumina grit) with a polishing machine (shown in Figure 3.9). During the polishing, the disks were secured in a holed plate glued to the polisher with CrystalBond. About 400 glassy carbon disks were prepared this way. Previous attempts in the Dahn Lab at making glassy carbon disk electrodes focused on small batches and required custom u-cups sizes because the diameter along the rod length was not consistent. Due to the brittleness of glassy carbon, the described system of making polished disks from rods was a result of trying many other pathways.

3.2.2 NSTF Growth on Glassy Carbon Disks

To coat the disks with NSTF, the following steps were taken: The mirror polished disks were released from the CrystalBond with acetone. The disks were then meticulously cleaned by ultrasonication in ethanol, then pure (18.2 $M\Omega$) water, followed by boiling in pure water. The drying step had to be rapid (seconds) otherwise spots would be left and these spots would remain visible after the NSTF coating (such a spot can be seen in Figure 3.9(d)). The disks were then loaded into a 'disk jockey' holder which exposed only one planar face of the disk and could be inserted into 3M's 'mach3' NSTF coating machine. The 'disk jockey' was made by Simon Trussler for the NSTF coating of Poco Graphite disks. The conditions of NSTF growth are proprietary. NSTF coating runs were performed by George D. Vernstrom (gdvernstrom3mmm.com). Figure 3.9(c) shows the 'disk jockey' holder. Figure 3.9(d) shows a close up of coated disks in the holder. A spot, left by the drying process, is visible on the second disk down on the right edge of the photograph.

(a) low-speed saw

(b) sanding and polishing machine



(c) ‘disk jockey’

(d) NSTF coated disks back from 3M

Figure 3.9: Some of the equipment used to prepare glassy carbon disks for sputter coating with Pt/Ir/Ru. **(a)**: the low-speed saw (used to cut the rods into disks), **(b)**: the sanding and polishing machine (holed plate for securing disks also visible), and **(c)** and **(d)**: the ‘disk jockey’ holder for 3M’s NSTF coating step. Other equipment used in the process, but not shown, is the rod-holding-jig for the low-speed saw, the drill press and the ultrasonic bath.

The ‘disk jockey’ cover plate (seen in upper right of Figure 3.9(c)) holds down the disks and leaves a small circumferential ring on the disk face which does not get coated by NSTF. This ring is shown in the next section, in Figure 3.12.

3.2.3 Sputtering

Sputtering is a physical vapour deposition technique used for the synthesis of thin films. For sputtering to occur, a voltage must be applied across two electrodes in a low pressure ($\sim 1\ mTorr$) chamber. This will light a plasma, which enables an electric current to pass between the electrodes. If argon is the gas in the chamber, positively charged argon ions will impinge on the cathode. The impact of the positive ions on the cathode will impart energy which will eject some material from the cathode surface, analogous to a the formation of an impact crater. The cathode material is therefore called a target. The ejected target material travels ballistically and lands on the substrate, which is placed opposite the target. The substrate is grounded to neutralize any ejected material which may be charged. The anode is a tunnel between the cathode and substrate. The yield of material ejected can be substantially increased if the plasma is confined with a magnetic field, so magnets are often arranged behind the target and this is known as magnetron sputtering. A circular erosion trench forms on the target as a result of the magnet. The target is recycled when the erosion trench wears down to the copper plate to which the target material is affixed.

3.2.3.1 The Dahn Lab Sputtering Machines

The Dahn Lab at Dalhousie University has two VT-3 multi-target magnetron sputtering machines made by Corona Vacuum Coaters Inc. (no longer in business). Important features of this machine are the toroidal arrangement of the targets and a rotating substrate table (diameter 40 cm). This, combined with the application masks at the end of the tunnel (as close as possible to the substrate), enables an areal loading which varies linearly along the toroid radius. All targets deposit along a single toroidal sputtering track. Three types of masks can create three types of thin films: 1) films where the maximum thickness runs along the inside of the toroid and zero thickness along the outside edge, 2) vice versa (maximum thickness along the outside toroid edge and zero along the inside) and 3) films with constant thickness along the toroidal radius. The amount of material deposited on the substrate can be adjusted by varying the sputtering power. A rotating table with multiple

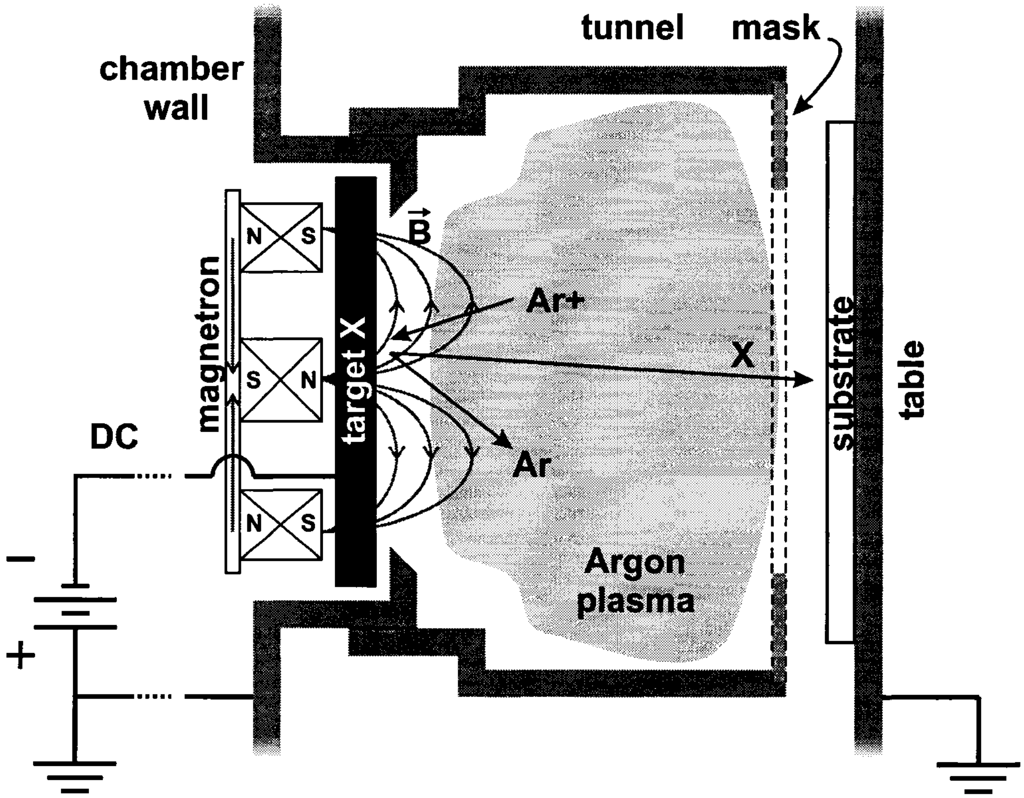


Figure 3.10: A schematic of a target assembly found in one of the multi-target magnetron sputtering machines in the Dahn Lab at Dalhousie University. The target is circular and the tunnel is cylindrical. Two magnets behind the target (a ring and a cylinder) are used to confine plasma electrons in a torus adjacent to the target. In the cross sectional schematic, the ring magnet appears twice. Used with Permission of copyright holder Vincent L. Chevrier, from *Chevrier* (2006).

targets simultaneously powered will produce thin films composed of 'intimately mixed' materials. Power and rotation speed are in ranges where less than an atomic monolayer is deposited with each pass of a point on the sputtering track. Therefore the sputtering machine can easily deposit a thin film which varies in a full binary composition range along the toroidal radius. Also, the machines in the Dahn Lab have been modified to enable the creation of thin films with a full range of ternary (*Dahn et al.*, 2002) and even quaternary (*Chevrier and Dahn*, 2006) stoichiometries on a single flat substrate, though these capabilities were not used for this project. Such films are often called libraries. More details on the system, such as the mask shapes, can be found in *Bonakdarpour et al.* (2003), *Barkhouse et al.* (2003), and *Hatchard et al.* (2003) Figure 3.10 shows a side-on view of a target assembly. Figure 3.11 shows a Dahn Lab sputtering machine with the door open.

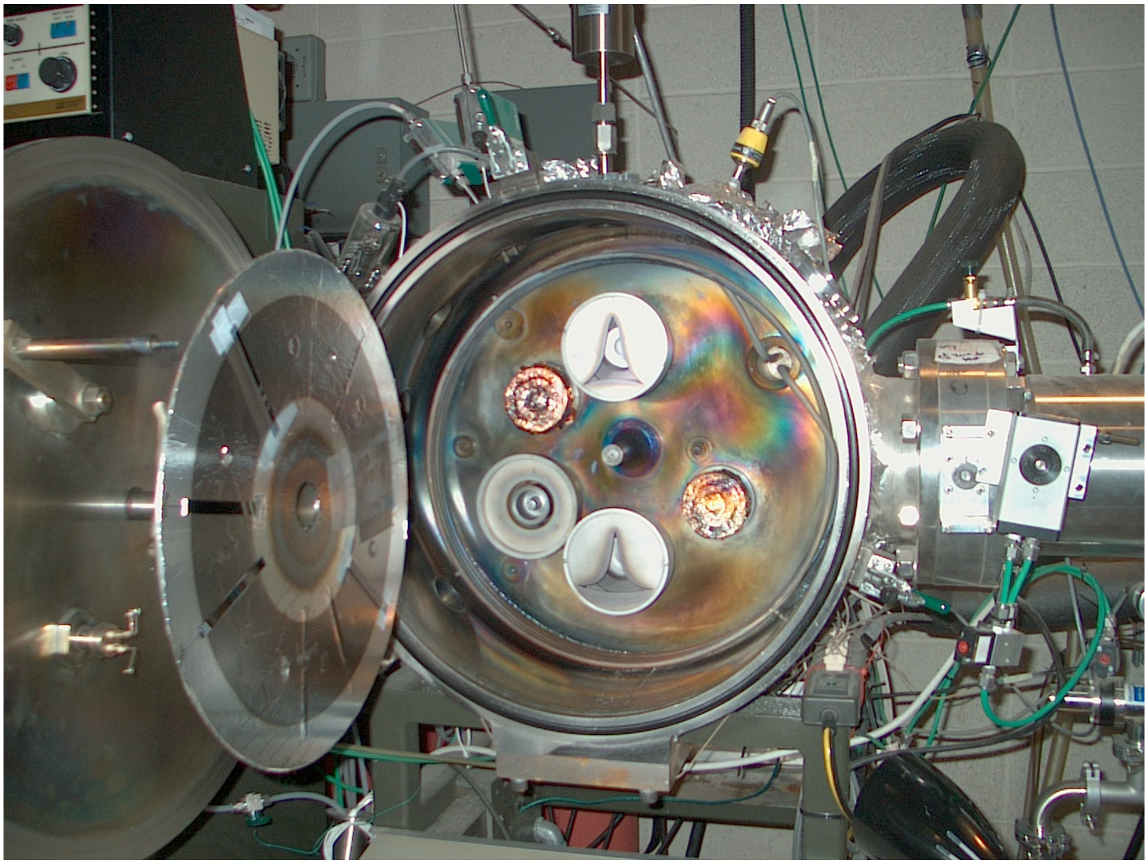


Figure 3.11: A sputtering machine showing two masked targets (both linear), two targets covered with copper foil, one sputter cleaner in the chamber. The door is open with the rotating table still attached. On the table can be seen a dark toroid, which is a thin film of the sputtered material.

Sputtering chamber walls are heated to desorb water and other contaminants. A R2000 series Polycold (now owned by Brooks Automation Inc.) fast cycle cryocooler supplies a coil inside the sputtering chamber which traps water vapour to achieve a vacuum faster than would be normally possible with just a turbo pump.

3.2.3.2 Sputtering Machine Procedures and Deposition Calibration

Before any sputtering run, the chamber is pumped down to low vacuum (10^{-7} $Torr$) with a turbo pump; a rotary vane 'roughing pump' first provides an initial vacuum. Ar gas is then introduced into the chamber at a controlled rate and the turbo pump speed is lowered to achieve a steady state pressure between 1 to 30 $mTorr$. All catalyst materials for this thesis project (Pt, Ru, and Ir) were sputtered in an Ar atmosphere and therefore deposited in the metallic state.

To measure the deposition rate, the mass of material deposited at a known sputtering pressure, power and number of rotations was measured with a Satorius SE-2 electronic micro-balance that has a resolution of 0.1 μg. To determine the mass of deposited material, the mass of punched circles of Al foil, called 'weigh disks' were measured before affixing them to the substrate table. After sputtering, the weigh disks were measured again, and the original masses subtracted to obtain the mass of sputtered material. Mass loading calibration procedures can also be found in *Liu et al.* (2010). These sputtering rate calibrations for each target were performed within about three months before a sample synthesis because the magnet strength changes over time, and the erosion trench on the target deepens with use, both of which can influence sputtering rate. During deposition, the Ar flow rate through the sputtering chamber was ~2.3 *sccm* and the pressure inside the sputtering chamber was ~0.8 $mTorr$. The target power was set to 50 *W*, 75 *W* and 65 *W* for Pt, Ru and Ir respectively. The actual power through the target could differ from the set power by up to ±4 W.

The disks are affixed on the sputtering table with holders which snugly fit into recessed slots machined into the flat table. Figure 3.12 shows a close-up photo of a holder with disks in a slot after a sputtering run. A holder can accommodate five disks. The slot positions and holder lengths are designed such that two holders can evenly space nine disks along the sputtering track radius, allowing for nine uniquely loaded disks using a linear mask.

Assembling the disk holder with nine disks is actually a difficult task, as is removing the disks from the holder after a sputtering run because they tend to get firmly stuck to one side of the holder. There is a big risk the disk surface will get scratched during assembly and removal. Figure 3.13 shows a disk for which the NSTF coating was damaged before the sputtering run, because the scratch and spots show up as highly reflective.

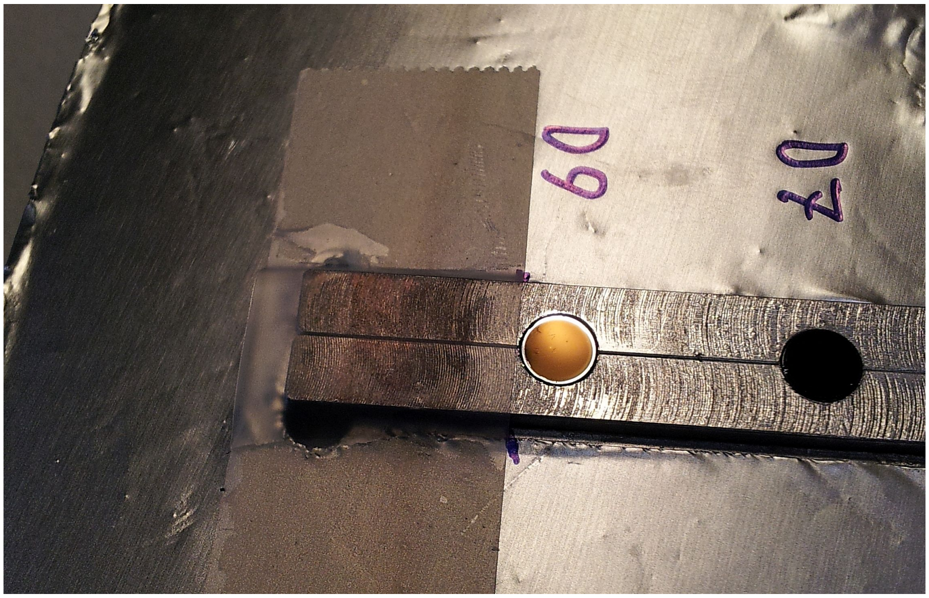


Figure 3.12: A close-up of the outer end of disk holder on the sputtering table after a sputtering run. The 9th and 7th of 9 possible disk positions are labelled as D9 and D7. Visible in the upper left is the outer edge of the sputtering table. The camera was positioned such that a reflective glare was on D9. This brings out the reddish colour of the NSTF and clearly shows the outer ring left by the 'disk jockey' cover plate. The ring is highly reflective because Pt/Ir/Ru deposits as a flat thin film on the polished glassy carbon in this area due to the absence of NSTF.

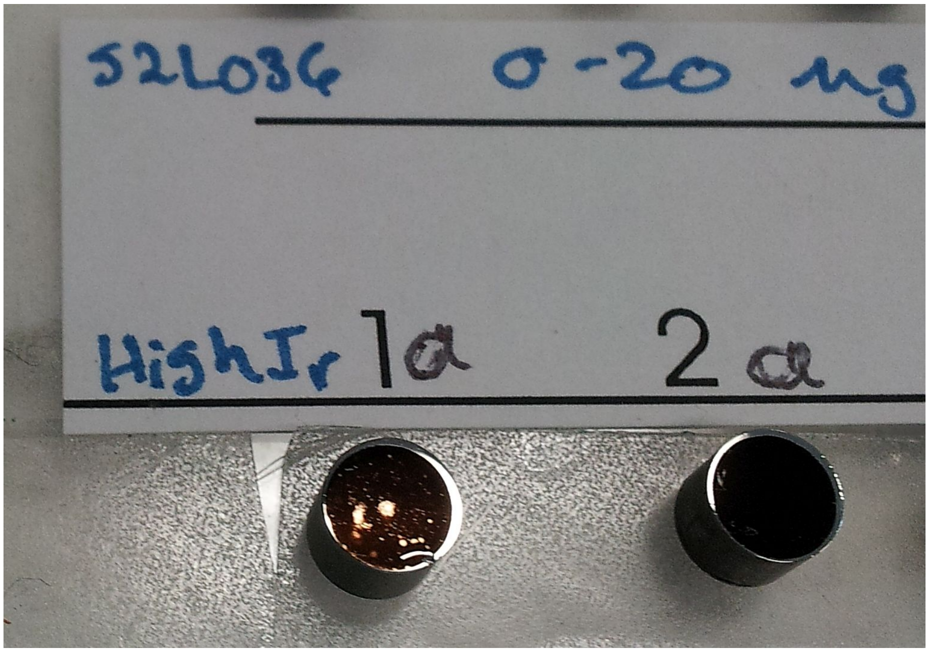


Figure 3.13: Damage and scratches done to disk 1a after the NSTF coating step, became highly visible after sputtering run S2L036.

3.3 Developing an RDE Durability Test for a Fuel Cell Cathode Catalyst Material

After synthesis, the samples must be tested for durability, but how? The catalyst should be deliberately degraded and the decline of some indicator of ORR activity with time could be the quantifier for durability. The ideal way to degrade a catalyst would be to subject an actual fuel cell to actual start and stop events. Probably the next best method would be to alternate the anode gas stream leading into a fuel cell between hydrogen and air. This was the approach of much of the early start/stop literature, particularity that from industrial researchers (For example *Reiser et al.* (2005) (UTC) and *Tang et al.* (2006) (Plug Power)). For RDE testing however, the degradation must be simulated with electrochemical control of the working electrode. It is therefore necessary to design some type of repeating experimental protocol designed to degrade the catalyst. Such a protocol is often called an accelerated stress test (AST). In the interest of laboratory efficiency, the AST should inflict as much damage as possible to shorten the length of the test. At the same time, its harshness should not exceed 'real-world' degradation conditions. For example, potentials of the test should be within the range of those caused by the degradation mechanism. Knowing how the start/stop potential changes with time, and the maximum value it could reach, is important for accurately simulating 'real-world' conditions.

3.3.1 Simulating Fuel Cell Start/Stop

A start/stop event raises the potential on the cathode. How should a start/stop event be simulated with the RDE? What is the nature of the rise (i.e. how does it proceed with time?)? How high does the potential climb during fuel cell start/stop? Attempting to answer these questions guided the development of the durability testing protocol used for this thesis project.

At the beginning of the USDOE durability contract, start/stop events were simulated by the RDE with potential holds (*Stevens et al.* (2010) and *Hatchard et al.* (2011)). Many RDE studies on cathode catalyst durability (start/stop simulations) use CVs (i.e. a saw-tooth/triangular potential waveform) with lower and upper limits of 1 and 1.5 V_{RHE} (*Huang et al.* (2011), *Binninger et al.* (2013), and *Parrondo et al.* (2014)). Later in the USDOE durability contract, the Dahn Lab also used saw-tooth potential waves to simulate start/stop, but these studies were not published. Some fuel cell durability studies (no RDE) also used triangular waveforms going up to 1.65 *V* (*Atanasoski et al.* (2012) and *Atanasoski et al.* (2013)). However we had an intuition these types of simulations were inadequate. What was the true nature of a start/stop potential transient? To answer this, a direct measurement of the cathode potential during a start/stop event is needed.

3.3.1.1 Temporal Nature of the Start/Stop Potential Excursion

Kim et al. (2009) invented a way to connect a reference electrode to a fuel cell membrane (the electrolyte), enabling a potentiostat to measure the potential of a fuel cell cathode during start/stop. Figure 3.14, taken from their study, shows the potential vs. time for the cathode, anode, and full cell when the anode gas stream is switched from hydrogen to air, and back to hydrogen. The shape of the first transient does not have the appearance of a saw-tooth wave. If anything, the first half of the first cathode potential transient (resulting from the air entering the anode) looks more like the potential response at the sudden start of a constant current. This led to the idea that pulses of constant current could be a more accurate simulation of the start/stop potential spikes. There is another reason to simulate start/stop events with galvanostatic holds. Pulses of constant current allows the potential reached during simulated start/stop to change as the catalyst degrades; OER catalyst loss results in a higher voltage for a given current. The next logical question in the durability protocol development is how high should the potential be allowed to go during the galvanostatic holds?

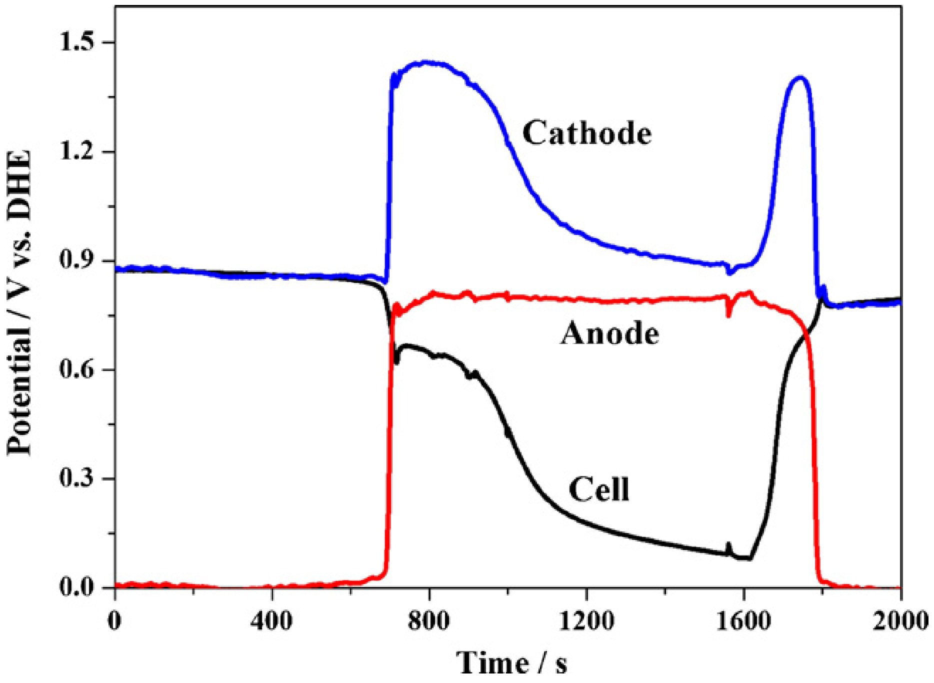


Figure 3.14: Electrode potentials of an actual fuel cell undergoing start/stop (simulated by switching the anode gas flow to air, then back to hydrogen). The dynamic hydrogen electrode (DHE) was the name they gave for their novel reference electrode inside the fuel cell, but is essentially equivalent to an RHE. Reprinted from Journal of Power Sources, 192, Kim, J., Lee, J. & Tak, Y., Relationship Between Carbon Corrosion and Positive Electrode Potential in a Proton-Exchange Membrane Fuel Cell During Start/Stop Operation, pg. 674-678, Copyright (2009) with permission from Elsevier (*Kim et al.*, 2009).

3.3.1.2 Upper Potential Limit of the Start/Stop Potential Excursion

Sidik (2009) showed the RCDM could be simply modelled with a set of Tafel equations if one understands the system as a ‘driving cell’ and a ‘driven cell’. *Sidik* (2009) also pointed out that *Reiser et al.’s* (2005) RCDM model, a second order differential equation of a heuristically introduced “electrolyte potential”, is incorrect. This is the approach used to make Figure 2.14, except with an added improvement over Sidik’s approach.[9] The main point in *Sidik* (2009) is “the maximum potential experienced by a (fuel cell) cathode under (start/stop) is about twice the potential observed when one connects a driving fuel cell to a driven cell (electrolyzer), both of which having the same physical characteristics and operating under the same conditions.”. The equation on Figure 2.14 ($V_{fuel\ rich} = V_{fuel\ starved}$) is based on Sidik’s driving cell/driven cell understanding of the RCDM.

---

[9] *Sidik* (2009) assumes the same kinetics for the ORR on both the anode and cathode, while Figure 2.14 simulates two different ORR equations for the anode and cathode for scenario Ⓑ.

Open circuit voltage for a state-of-art NSTF fuel cell is about 0.95 V. (*Steinbach*, 2016). One would expect the RDCM to slightly polarize this voltage due the corrosion current. Therefore if we assume the highest voltage the fuel rich region (driving cell) can reach is 0.9 V, the potential on the cathode in the fuel starved region would climb to a maximum of 1.8 V_{RHE}. This is the maximum potential a constant current hold delivered by the Keithley 2400 was allowed to reach. After 1.8 V_{RHE} is reached, the hold is continued for the planned duration, but the current is adjusted to maintain 1.8 V_{RHE}.

3.3.2 The RDE Durability Testing Protocol for this Thesis

When a fuel cell operates, the cell voltage gets down to approximately 0.65 V. When a fuel cell idles, the cathode potential is the open circuit voltage (i.e. ~0.95 V (*Steinbach*, 2016)). When a fuel cell is completely off, the cathode of the fuel cell is filled with air, so the potential can be assumed to be the oxygen rest potential, which is also about ~0.95 V_{RHE}. The oxygen rest potential for Pt is 1.046 V_{RHE} (*Hoare*, 1962), for IrO_2 is 0.94 V_{RHE} (*Hoare*, 1964), and for RuO_2 is 0.9 V_{RHE} (*Burke and O'Meara*, 1972). Therefore a series of potentiostatic and galvanostatic holds were performed, to simulate the effect rest (fuel cell off), start-up, operation, idle and shut-down on a fuel cell cathode. Figure 3.15 shows these sequence of holds, hereafter called one SU/SD cycle, applied to pure Pt on NSTF on glassy carbon. The electrolyte was kept saturated with O_2 to simulate a fuel cell cathode environment. Also, *Matsumoto et al.* (2011) showed the presence of O_2 enhances Pt dissolution. The galvanostatic holds in Figure 3.15 were set to 200 μA, or 0.942 $mA\,cm^{-2}$, which provided a rise in potential to an acceptable range. ASTs performed for the study in Chapter 4 maintained 200 μA, while ASTs shown in Chapter 5 used an increased start/stop of 500 μA to shorten test duration while keeping beginning-of-test potential for the benchmark Pt sample below 1.8 V_{RHE}.

CVs were performed every 200 SU/SD cycles to characterize ORR. A CV going up to 1.55 V_{RHE} was also usually included to possibly aid in a more detailed characterization of OER activity than the galvanostatic pulses could provide. When this high potential CV was included, ORR CVs were usually done before and after it, to determine if this CV had any influence on ORR activity. It most cases the influence was insignificant. Figure 3.16 shows an example of the initial set of characterization CVs, the first set of 200 SU/SD cycles, and the second set of characterization CVs. The characterization CVs data was collected with the Pine potentiostat and the holds for the start/stop simulations were performed with the Keithley 2400 series source measure units.

In addition to the galvanostatic holds, this testing protocol has key differences when compared with most other RDE ASTs found in the literature; virtually all published RDE AST studies simulate SU/SD separately from load cycling. Although not mentioned specifically in Section *Pt Instability* (pg. 23), load cycling and idling are other ways the two Pt degradation mechanisms and are activated. For instance, a study from Nissan (*Shimoi et al.*, 2009) attributes almost half (44%) of fuel cell performance decline (which would include the effects of carbon corrosion) to SU/SD, with load cycling and idling evenly responsible for the other half. A standardized AST for RDE from the Fuel Cell Conference of Japan (FCCJ) uses triangular waves between 1.0 and 1.5 V_{RHE} for start/stop simulation and another test (square waves between 0.6 and 1.0 V_{RHE}) to simulate load cycling and idling (*Ohma et al.*, 2011). The USDOE also proposed two tests designed to simulate load cycling and SU/SD, also on either side of 1.0 V. The tests were part of a Request for Information (*United States DOE*, 2013), but have not yet been incorporated into the USDOE's master document for fuel cell research targets and standards (the "Multi-Year Research, Development, and Demonstration Plan" (*United States DOE*, 2016)) The AST designed for this thesis project is unique among RDE ASTs in that it simulates start/stop events, load cycling and idling. Therefore it can be considered much more aggressive (though still realistic) than virtually all the other RDE AST studies reported.

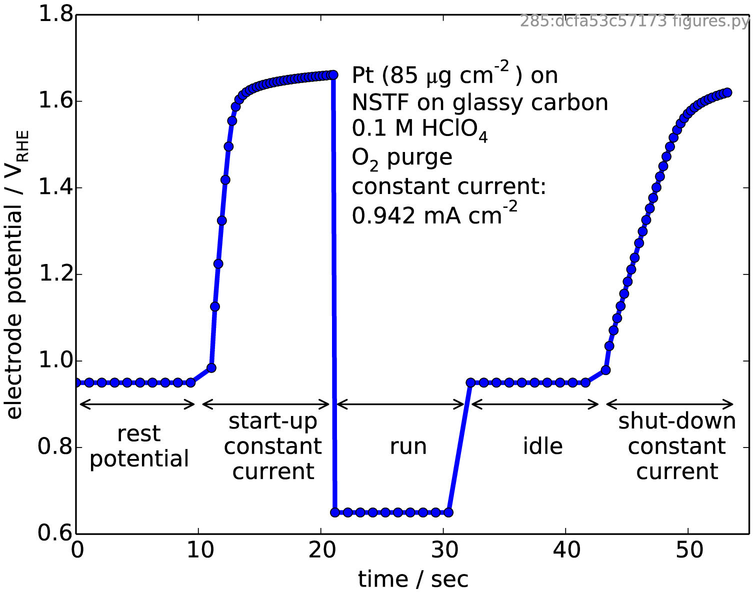


Figure 3.15: An example of a sequence of potentiostatic and galvanostatic holds designed to simulated the potential on a cathode during fuel cell start-up, run, idle, and shut-down, performed on a pure Pt RDE sample. The sequence of five holds constituents one SU/SD cycle.

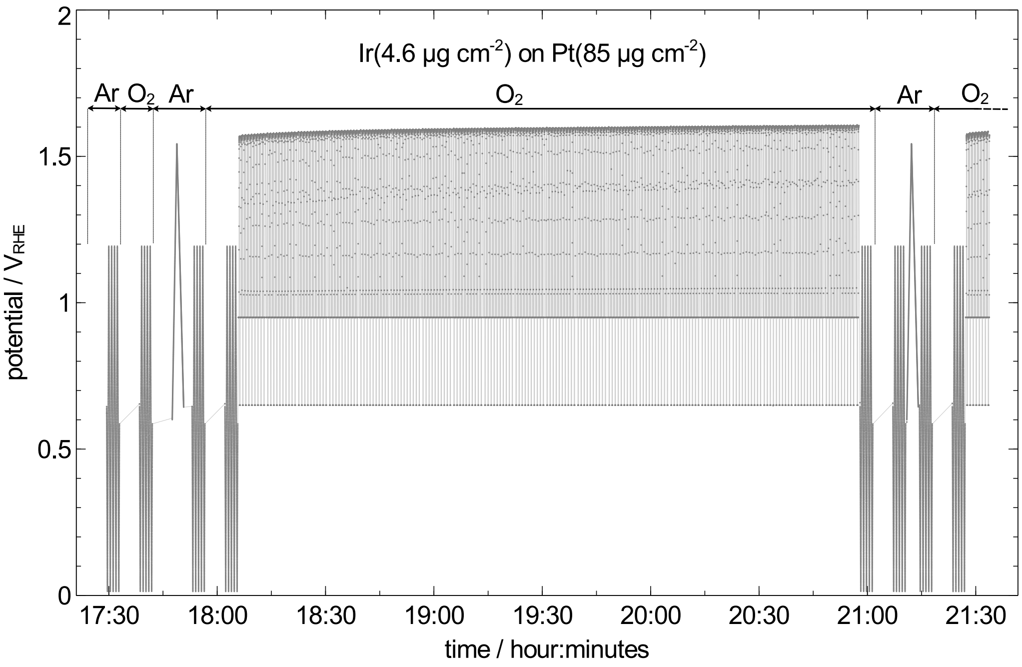


Figure 3.16: An example of one of the many ASTs done for this project. Shown is the initial set of characterization CVs, followed by 200 SU/SD cycles, followed by the second set of characterization CVs, followed by a few SU/SD cycles. The AST was generally stopped when the potential of the constant current holds reached their allowed maximum, 1.8 V_{RHE}, or when 4000 SU/SD cycles were completed. Gas purging of either Ar or O_2 is indicated.

3.3.3 Additional Data on the Nature of Start/Stop

After the AST for this project was designed and put to use, published studies of measured fuel cell potentials during start/stop came to light which demonstrate a discrepancy concerning the temporal nature of the potential transient during a start/stop event.

Dross and Maynard (2007) fitted a fuel cell with two RHEs, one at the anode inlet and the other at the anode outlet. From their study, Figure 3.17 shows potentials during an actual start-up and Figure 3.18 shows potentials during an actual shut-down. The start-up potential transient looks very much like the potential response from the initiation of a constant current. The shut-down potential transient looks very much like a triangular (saw-tooth) potential wave. The FCCJ also performed potential measurements a fuel cell fitted with a reference electrode to assist in the development of their AST (*Ohma et al.*, 2011). From their study, Figure 3.19 shows the potentials during a simulated start-up. They do not provide details on the their reference electrode, so an RHE is assumed. In contrast to *Dross and Maynard* (2007), the start-up potential transient looks very much like a triangular (saw-tooth) potential wave. The location of the reference electrode for the studies by *Ohma et al.* (2011) and *Kim et al.* (2009) was not specified. Perhaps this is the reason for the discrepancy. Because of the specification of the reference electrode locations, the study by *Dross and Maynard* (2007) seems the most trustworthy. If this study had been known during the development of the AST for this project, perhaps the shut-down potential transient would have been simulated with a triangular wave. Also, a further improvement on the AST for this project would be to let the shut-down potential relax to the rest potential naturally, but this would prolong the duration of the experiment. This could also influence the degradation to be less severe; recall the study by *Topalov et al.* (2013) indicates the rate of potential change is an important factor in the amount of Pt loss (see Figure 2.7).

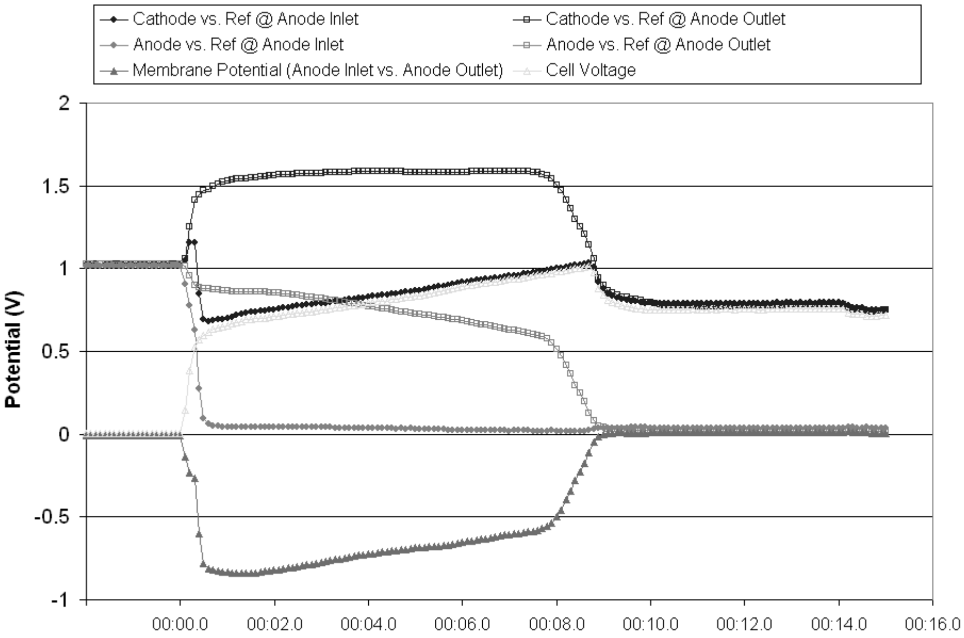


Figure 3.17: Start-up potentials of a fuel cell. “Cathode vs. Ref @ Anode Outlet” shows the maximum potential on the cathode reaches 1.59 V_{RHE}. The shape looks like the potential response of a constant current. Reprinted with permission from ECS Trans. 11, 1059-1068 (2007). Copyright 2007, The Electrochemical Society (*Dross and Maynard*, 2007).

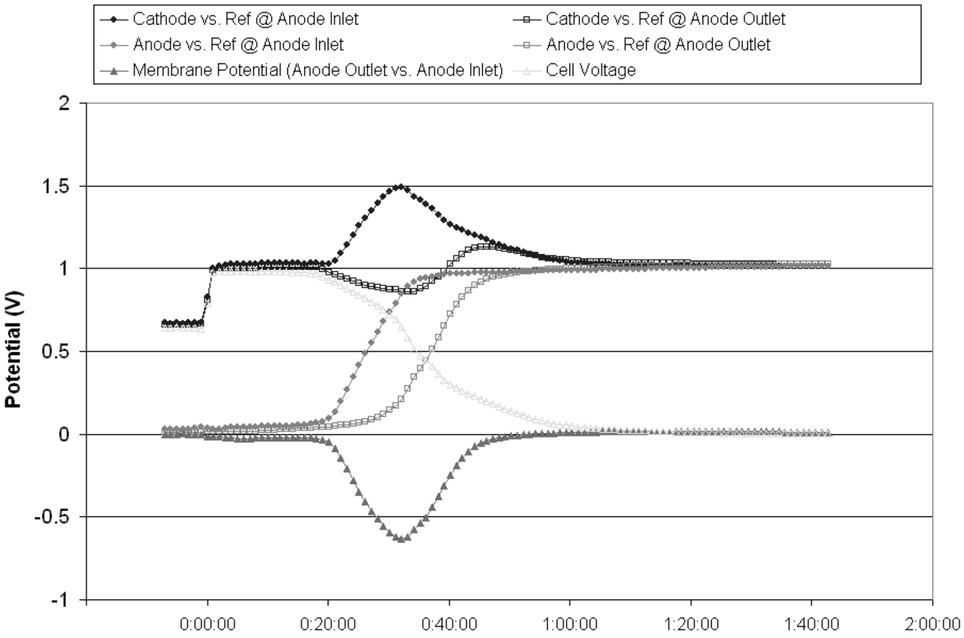


Figure 3.18: Shut-down potentials of a fuel cell. “Cathode vs. Ref @ Anode Inlet” shows the maximum potential on the cathode reaches 1.5 V_{RHE}. The shape looks like a triangular (saw-tooth) potential wave. Reprinted with permission from ECS Trans. 11, 1059-1068 (2007). Copyright 2007, The Electrochemical Society (*Dross and Maynard*, 2007).

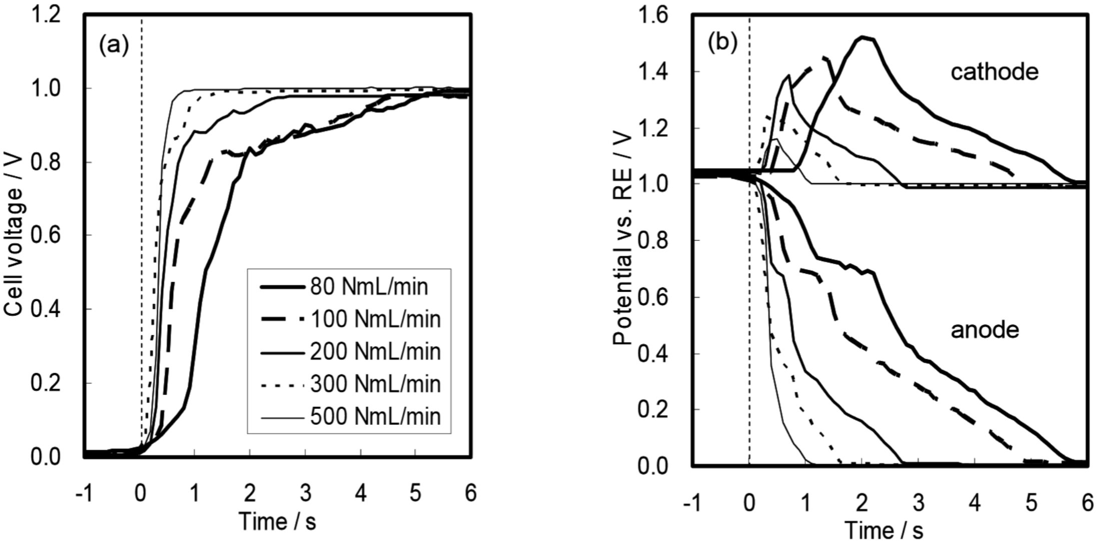


Figure 3.19: Full cell voltage **(a)** and potentials **(b)** of a fuel cell undergoing a simulated start-up event (beginning with air in both anode and cathode). Legend in **(a)** is flow of hydrogen gas in anode. The cathode potential transient **(b)** shows that the maximum potential on the cathode reached 1.5 V_{RHE} for slowest anode flow (80 $NmL\,min^{-1}$), and the shape looks very much like the a triangular (saw-tooth) potential wave. Reprinted with permission from ECS Trans. 41, 775-784 (2011). Copyright 2011, The Electrochemical Society (*Ohma et al.*, 2011).

Chapter 4

A Comparison of Intermixed and Overlayered Ru and Ir Compositions[1]

This study was meant to serve as a baseline for subsequent RDE studies on the Ir-Ru-Pt NSTF catalyst system. As stated in *Structure of this Thesis* (pg. 21), this study should be viewed as a learning experience. Included in this chapter, but not in *Crowtz et al.* (2014), are more details on the numerical methods used for the necessary ORR corrections, the experimental problem of glassy carbon current collector corrosion, ECSA inaccuracies stemming from the presence of Ru/Ir, Tafel slope analysis, and several additional types of plots.

Ideally, both Ir and Ru will be part of the materials solution to mitigating the RCDM, but the simpler systems, that is either Ru or Ir along with Pt should be studied first. A study was conducted which hoped to answer one of the questions posed in the Section *Project Motivation*: What is the best manner of sputtering deposition for Ru and Ir when combined with Pt on NSTF? Specifically, this question had a view toward creating alloy thin films with the sputtering machine known as 'intimately mixed', or 'intermixed' films. A more focused question would therefore be: is it better to sputter Pt and Ru/Ir intermixed (as an alloy), or with the OER catalyst deposited after (on top of) the Pt? Ru or Ir deposited under Pt was not considered because it was assumed the overlayer of Pt would effectively cover and therefore block the action of the OER catalyst.

4.1 Numerical Methods for Determining ORR Activity

None of the data presented in this Chapter is corrected for ohmic drop. Figure 4.1 shows the steps in applying the ORR corrections with the processing techniques used for this

---

[1] Portions of the data shown in this chapter (about a third of the figures) were published in *Crowtz et al.* (2014). The author's contribution to *Crowtz et al.* (2014) included writing all the text, all the data analysis (numerical processing and figures), all the sample synthesis except the sputtering, and about half of the RDE experimental work. Unfortunately there was a data processing mistake in the original publication affecting the pure Pt sample. This mistake is corrected in this chapter.

Chapter. The following two sections explain some details for ORR numerical processing which were not covered in Chapter 3.

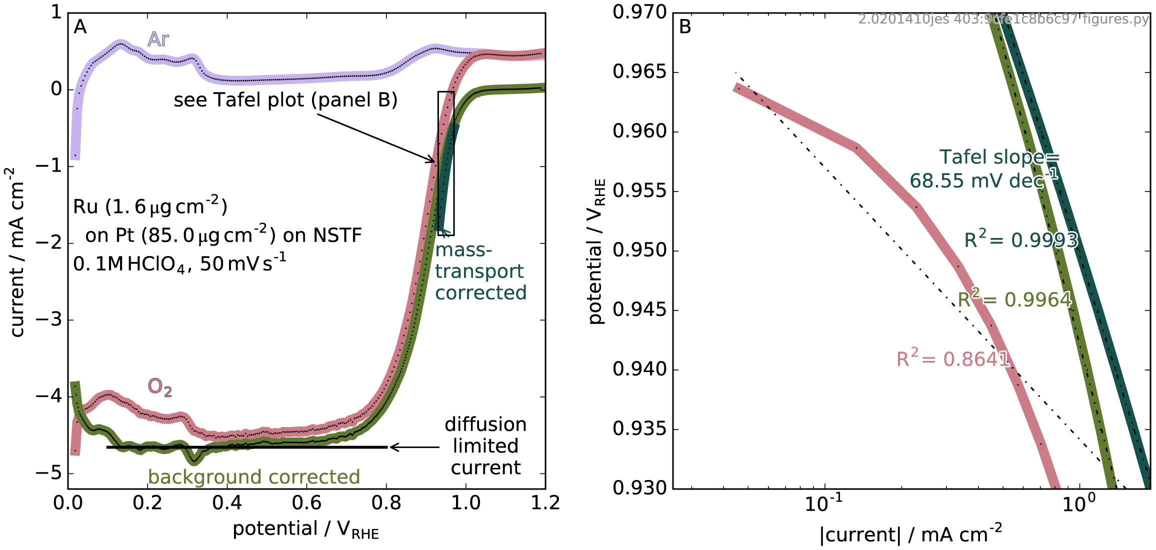


Figure 4.1: **A**: The final up-sweep of an Ar and O_2 CV, their resulting background corrected up-sweep, and a small segment of the result of the application of the Koutecký-Levich equation (labelled mass-transport corrected). **B**: A Tafel style plot showing how each correction improves the goodness-of-fit to the Tafel equation.

4.1.1 Sweep Cusp Determination: Moving Regression Sign Change

To separate the raw CV data into sweeps, a moving linear regression window was applied to the potential vs. time data. The potential-time cusps (locations where the sweep switched direction) were the points when the slopes change sign (from negative to positive or vice versa). There were two points for each cusp, corresponding to the two slopes closest to zero. The window data bin (about $^1/_{10}{}^{\text{th}}$ the length of a sweep) was an odd number so the regression slope was based on the same number of points ahead and behind.

4.1.2 Sweep Monotonicity: Noise Removal with Regression Estimate

The CV subtraction requires that the two *I*-*V* sweeps have equivalent potentials. Interpolating the current to a list of potentials required that the raw potential data be monotonic, (i.e. constantly increasing). The monotonicity of the raw data was often interrupted by noise. Therefore to simplify the processing, a linear regression was performed on the raw potential vs. time data. The potential values from the regression equation were then substituted for the raw potential data. The current for the CV sweeps (Ar and O_2) were then interpolated to a list of potentials to perform the subtraction.

4.2 A Study on Binary Ru/Ir with Pt Intermix and Overlayer Compositions

The areal mass loadings of Pt, Ir and Ru in this project were guided by United States USDOE targets for the total mass of platinum group metals (PGM) on both anode and cathode from the "Multi-Year Research, Development, and Demonstration Plan" (*United States DOE*, 2016). The catalyst target for 2020 specifies 125 $\mu g\, cm^{-2}$ total PGM loading for both anode and cathode. 3M directed that Pt loading be set at 85 $\mu g\, cm^{-2}$ for all work performed for the 3M durability contract. As of 2015, 3M's state-of-the-art hybrid[2] NSTF fuel cell had about 20 $\mu g\, cm^{-2}$ of Pt on the anode (*Steinbach*, 2016). Therefore, there was enough flexibility for the remaining Pt or PGM to go toward the OER catalysts (125 – 85 – 20 = 20 μg).

NSTF disks were coated with Pt and Ir or Ru via either an overlayer or intermix sputtering technique. Figure 4.2 shows a simple sketch which illustrates the difference between the different deposition configurations. Three binary compositions were prepared in each of the four sputtering runs resulting in twelve compositions with stoichiometries of $Pt_{1-x}Ir_x$ and $Pt_{1-x}Ru_x$, where x = 0.035, 0.15, and 0.33 (except for the highest Ru content overlayered on Pt, where x = 0.22 instead of 0.33). This resulted in mass loadings of 3, 15.3, and 42 $\mu g\, cm^{-2}$ for Ir (intermix and overlayer), 1.6, 8.1, and 22 $\mu g\, cm^{-2}$ for Ru intermixed and 1.6, 8.1, and $\underline{12.3\ \mu g\, cm^{-2}}$ for Ru overlayer.[3] A fifth series of samples consisting of 6 $\mu g\, cm^{-2}$ Ir overlayered on a Ru-Pt intermix composition spread (Ru: 1.6 to 22 $\mu g\, cm^{-2}$) was also tested.

---

[2] The latest NSTF fuel cells from 3M now add a thin layer of Pt\C on the NSTF cathode

[3] The highest Ru on Pt has a different stoichiometry because the $Pt_{1-0.33}Ru_{0.33}$ sample was unfortunately damaged.

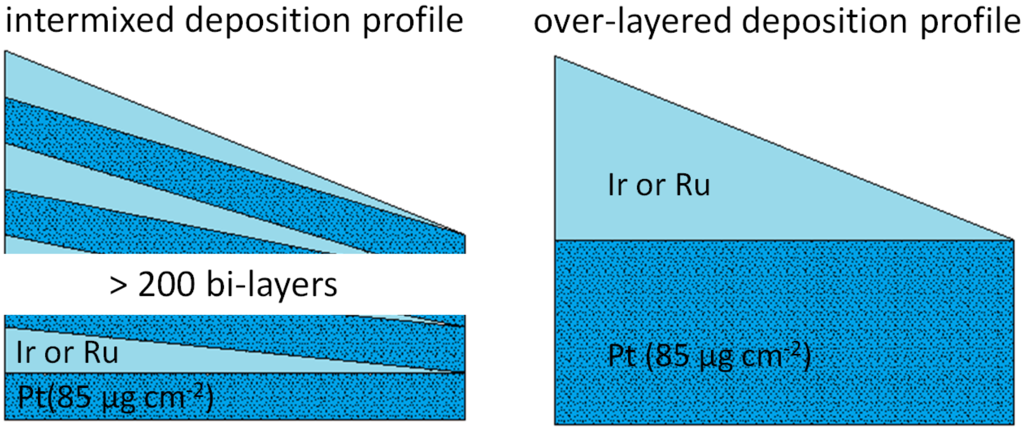


Figure 4.2: A simple diagram highlighting the difference between the intermix and overlayer sputter deposition techniques. Less than atomic monolayer is deposited in each intermixed wedge.

4.3 Results of Binary Compositions

Experiments were carried out with the AST described in Section *The RDE Durability Testing Protocol for this Thesis* (pg. 119). Figure 4.3A shows the potentials of the experiment for pure Pt, which serves as the baseline for comparison to all the other compositions. The zoomed inset panels B and C are referred to later in this section to explain the determination of ORR and OER activity. Figures 4.8 through 4.11 show the progression of ORR and OER activity for all twelve compositions. The ORR and OER activity for one sample are tracked together by using the marker colour as the indicator of OER activity.

General Remarks on OER Activities:

The OER activity can be easily characterized with the highest potential reached during a constant current hold. The start-up end-potential was selected as a performance metric of OER activity because the potential at the end of the start-up hold is always higher than the potential at the end of the shut-down hold. Figure 4.3C shows encircled, a start-up end-potential just prior to ORR characterization This was used as the OER activity to colour the markers in Figures 4.8 through 4.11. Figure 4.4 shows all the start-up end-potentials for all compositions except pure Pt. Figure 4.5, shows a plot of start-up end-potentials for the first 50 SU/SDs. Initial OER activities correlate to Ru loading and deposition methods as one would expect.

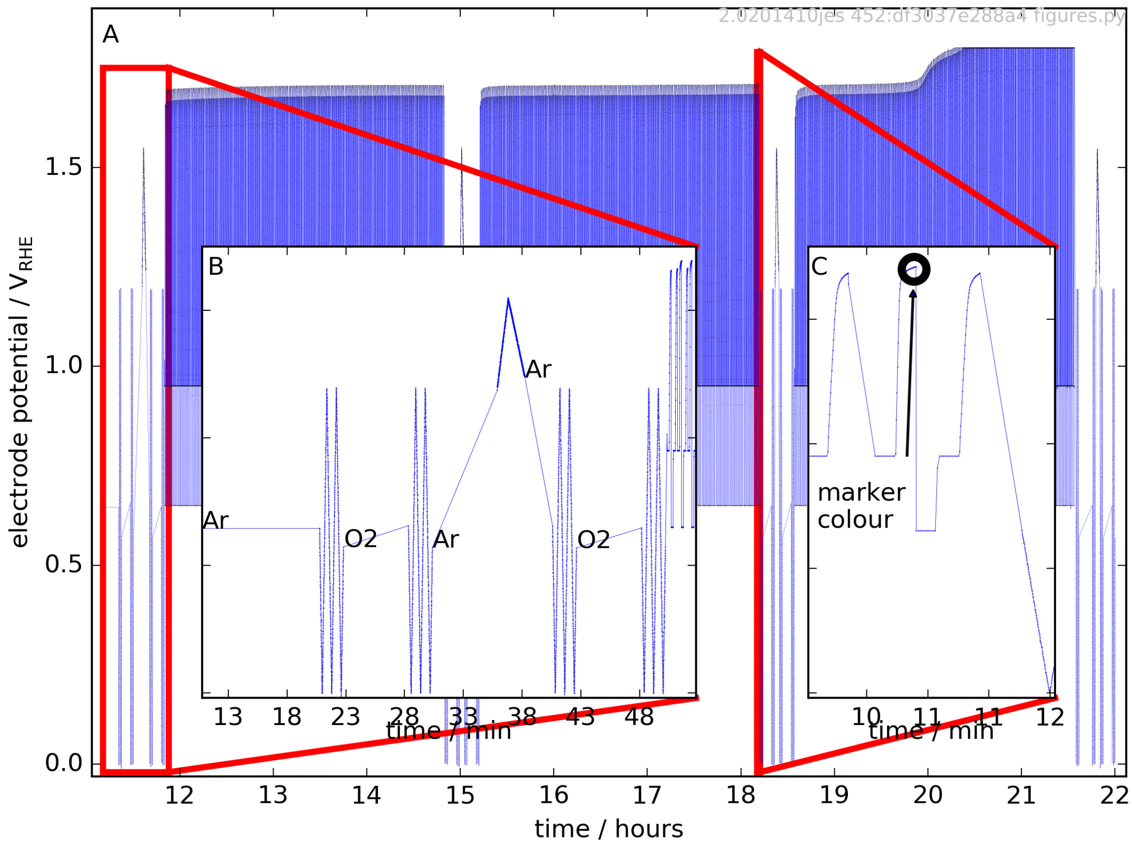


Figure 4.3: **A**: Complete SU/SD RDE experiment of pure Pt (85 $\mu g\, cm^{-2}$). Sets of 200 SU/SD cycles are separated by sets of ORR characterization CVs. **B**: The first set of characterization CVs with commencement of gas purging indicated. **C**: The final potential (circled) at the end of a start-up hold immediately prior to a set of ORR characterization CVs. This value is used to colour the markers in Figures 4.8 through 4.11.

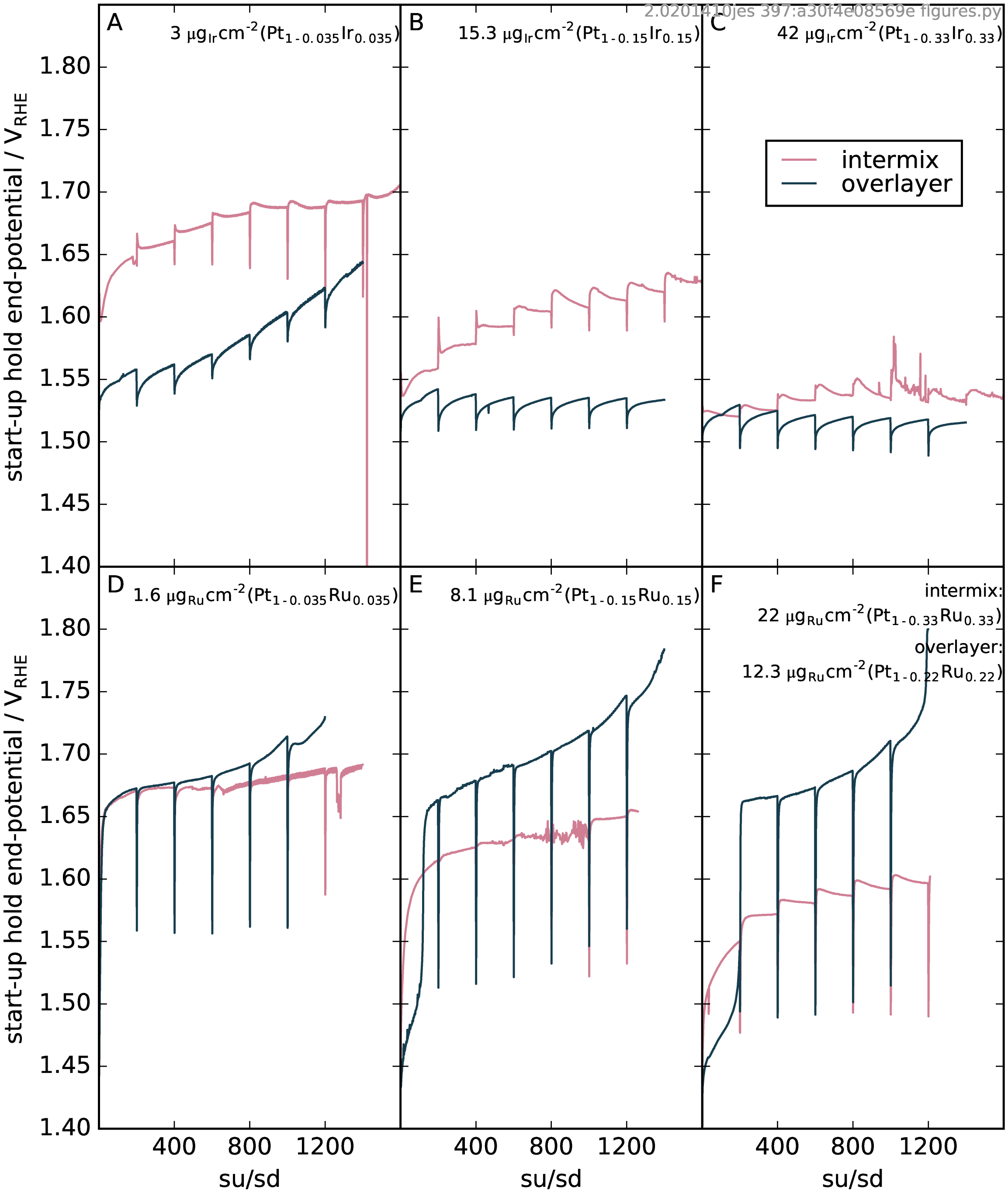


Figure 4.4: Start-up end-potentials for all twelve Ru/Ir intermix and overlayer compositions except pure Pt. Top row: Ir, bottom row: Ru, SU/SD current: 0.942 $mA\ cm^{-2}$.

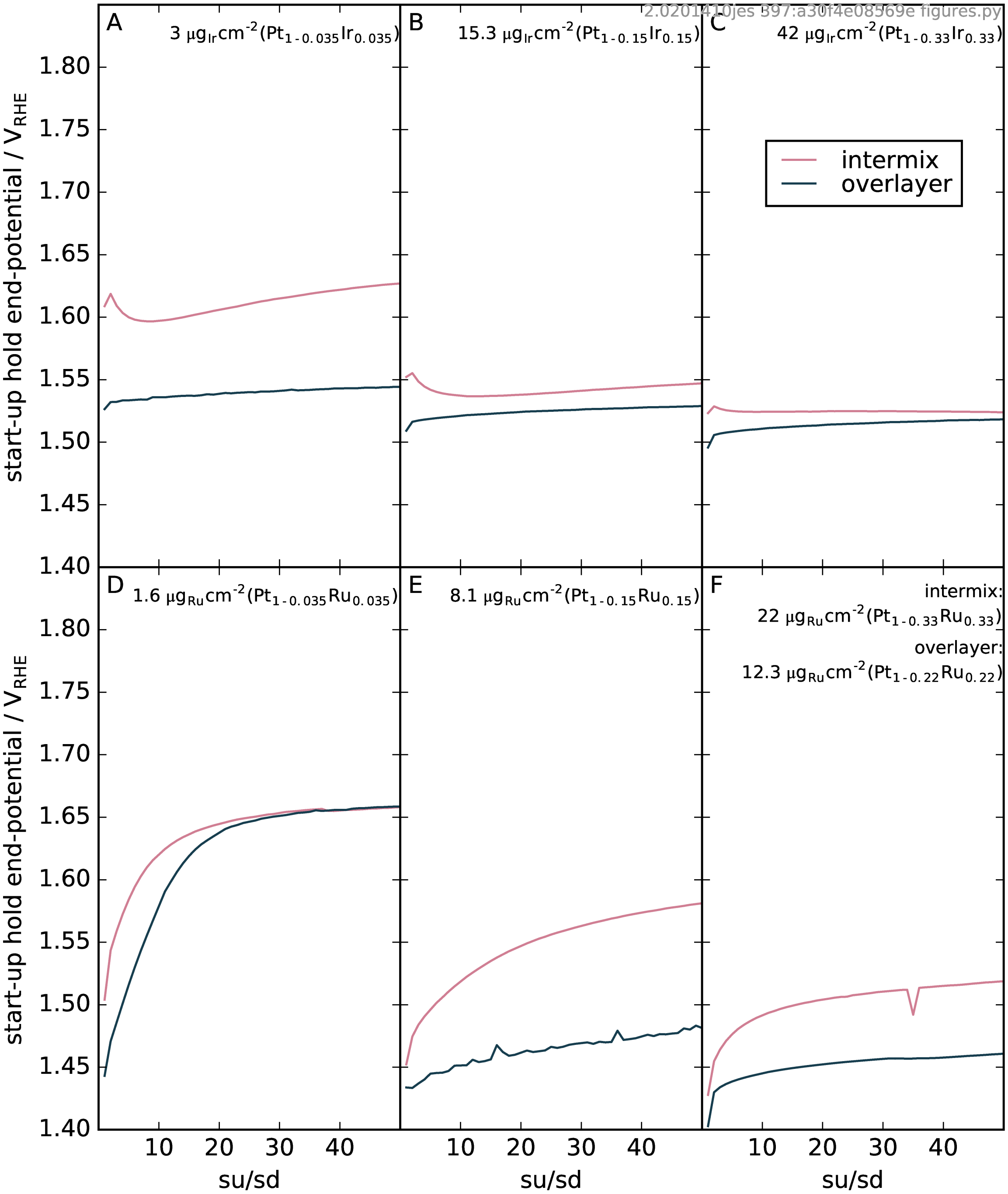


Figure 4.5: The first 50 start-up end-potentials for all twelve Ru/Ir intermix and overlayer compositions except pure Pt. Top row: Ir, bottom row: Ru, SU/SD current: 0.942 $mA\ cm^{-2}$.

General Remarks on ORR Activities:

As mentioned in Chapter 3 (on pg. 95), the ORR activity is characterized with the last full up-sweep from the Ar and O_2 CVs (0 to 1.2 V_{RHE}). For the data in this chapter, this is the fourth full up-sweep, with the exception of pure Pt, for which it is the second.

There are two sets of CVs which can be used to characterize the ORR: the CVs before the CV to 1.55 V_{RHE}, and the CVs after. Figure 3.16 clearly shows these CVs and the difference in the CV set order between the first (pre-SU/SD) set and the remaining CV sets.[4] The ORR activity used for plotting figures in this Chapter is always from the CVs after the CV to 1.55 V_{RHE}. Most often the difference between the ORR before and after the CV to 1.55 V_{RHE} was insignificant, but sometimes it was noteworthy. All differences are shown in Figures 4.14 and 4.15 in Section 4.4.5.

The ORR activity plotted is the background and mass transport (Koutecký-Levich) corrected current at 0.96 V_{RHE}. This is lower than the potential used for the last published study on NSTF grown on glassy carbon (1.0 V_{RHE} in *Liu et al.* (2010)) because at 1.0 V_{RHE}, there was no clear ORR current for some of the samples at the end of the test. 0.96 V_{RHE} seemed like a good compromise between ensuring ORR current (i_k) at the end-of-test, and keeping the highest $|i_k|$'s (beginning-of-test) $< |i_d|/2$. ORR currents are made positive for plotting.

When most of the Pt was dissolved due to the AST, it was visually evident in the Ar and O_2 CVs. In an Ar CV, the Pt H_{UPD} and oxide features disappear. In an O_2 CV, current (which is negative) in the diffusion limited potential range (about 0 to 0.7 V_{RHE}, see Figure 4.1A) increases due to a kinetic limitation (which is explained further in the second paragraph of Section 5.4). After the a kinetic limitation appeared, it quickly (within 200 to 400 SU/SD cycles) increased to a value between -1 and 0 $mA\,cm^{-2}$. The appearance of a kinetic limitation effectively means the ORR catalyst has reached the end of its life. Therefore the ORR is shown as zero if the diffusion limited current (negative) started to increase. A good quantitative indicator of the appearance of a kinetic limitation is the ORR current at some lower potential. For the data shown in this Chapter, if the ORR current at 0.86 V_{RHE} was less than 1.5 $mA\,cm^{-2}$, the ORR activity (current at 0.96 V_{RHE}) was declared to be zero.

---

[4] Order of first CV set: Ar-CV, O_2-CV, Ar-CV-to-1.55, Ar-CV, O_2-CV. Order of second and remaining sets: O_2-CV, Ar-CV, Ar-CV-to-1.55, Ar-CV, O_2-CV.

Surface Area Correction:

Although great care is taken in preparing the samples, there are factors that can introduce errors in the surface area. The drying step can leave spots, which influences whisker growth (Figure 3.9(d)) and presumably whisker density. The disks are frequently handled during the sputtering and tip assembly steps, so sometimes small scratches are introduced on the NSTF surface. These patches and scratches on the disk surface (see Figure 3.13) introduce errors in the catalytic surface area. Applying a surface area correction (division by SEF) should help correct these errors. This was done in the A panels of Figures 4.8 through 4.11. The SEF is determined from the same full up-sweep from the Ar CV after the CV to 1.55 and before any SU/SDs. All the ORR activities for a given composition were normalized to this SEF. Figure 4.6 shows how the SEF was determined for the pure Pt sample. Figure 4.7 shows the CVs along with their SEFs for the other 12 Ru/Ir samples. There are some issues with using these SEFs to determine Pt specific current density, discussed in Section 4.4.2.2.

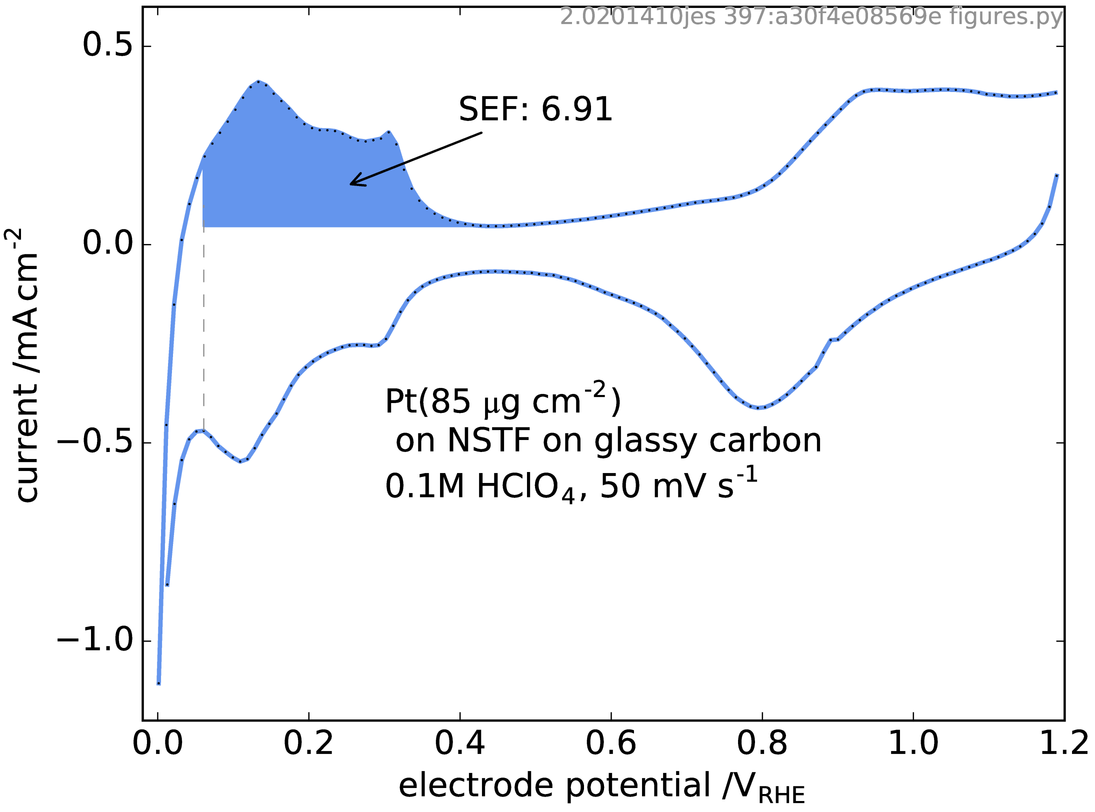


Figure 4.6: The final full up-sweep and down-sweep from the CV at 40 minutes in Figure 4.3 panel B, with shaded H_{UPD} region used for determining SEF.

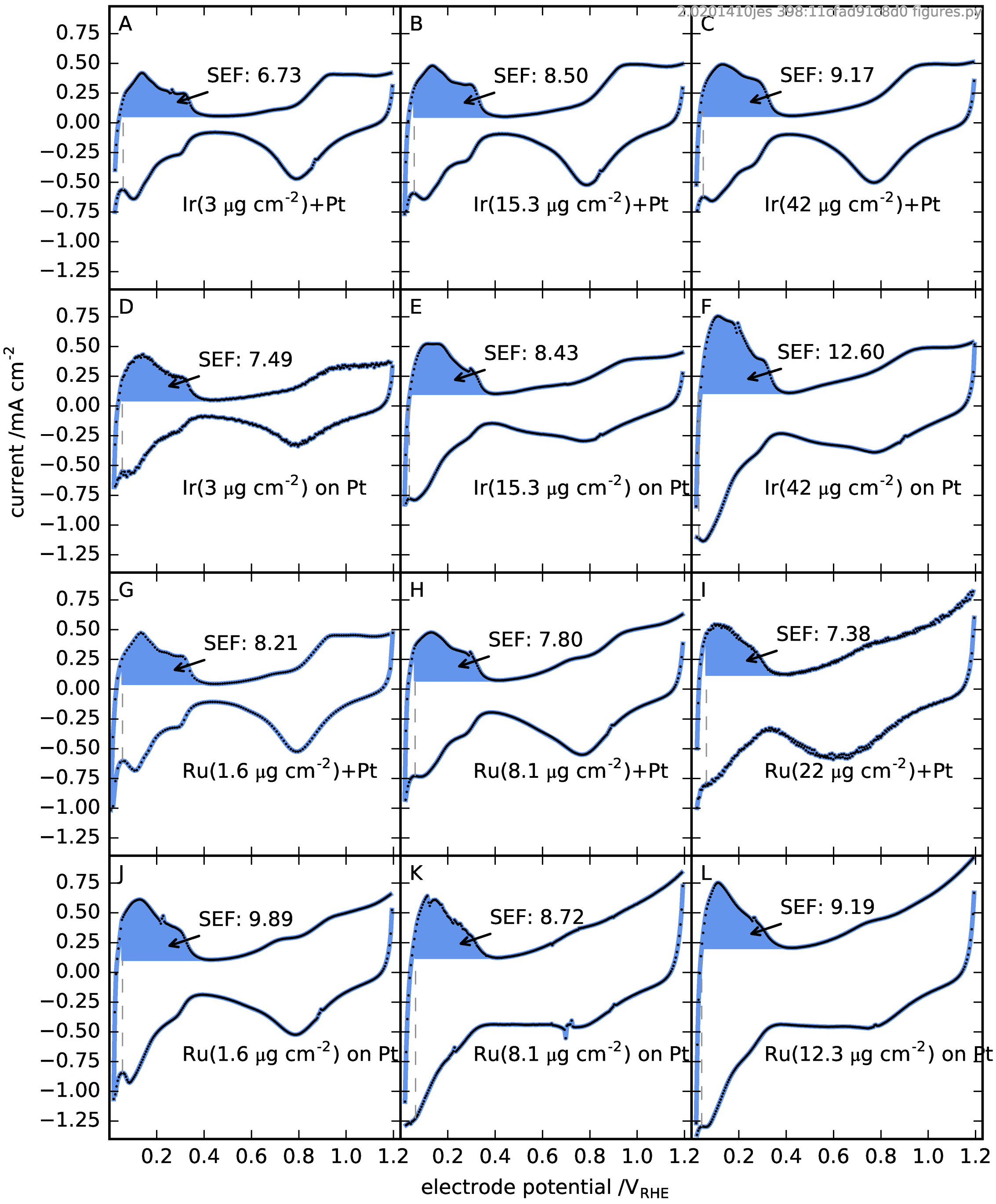


Figure 4.7: Shaded H_{UPD} desorption areas (along with their SEFs) of the 4th full up-sweep from the Ar CV after the CV to 1.55 V_{RHE} and before any SU/SDs. These SEFs were used for the A panels in Figures 4.8 through 4.11. (Electrolyte: 0.1 M $HClO_4$, sweep rate: 50 $mV\ s^{-1}$)

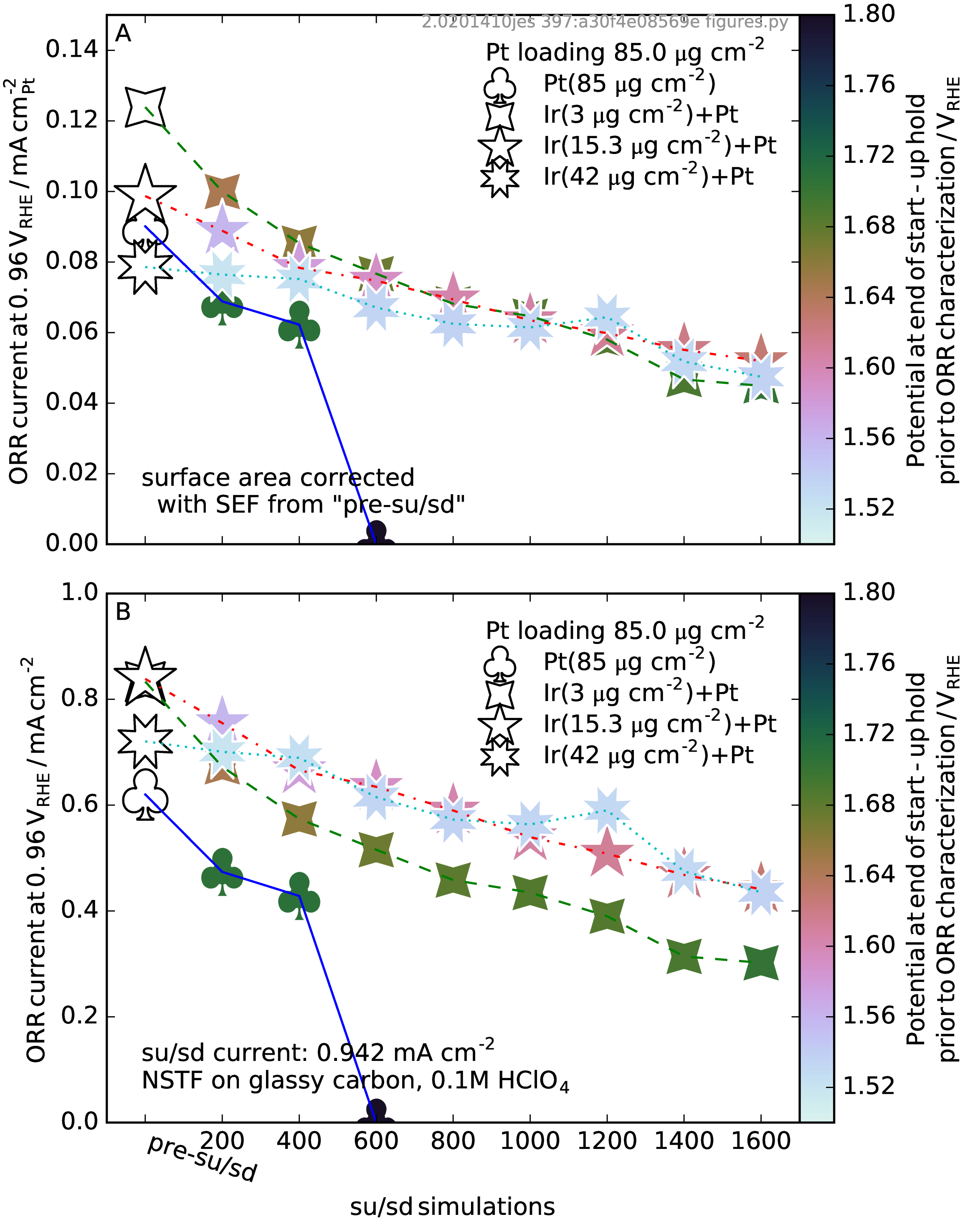


Figure 4.8: The progression of ORR and OER activity for the compositions of Ir intermixed with Pt. **A**: normalized to initial SEF and **B**: geometric current density. ORR is background and mass transport (Koutecký-Levich) corrected. The marker colour corresponds to highest potential reached by SU/SD cycle prior to ORR characterization, therefore a more pale/lighter colour represents higher OER activity. Pure Pt included for reference.

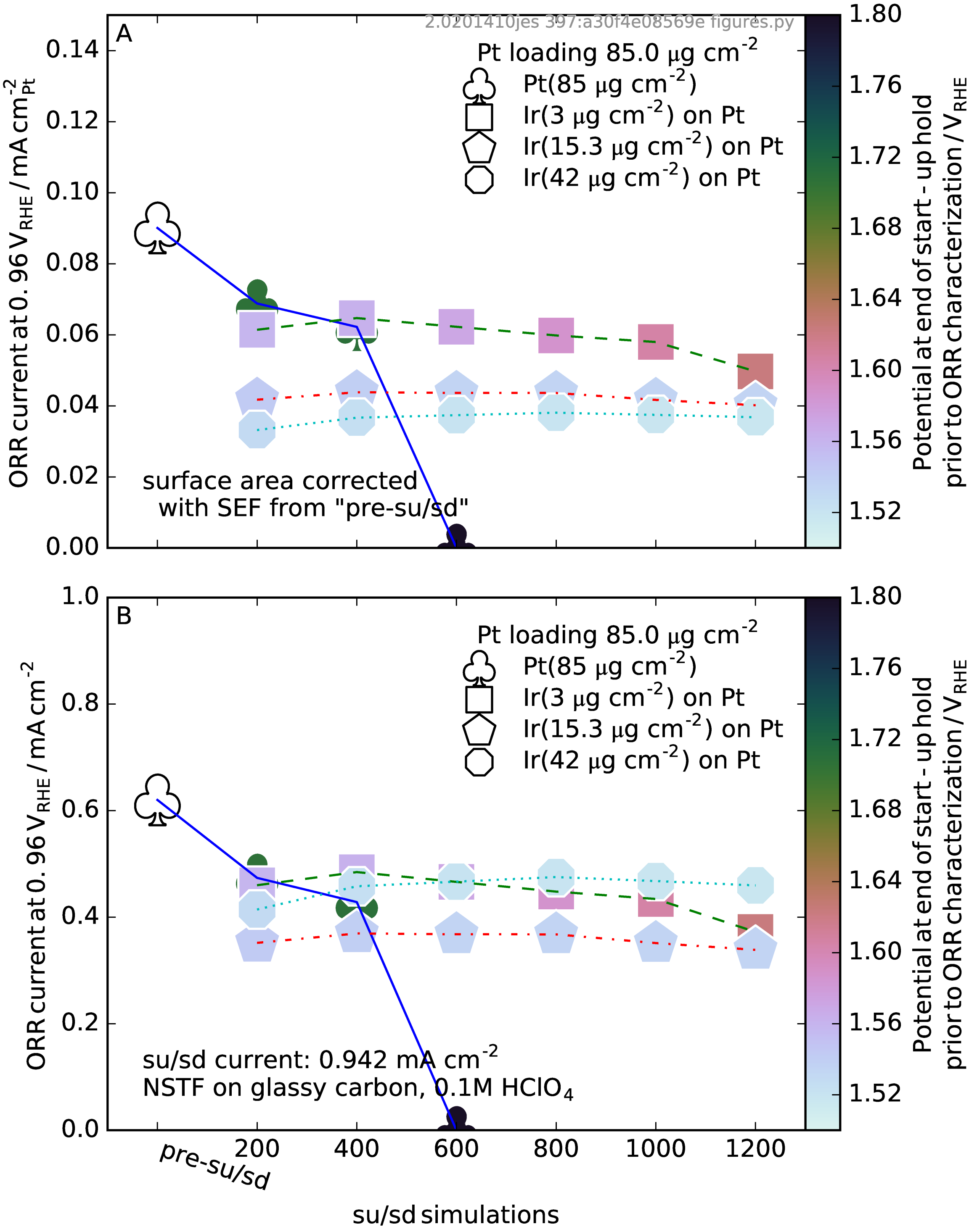


Figure 4.9: The progression of ORR and OER activity for the compositions of Ir sputtered on top of Pt. **A**: normalized to initial SEF and **B**: geometric current density. ORR is background and mass transport (Koutecký-Levich) corrected. The marker colour corresponds to highest potential reached by SU/SD cycle prior to ORR characterization, therefore a more pale/lighter colour represents higher OER activity. Pure Pt included for reference.

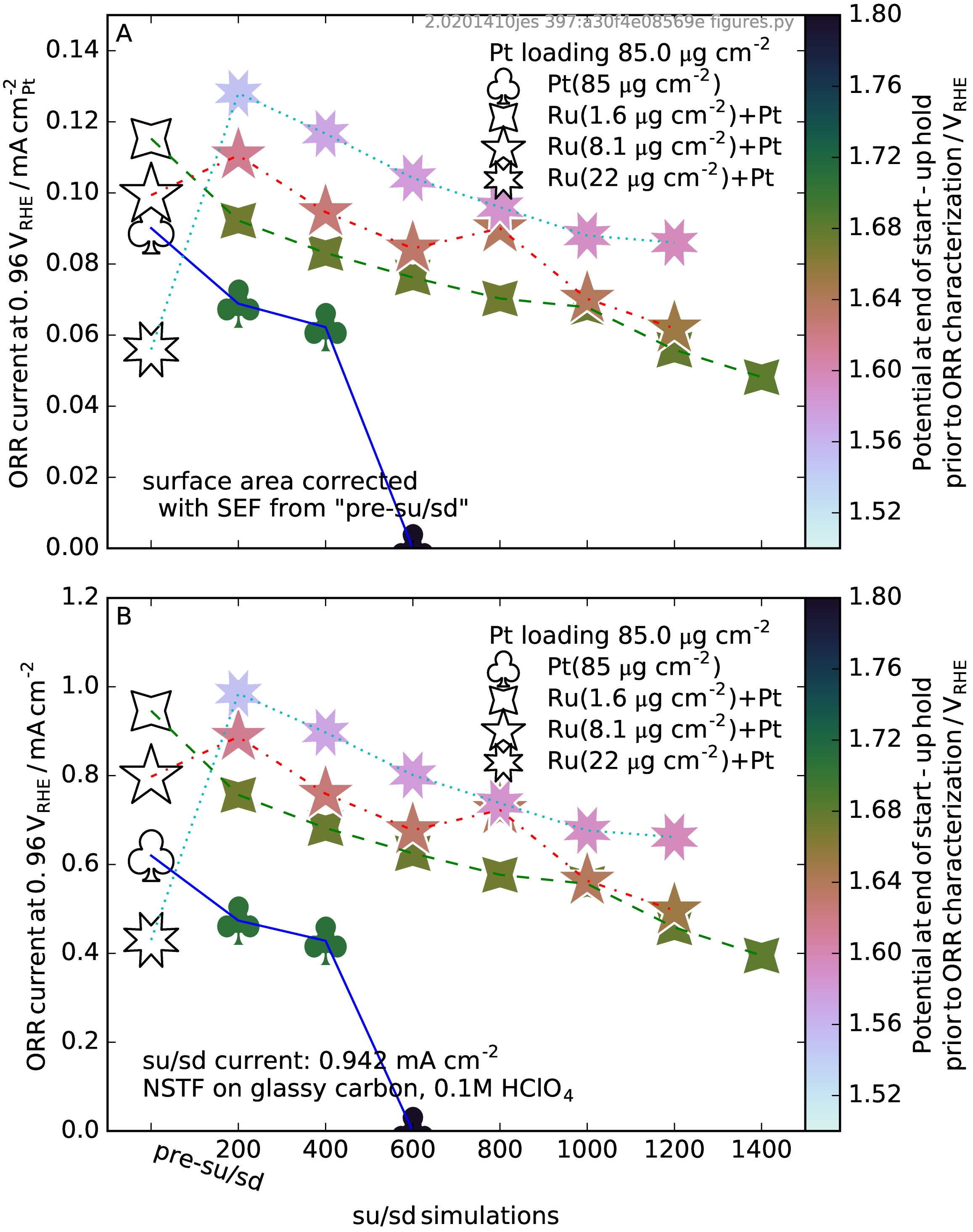


Figure 4.10: The progression of ORR and OER activity for the compositions of Ru intermixed with Pt. **A**: normalized to initial SEF and **B**: geometric current density. ORR is background and mass transport (Koutecký-Levich) corrected. The marker colour corresponds to highest potential reached by SU/SD cycle prior to ORR characterization, therefore a more pale/lighter colour represents higher OER activity. Pure Pt included for reference.

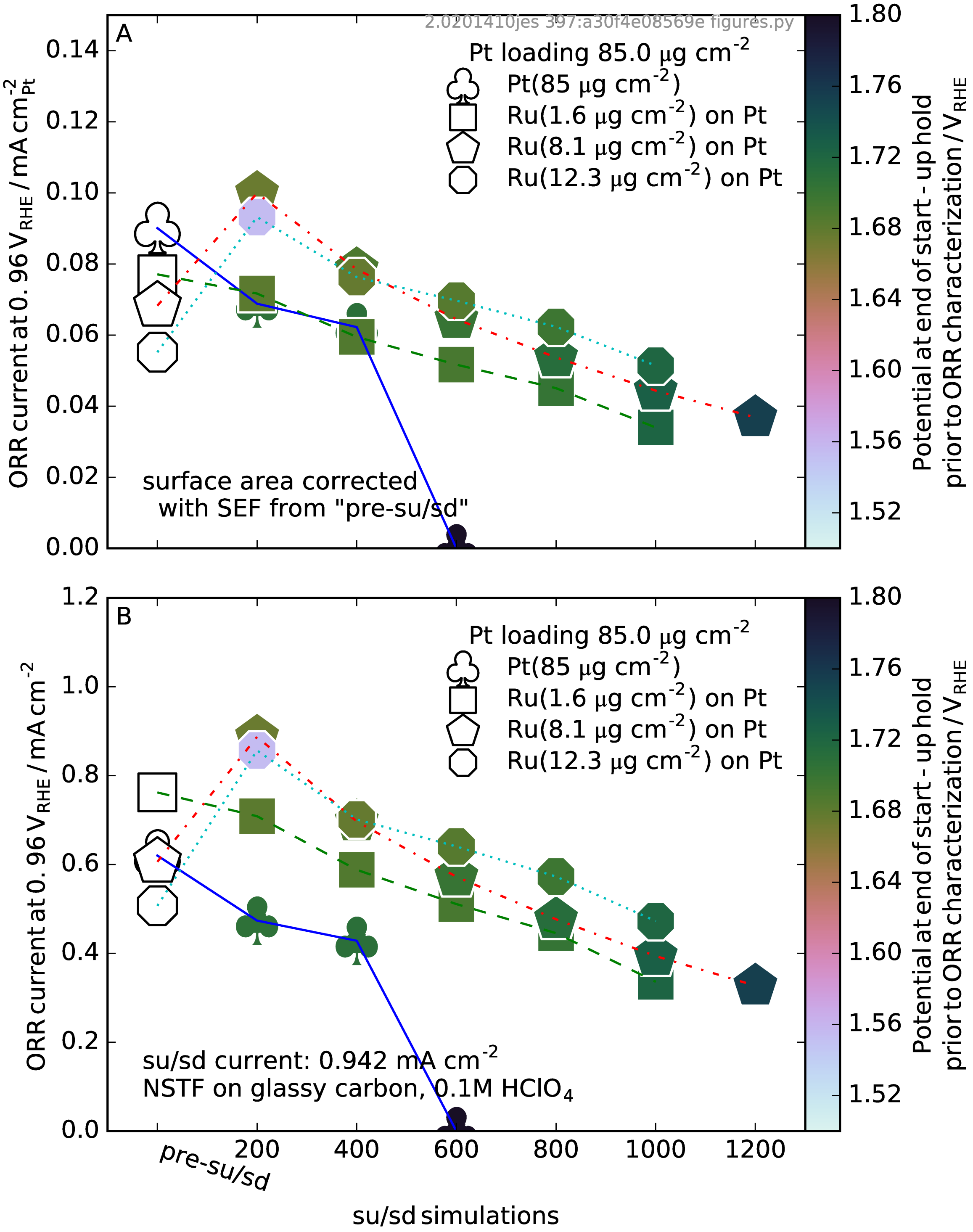


Figure 4.11: The progression of ORR and OER activity for the compositions of Ru sputtered on top of Pt. **A**: normalized to initial SEF and **B**: geometric current density. ORR is background and mass transport (Koutecký-Levich) corrected. The marker colour corresponds to highest potential reached by SU/SD cycle prior to ORR characterization, therefore a more pale/lighter colour represents higher OER activity. Pure Pt included for reference.

4.4 Discussion of Binary Compositions (Figures 4.8 to 4.11)

4.4.1 General Remarks

OER Activities: All compositions have a higher OER activity than pure Pt, as expected. Figure 4.5 shows the OER activities consistently order as one would expect: loadings increase activity, and overlayer has a higher activity than intermix. Details will be discussed later for the Ir and Ru containing compositions in the OER subsection of Sections 4.4.3 and 4.4.4 respectively.

ORR Activities: All compositions last longer than pure Pt. It is very apparent that Ru or Ir addition provides protection against ORR activity loss due to repeated SU/SD. Only the Ir overlayer compositions (Figure 4.9) clearly suffer from decreased initial ORR activity compared to pure Pt. The initial ORR activities of the Ru intermix compositions (Figure 4.10) actually seem to be better than pure Pt (discussed in Section 4.4.4). The other compositions are too close to discern a definitive ORR benefit or detriment. Details will be discussed later for the Ir and Ru containing compositions in in the ORR subsection Sections 4.4.3 and 4.4.4 respectively.

4.4.2 Remarks on the Pt Specific ORR Activities

4.4.2.1 Effect of SEF Corrections on ORR Activity Ordering

Figure 4.9B (Ir overlayer) shows the middle loading (15.3 $\mu g_{Ir}\, cm^{-2}$) at 200 SU/SDs has the lowest ORR activity, but one would expect the highest loading (42 $\mu g_{Ir}\, cm^{-2}$) to have the lowest activity because there is more Ir covering the Pt (the ORR activity of Ir is less than that of Pt (*Cardarelli*, 2008).). Figure 4.9A shows the Pt specific ORR activities are ordered as one would expect. The same effect can roughly be seen in the intermix samples (Figure 4.8). Applying a surface area correction does not change the ordering of ORR activity for Ru compositions

4.4.2.2 SEF Inaccuracies

The presence of metallic Ir or Ru presents problems for obtaining the Pt specific current when dividing by the SEF because metallic Ir or Ru will add hydrogen adsorption/desorption current to the H_{UPD} region (shown in Figures 2.29 through 2.32 and discussed in Section *The Anodic Oxidation of Ru and Ir Supported on NSTF and Flat Glassy Carbon*, pg. 61). Figure 4.7 shows a positive correlation between the Ir loading and the SEF. The same correlation is not found for Ru compositions; why not?

As the AST progresses, the ECSA (H_{UPD} desorption area) is expected to shrink due to Pt loss, but for the highest intermix and overlayer Ru loadings, SEF actually increases after the first 200 SU/SDs. Figure 4.12 shows the shrinkage and increase in a bar chart of SEFs before and after 200 SU/SDs for all compositions; the shrinkage of Pt CV features can also be seen in Figure 4.19.

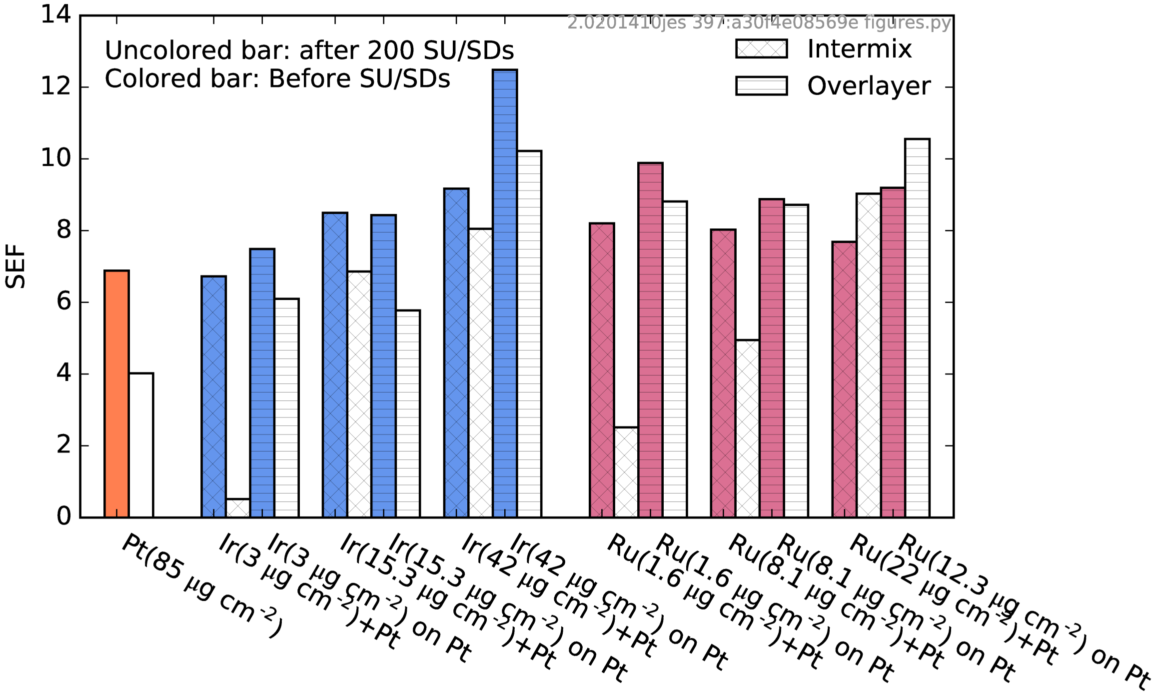


Figure 4.12: SEFs from the Ar CVs before and SU/SDs (coloured) and after 200 SU/SDs (uncoloured) for all compositions. Sweep details in the caption of Figure 4.7.

Figures 4.13D and E shows the two Ar CVs for the highest loaded Ru overlayer composition (12.3 $\mu g_{Ru}\, cm^{-2}$ on 85 $\mu g_{Pt}\, cm^{-2}$), and their precise times within the AST (panels A, B, and C). Why did the SEF increase after SU/SDs? Figure 4.13 shows the SEF before any

SU/SDs was an underestimate of the actual Pt-based SEF because of a ‘widened’ double-layer region. This widening is probably due to some overlap between H_{UPD} and reversible oxide currents on Ru. Figure 4.7 shows this widening effect correlates with Ru loading. The same widening can be seen for Ir compositions (in Figure 4.7), but the effect is not as pronounced. Figure 4.13E shows that, after 200 SU/SDs, the CV looks much more like a Pt CV because the surface Ru has been lost to solution.

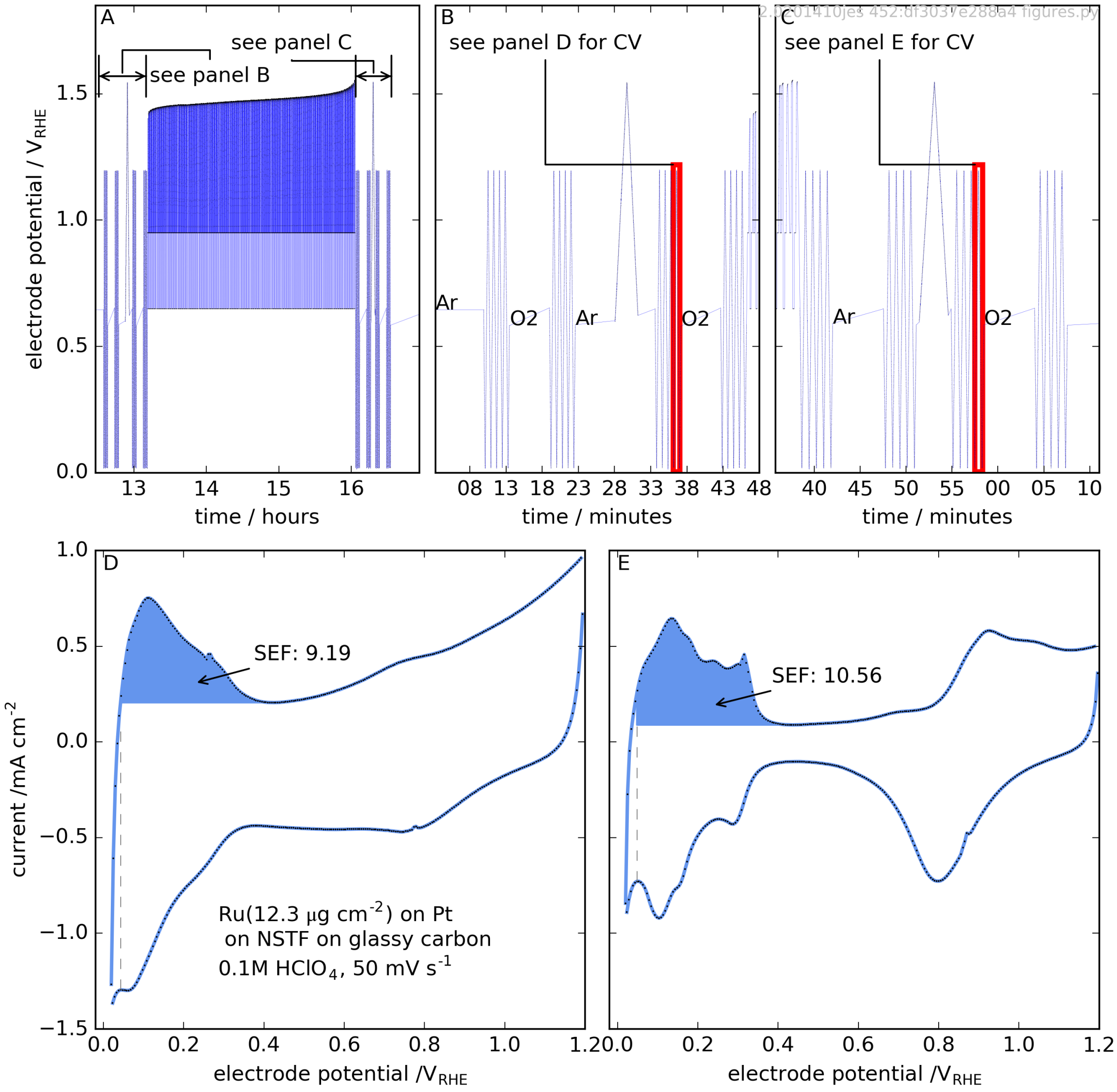


Figure 4.13: An example of when the SEF of a CV after the first 200 SU/SD cycles was greater than SEF from the pre-SU/SD CV.

Metallic Ir and Ru are problematic for ECSA quantification using the H_{UPD} region because these elements have H_{UPD} features of their own, which lead to an over estimation of the Pt surface area. Ru underestimates Pt ECSA at high loadings because of the strong widening effect in double-layer region. Can anything be done to determine the Pt ECSA of Ru/Ir containing compositions? Depositing as oxides, or electrochemical pre-oxidization may help for Ir, but would make matters worse for Ru compositions because RuO_x pseudocapacitance covers the H_{UPD} region (see Figures 2.29 and 2.30).

The problem has been solved by *Binninger et al.* (2014) with CO gas, which produces a strong anodic current desorption feature between ~0.75 to 0.95 V_{RHE} (known in the literature as "CO-stripping"). In their work, a CV in Ar and a CO-stripping CV are subtracted to obtain the Pt ECSA in the presence of pseudocapacitive metal oxides. Unfortunately, our research was carried out before this method was published. The surface area corrections should be viewed with caution, i.e. they are not perfect due to the presence of Ir and Ru, but are provided nonetheless because it is a standard practise to apply H_{UPD}-based corrections to Pt catalysts under RDE study.

4.4.3 Remarks on Ir Samples

ORR Activities:

Figure 4.8 shows that intermixing Ir in Pt does not have a strong influence on ORR activity. This agrees well with the work of *Liu et al.* (2010) which showed similar slight differences in ORR activity for a spread of similar samples under similar testing conditions.

Figure 4.9 shows Ir overlayer produces more stable ORR catalysts than Ir intermix (Figure 4.8), but probably at the cost of a lower initial ORR activity. The metallically deposited Ir electrochemically oxidizes to iridium oxides, and compared to Pt, Ir oxides are ORR inactive. Even though the Ir intermix starts out higher, the end-of-test (1600 SU/SDs) ORR activities of intermix compositions are on average lower than their overlayer counterparts. It is truly remarkable that the ORR activity for the two higher Ir overlayer loadings remains more-or-less stable over 1600 SU/SDs. All the knowledge disclosed in Section *Pt Instability* (pg. 23) indicates that Pt ought to be unstable if subjected to this AST protocol, therefore this behaviour is somewhat suspicious. Some samples from the next study also exhibited an ORR activity which reached a value which did not decrease with SU/SD cycles (see pg. 187 for a list and brief discussion).

OER Activities:

Figure 4.9 shows that the magnitude of OER activity decrease (marker colour darkening) for 3 $\mu g_{Ir}\,cm^{-2}$ overlayer is approximately the same as it is for the 3 and 15.3 $\mu g_{Ir}\,cm^{-2}$ intermix samples (Figure 4.8). This is easier to gauge in Figure 4.4, which shows that while the magnitude decrease is the same for these three compositions, the stability trend is different. The OER activity of 15.3 and 42 $\mu g_{Ir}\,cm^{-2}$ overlayer barely changes over 1400 SU/SDs. Figure 4.4 shows an Ir overlayer produces more stable OER catalysts with the exception of the lowest loading (3 $\mu g_{Ir}\,cm^{-2}$) for which the intermix becomes more stable. However this stability could be the result of increasing carbon corrosion, which is explained in Section 4.6. Ir overlayer seems to be the better deposition technique.

Does the remarkable OER stability of 15.3 and 42 $\mu g_{Ir}\,cm^{-2}$ overlayer compositions mean that Ir at these loadings are completely stable and none is lost? Probably not. Recall Ir loss is positively correlated to oxygen evolution (see Figures 2.34B and 2.35). The Ir intermix compositions have less Ir at the surface. One could imagine as the intermix Ir is lost, the active sites decrease (recall less than an atomic monolayer is deposited with each rotation of the table for intermix compositions (pg. 112). As overlayer Ir is lost, it is replenished by Ir underneath the active sites. Ir ($\sim 10\ \mu g\,cm^{-2}$) sputtered overlayer on Pt on NSTF under similar sputtering conditions as for this project (see Section 3.2.3.2 for sputtering parameters) forms discrete particles several nanometres in diameter (*Cullen et al.* (2011) and *Atanasoski et al.* (2012)), so a replenishment is conceivable, given the extremely low dissolution rates for anodically grown Ir oxide (see Figure 2.35).

Does the remarkable OER stability of 15.3 and 42 $\mu g_{Ir}\,cm^{-2}$ overlayer compositions mean that less Ir is lost than for the intermix counterparts? Probably, but not necessarily. Ir loss is positively correlated to oxygen evolution (see Figures 2.34B and 2.35). The active Ir surface area of an overlayer composition is greater than its stoichiometric intermix counterpart. Based on the assumption that Ir loss occurs at a rate proportional to oxygen evolution (from the mechanism proposed in Figure 2.34B), if each active Ir site is turning over less oxygen, than Ir loss should be reduced. However, Figures 2.37 and 2.38 show Ir stability is highly dependant on its anodic electrochemical history. Figure 2.39 also demonstrates a stability, in addition to an activity, dependence on anodic history. Furthermore, Figure 2.39 shows that for a pulse of constant current, most of the Ir is dissolved in the first 100 to 200 seconds, i.e during the charging process. It is possible that between the overlayer and intermix Ir samples, the proportion of current gone to charging, and extent of anodic oxidation could be very different. The nature of Ir stability is indeed complicated.

4.4.4 Remarks on Ru Samples

ORR Activities:

Figures 4.10 and 4.11 show that the ORR of the two highest intermix and overlayer loadings start out lower than their respective activities at 200 SU/SDs. This is probably due to dissolution of the surface Ru which initially covered Pt, blocking its ORR activity. Both intermix and overlayer Ru show a surprising trend, in that once the sample has undergone 200 SU/SDs, Ru loading positively correlates to ORR activity. This correlation is the opposite of what would be expected, at least for overlayer compositions; It is opposite to what is seen for the Ir compositions. It is possible the increase in ORR activity is due to a dealloying process, similar to what happens in transition metal-Pt alloy ORR catalysts; the loss of the alloying metal leaves the Pt surface roughened on the atomic scale, increasing surface area (*Liu*, 2011). The increase in activity could also be a result of an alteration of the electronic structure of Pt due to alloying, the so called "(strain induced) d-band centre shift" (see *Nørskov et al.* (2009) for a theoretical summary, *Adzic et al.* (2007), *Stamenkovic et al.* (2006) and *Strasser et al.* (2010) for experimental treatments). These two phenomena, along with the so called "particle size effect" (*Mayrhofer et al.*, 2005) have been the rationale behind fuel cell cathode catalysis development for the past decade. A detailed discussion of these phenomena is beyond the scope of this thesis project.

Figure 4.10 (intermix) shows the Ru loading has a large influence on OER activity but does not seem to have a significant influence on the ORR degradation trend, which appears to be approximately the same as the degradation trend of the Ru on Pt series in Figure 4.11.

OER Activities:

After 200 SU/SDs, the OER activity for all compositions is about the same and stays fairly consistent. Though most for the Ru is initially corroded, it would seem some of the Ru is resistant to loss and stays to provide some small amount of OER activity (compared to pure Pt). This corroborates with the work of *Atanasoski et al.* (2012), which provides

XPS evidence for the existence of chemical bonds between the Ru and the NSTF support. *Atanasoski et al.* (2015) proposes a location for such a bond. The chemical interaction between NSTF and Ru could help stabilize the Ru, while still allowing Ru to provide OER activity.

4.4.5 The Effect of the CV to 1.55 V_{RHE}

Sometimes the difference between the ORR activity before and after the CV to 1.55 V_{RHE} was noteworthy; Figures 4.14 and 4.15 show the ORR differences for all the Ir and Ru compositions respectively. If the ORR changes after the CV to 1.55 V_{RHE}, it could be due to either a change in the O_2 CV current or the Ar CV current. The two CVs may influence the ORR to change in the same direction or opposite directions. Therefore these CV currents at 0.96 V_{RHE} are also included on Figures 4.14 and 4.15.

Generally, the ORR current after the CV to 1.55 V_{RHE} is slightly higher. Panels C and F of Figures 4.14 (highest loaded Ir intermix and overlayer) show something interesting; the O_2 CV current is consistently improved after the CV to 1.55 V_{RHE} for the intermix, but is consistently worsened for the overlayer composition. It seems the ORR for the high ($42 \mu g_{Ir}\, cm^{-2}$) intermix composition is highly sensitive to the potential history of the electrode.

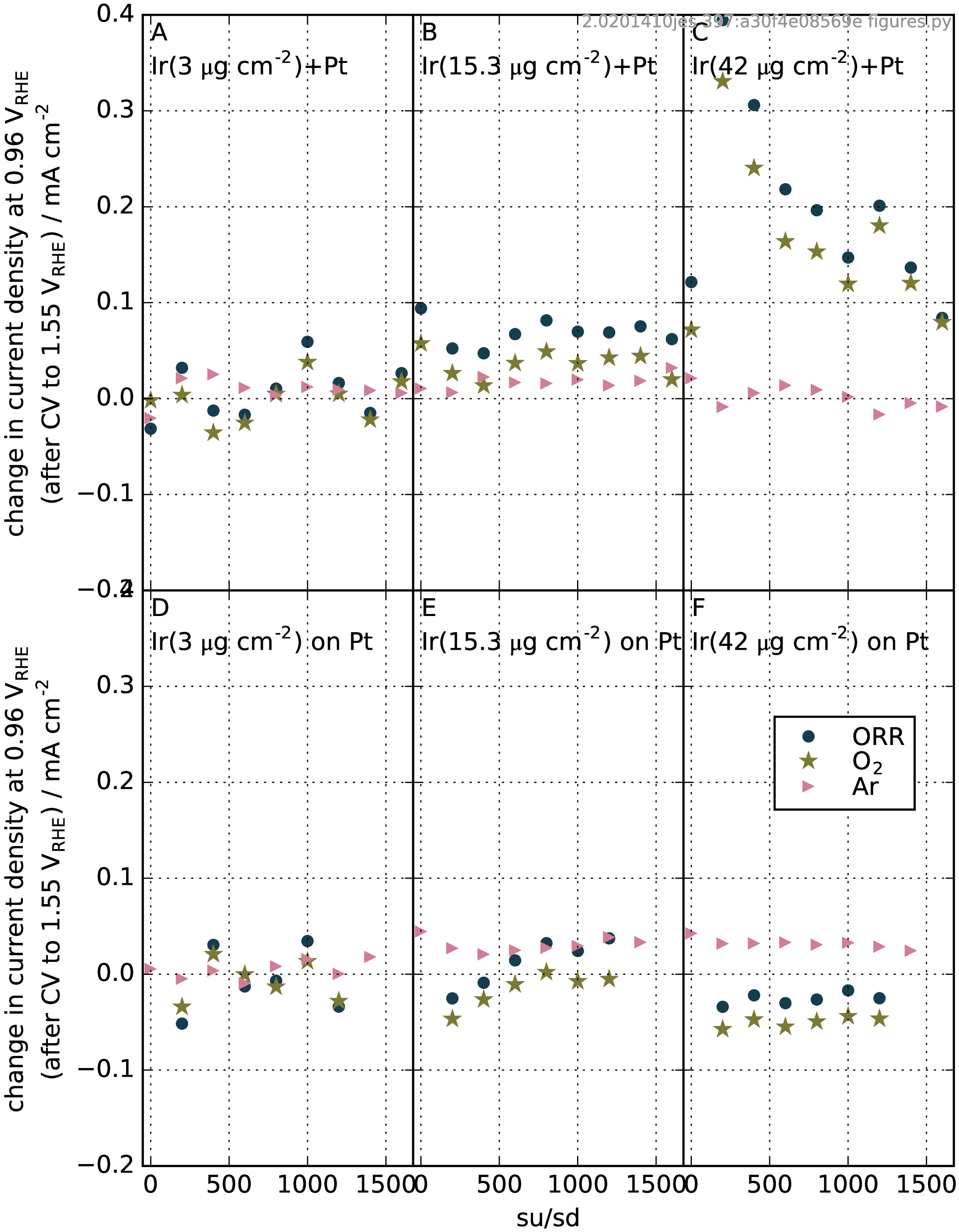


Figure 4.14: The difference between the ORR activity before and after the CV to 1.55 V_{RHE} for Ir compositions. Currents from the O_2 and Ar CV are also included to help discern the primary cause of ORR change. Data is missing in panels D, E and F at su/sd=0 because of an equipment malfunction with the oxygen gas (previously mentioned on pg. 132) and at su/sd=1400 because the test was stopped before the last O_2 CV in the final set began.

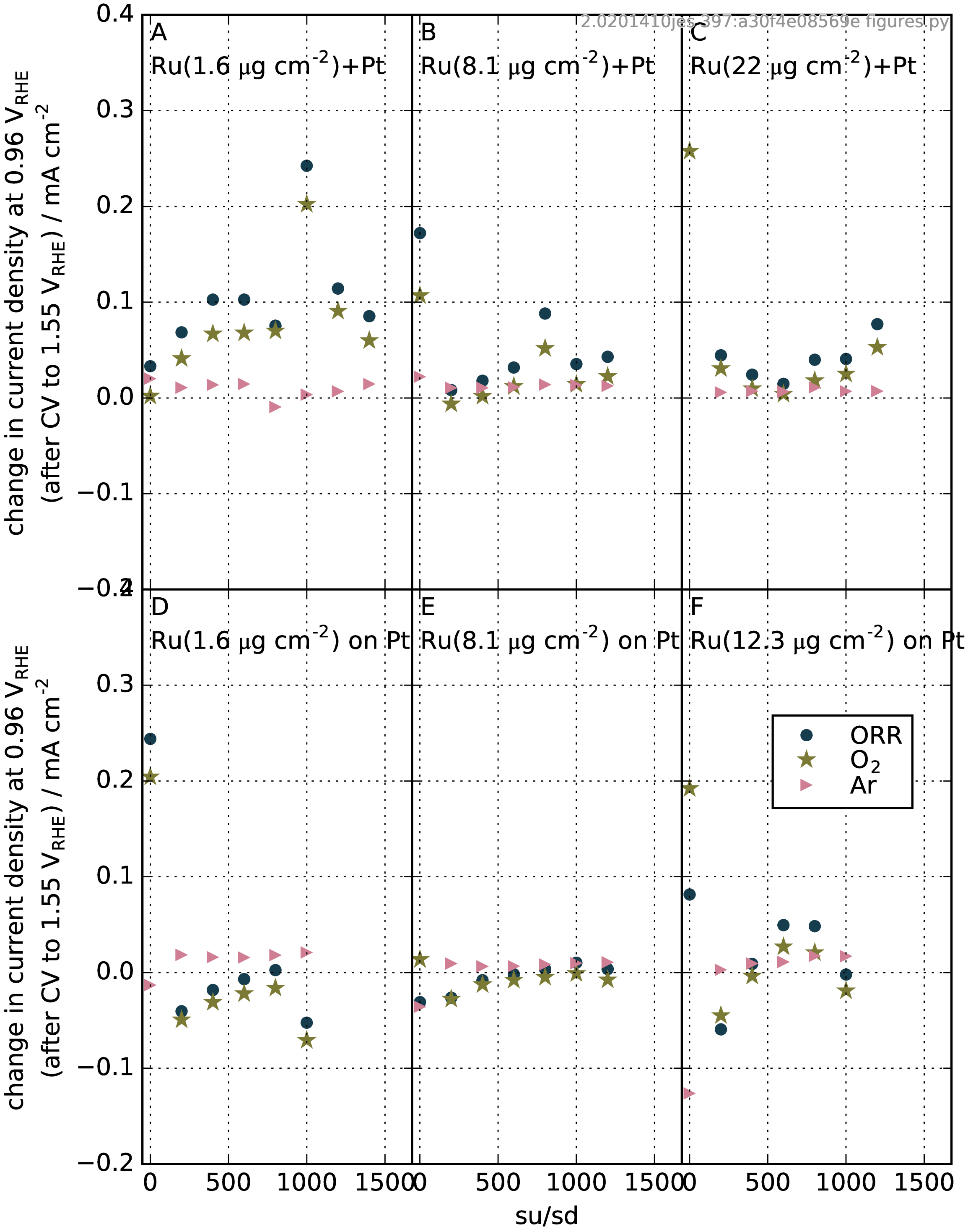


Figure 4.15: The difference between the ORR activity before and after the CV to 1.55 V_{RHE} for Ru compositions. Currents from the O_2 and Ar CV are also included to help discern the primary cause of ORR change. Data at su/sd=0 in panels C is missing because the first Ar CV was unusable, probably due to a large bubble on the RDE tip.

4.4.6 Brief Summary of Binary Compositions

Of the twelve compositions studied in this Section, the 22 $\mu g_{Ru}\,cm^{-2}$ intermix seems to be the best, providing high ORR and OER activities, in addition to good durabilities for both OER and ORR. In terms of the best deposition strategy, intermix is better for the Ru samples, and overlayer is better for the Ir compositions.

4.5 A Ternary Ru, Ir Pt Composition Spread with Variable Ru

Figure 4.16 shows data for 6 $\mu g_{Ir}\,cm^{-2}$ sputtered on a spread of Ru intermixed with a constant amount (85 $\mu g\,cm^{-2}$) of Pt. Why was this additional composition spread tested? Figure 4.9 showed that 15.3 $\mu g_{Ir}\,cm^{-2}$ on Pt was stable while 3 $\mu g_{Ir}\,cm^{-2}$ was not. Therefore the rationale behind the choice of loadings in Figure 4.16, was to determine if Ru could substitute for Ir to produce a stable composition at a lower Ir loading than 15.3 $\mu g_{Ir}\,cm^{-2}$ (Ru is less expensive than Ir). Unfortunately a mistake made in determining the loadings for the binary Ir samples was detected after the research for this first study (i.e. Chapter 4) was completed and published in *Crowtz et al.* (2014). At the time the research was being planned, we thought 15.3 $\mu g_{Ir}\,cm^{-2}$ was 9 $\mu g_{Ir}\,cm^{-2}$, so 6 $\mu g_{Ir}\,cm^{-2}$ was chosen as the intermediate loading for the ternary study presented in this Section. A more appropriate loading would have been 10 $\mu g_{Ir}\,cm^{-2}$.

None of the compositions exhibit the stability shown in Figure 4.9 by 15.3 $\mu g_{Ir}\,cm^{-2}$. The end-potentials (marker colour) for all samples are similar and follow a similar degradation trend probably because the Ir top layer (unchanging at 6 $\mu g_{Ir}\,cm^{-2}$) plays the dominant role in catalysing the OER. Figure 4.16 panel A shows the Pt specific ORR's are lower compared to the other Ru+Pt (intermix) data in Figure 4.10, but the geometric activities (B panels) are similar. This is because the SEFs in Figure 4.16 (which can be found in Appendix B, Figures B.14 through B.18) were higher than the SEFs in Figure 4.10. The higher SEF is probably due to the presence of metallic Ir (which adds to the H_{UPD} desorption current), near the beginning of the test, when the SEF is measured.

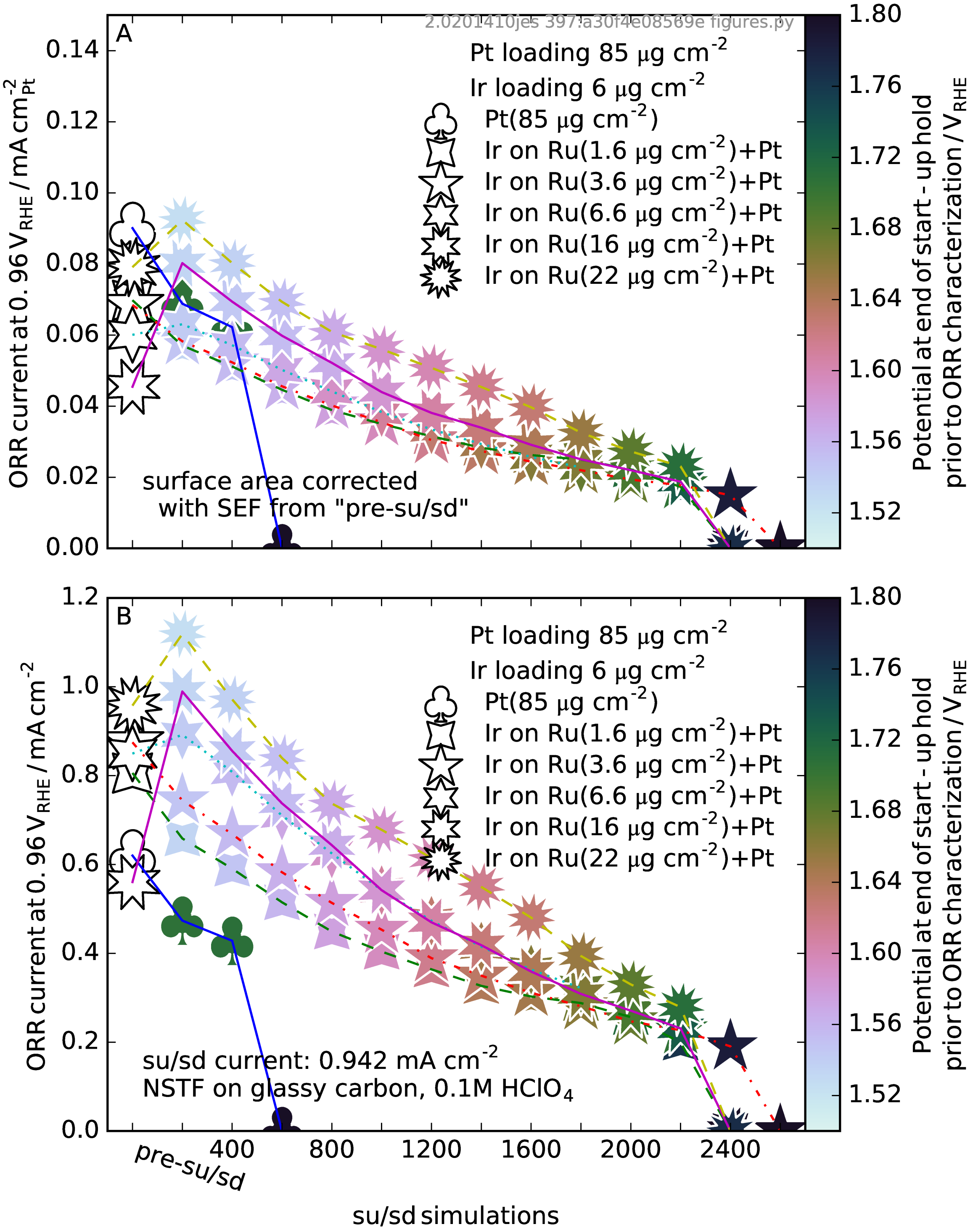


Figure 4.16: The progression of ORR and OER activity for the compositions of Ir sputtered on top of Pt intermixed with Ru. **A**: normalized to initial SEF and **B**: geometric current density. ORR is background and mass transport (Koutecký-Levich) corrected. The marker colour corresponds to highest potential reached by SU/SD cycle prior to ORR characterization, therefore a more pale/lighter colour represents higher OER activity. Pure Pt included for reference.

4.6 Glassy Carbon Corrosion Problem

Shortly after work for the durability contract began, it was noticed that many of the Ar CVs exhibited strange and unexpected shapes. For example, Figure 4.17 shows that the Ar CVs grew as the AST progressed. These are the Ar CVs for the 8.1 $\mu g_{Ru}\, cm^{-2}$ intermix, used in Figure 4.10. Figures like this for all twelve binary compositions and pure Pt can be found in Appendix B. The cause of this behaviour was a mystery. Work on solving the problem began before any of the data presented in this report was collected. That work is the reason why glassy carbon was the RDE disk material for all the work shown in this report. It was thought that perhaps the porous nature of the compressed graphite disks caused the problem seen in the Ar CVs when the pyrolytic coating was somehow compromised (explained in Section *Disk Preparation*, and footnote 8 on pg. 108). Glassy carbon did not fix this frequent problem. In hindsight, the use of compressed graphite disks could have continued. During the work dedicated to identifying the issue, it was noticed the walls of the glassy carbon disks were appreciably corroding. Figure 4.18 shows fine carbon particles washing off the side of a corroded disk when immersed in water, after removal from the Pine RDE tip assembly.

The increasing double-layer region current, seen in Figure 4.17 is attributable to the creation of graphitic oxide functional groups on the glassy carbon, which provide electrochemical pseudocapacitance.[5] Phenolic (*Nagaoka and Yoshino*, 1986) and quinoidal (*Engstrom and Strasser* (1984) and *Nagaoka and Yoshino* (1986)) functional groups have been proposed. Carboxyl functional groups have also been proposed for pyrolytic graphites treated by non-electrochemical methods, but which also display electrochemical pseudocapacitance (*Evans et al.*, 1977).

---

[5] This phenomena is often called "electrochemical activation" in the literature (*Kepley and Bard*, 1988). However, that terminology is avoided because it does not have a well defined meaning. It is also commonly used to describe the development of other types of electrochemical pseudocapacitance (for instance Pt, Ru, and Ir oxides).

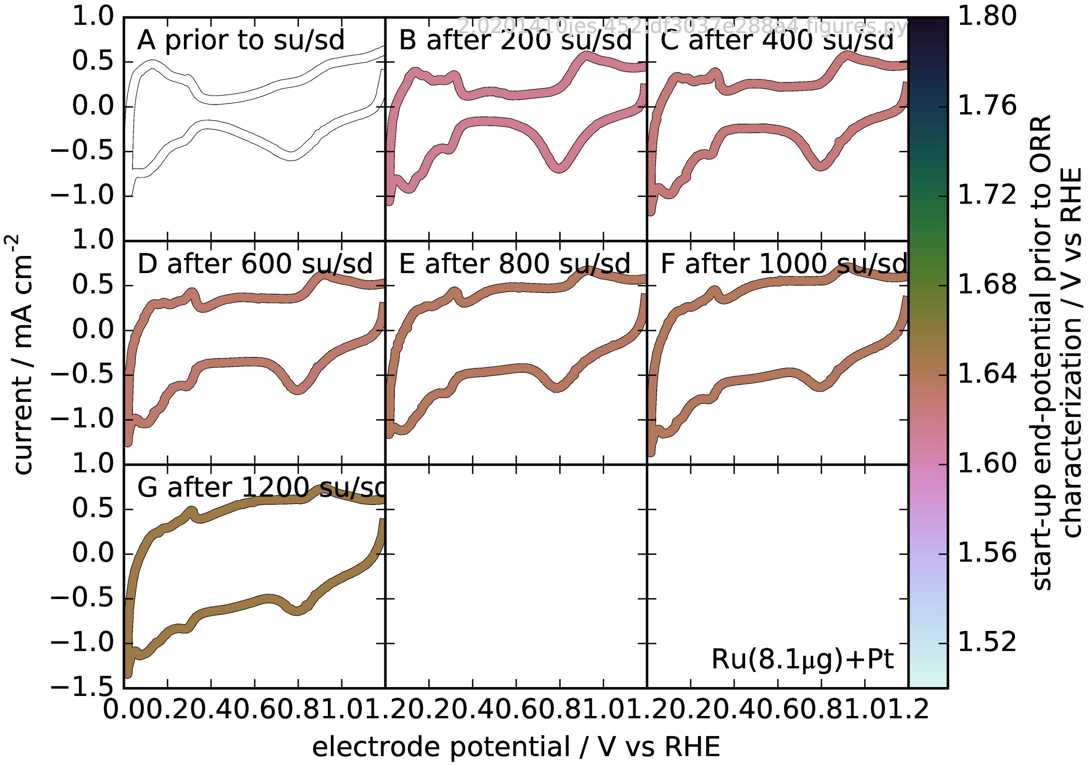


Figure 4.17: Ar CVs (from the intermix Ru (8.1 $\mu g\ cm^{-2}$)+Pt sample in Figure 4.10) showing the mysterious CV development behaviour seen in most of the binary composition samples, later determined to be the result of carbon corrosion.

Figure 4.18: Photo of the Ru (1.6 $\mu g\ cm^{-2}$) on Pt sample in Figure 4.11. The disk was submerged in a small pool of water immediately after SUSD testing. Note the fine carbon particles streaming off the side as indicated by the arrow.

To eliminate this problem, an extremely small amount (at little as possible) of high vacuum silicone grease (composed of polydimethylsiloxane and fumed silica (part no. 2021846-0702, Dow Corning Corporation) was applied to the inner wall of the u-cup. The disk was held with tweezers, inserted in the u-cup, and turned to 'wet' the disk wall prior to RDE tip assembly. The grease sealed the crevice between the glassy carbon disk and the u-cup and prevented carbon corrosion. Figure 4.19 shows the Ar CVs for a 6 $\mu g_{Ir}\, cm^{-2}$ on 1.6 $\mu g_{Ru}\, cm^{-2}$+Pt sample for which silicone grease was applied. A lack of carbon corrosion can be inferred from the consistent width of the double-layer region between panel B and G. Panels H and beyond show a widening of the double-layer region, while the $\mathrm{H_{UPD}}$ features continue to shrink, indicating the silicone grease fix only delays and lessens carbon corrosion. A major concern is that the silicone grease will block Pt from catalysing the ORR. The presence of minute amounts of organic chemicals are notorious for reducing the catalytic action of Pt. This was discussed briefly in Chapter 2 in Section *Electrochemical Cleaning* (pg. 68). The data in Figure 4.19 is for one of the experiments (Ir on Ru (1.6 $\mu g\, cm^{-2}$) intermixed with Pt) shown in Figure 4.16. The slightly lower ORR activity of this sample seen in Figure 4.16 simply aligns with the trend in Ru loading. It's ORR activity is not suspiciously low. The silicone grease had very little effect on the ORR activity of the sample. More experiments attempting to detect the effect of silicone grease on ORR activity were done and are shown in Section 4.6.1.

Figure 4.20 shows photos of the end of RDE tips, which demonstrate the visual effect of adding silicone grease, and the visual effects of carbon corrosion. Silicone grease would begin to creep along the surface of the disk if the RDE tip was allowed to sit for an hour or two after grease application, especially if there was a copious amount applied. Figures 4.20(a) and (b) show this creep from the edges. The longer the rest period, the greater the extent of the creep. Since it was impossible to fully wet the cylindrical wall of the disk before tip assembly (because the end of the disk must be held to turn it in the u-cup) the tip was purposely left to sit, hoping the silicone grease creep would seal the end region. Even with the addition of silicone grease, carbon corrosion occurs under the flat Pt ring (the area left devoid of NSTF whiskers due to the disk jockey cover plate). Figures 4.20(d) and (e) shows that sections of the Pt ring were gone after a finished AST. Some degree of carbon corrosion seemed unavoidable, especially after ~2 days of accelerated stress testing.

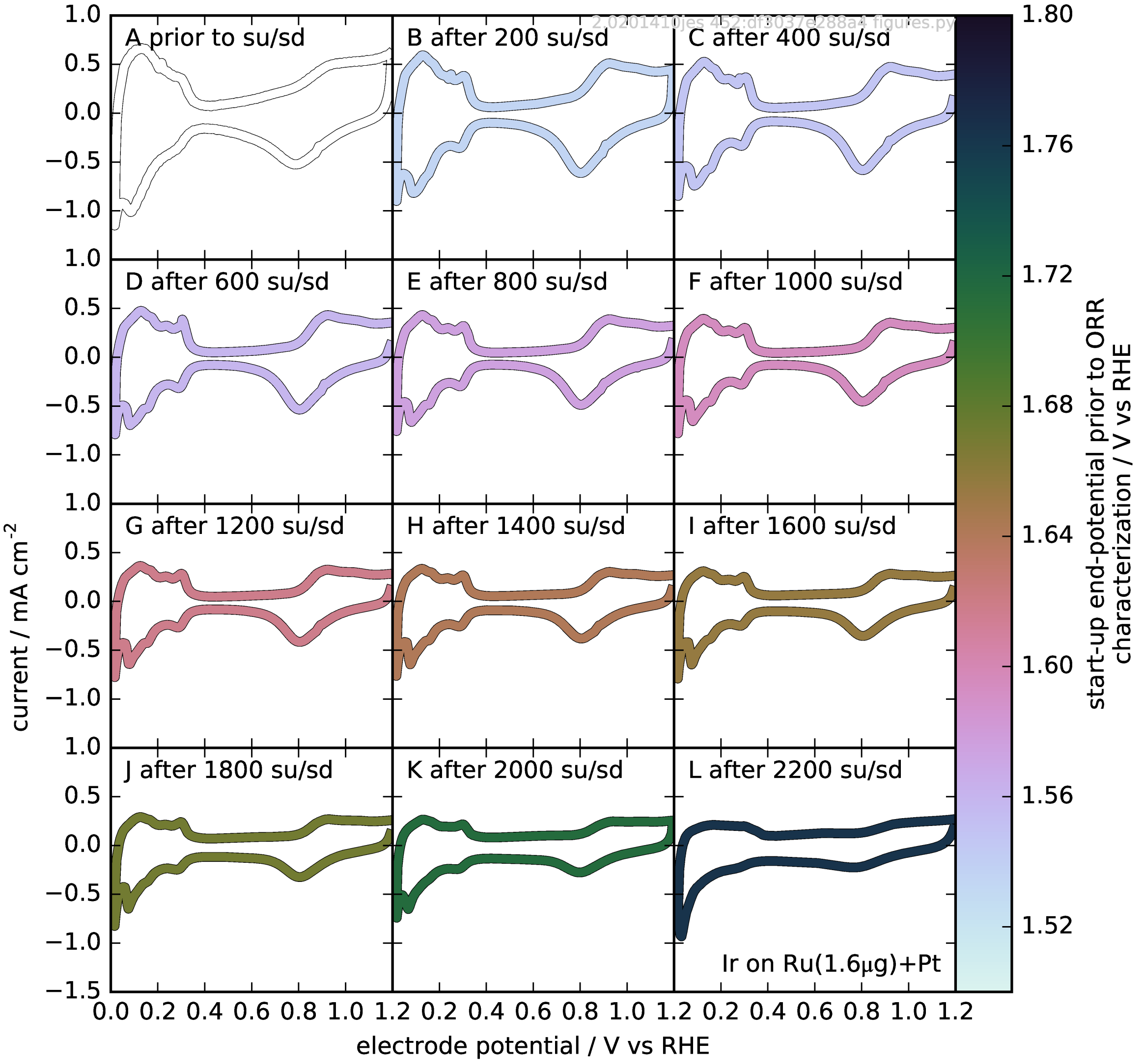
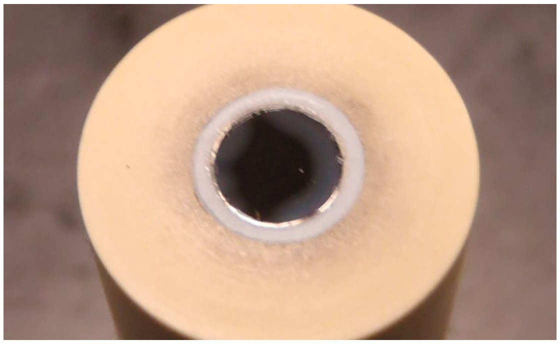
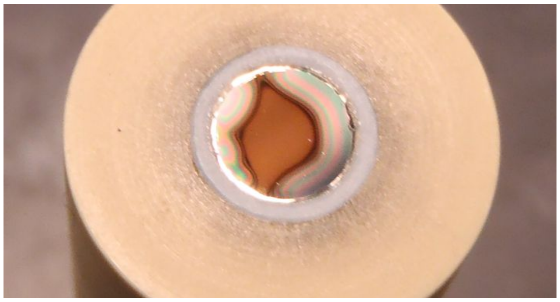


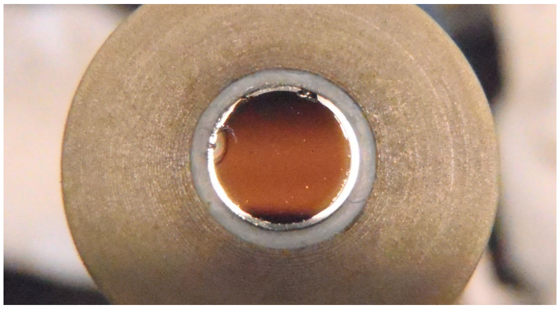
Figure 4.19: Ar CVs from the Ir on Ru (1.6 $\mu g\, cm^{-2}$) intermixed with Pt sample in Figure 4.16, which had a dimethicone based ‘high vacuum grease’ (silicone grease) applied to the inside of the u-cup prior to RDE tip assembly. The double-layer region is relatively stable compared to the sample in Figure 4.17.



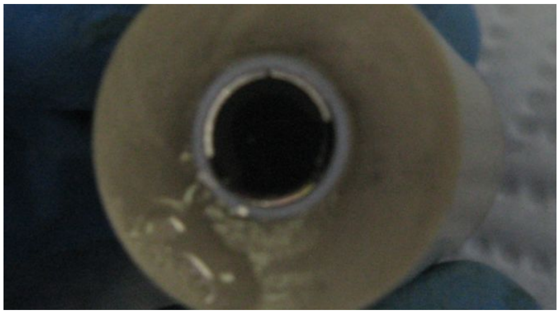
(a) before AST- copious silicone grease



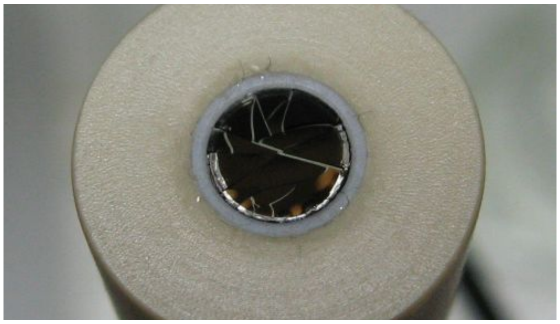
(b) same disk in panel (a), with glare



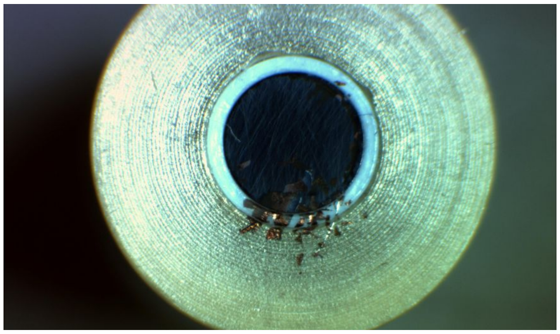
(c) before AST- small amount of silicone grease, Pt ring chipped



(d) immediately after an AST- sections of flat Pt ring have peeled off



(e) after an AST- soaked in pure water, then air-dried



(f) after a 3 day and 9 hour AST

Figure 4.20: **Left Column** (Effects of silicone grease): **(a)**: A copious amount of silicone grease on an untested disk, barely visible around the edge of the disk. **(b)**: The same disk in panel (a), with a reflective glare on the disk surface. **(c)**: A very small amount of silicone grease (on the left side, at 9 o'clock) on an untested disk. Also visible are small chips in the Pt flat film ring (an artifact of the disk jockey plate cover) at 1 and 9 o'clock. The chips probably was incurred when the tip was pushed into the assembly jig (see pg. 101). **Right Column** (Effects of carbon corrosion): **(d)**: A tip immediately after an AST (still wet) with pieces of the flat Pt ring missing due to corrosion. **(e)**: Post-AST, soaked in pure water overnight, then allowed to air-dry. Most of the flat Pt ring is gone. Tiny specks of Pt are on the shroud. **(f)**: A pure Pt sample after a three day and 9 hour AST with a low (0.16 $mA\,cm^{-2}$) SU/SD current with upper potential starting at 1.3 and finishing at 1.65 V_{RHE}. The NSTF film has detached and shifted partially onto the u-cup and shroud.

Eventually even the NSTF film would be compromised, presumably due to carbon corrosion underneath it. Figure 4.20(f) shows the NSTF film detached from the disk surface after one of the longest ASTs conducted. The effect of carbon corrosion on the results of the AST are shown in Section 4.6.2.

4.6.1 The Effect of Silicone Grease and CVs Only (no SU/SD) on ORR

Some experiments were done on pure Pt to test the effect of silicone grease, the effect of the extent of grease creep over the disk surface, and the effect of the CV characterizations only on the ORR activity. Figure 4.21 shows the results of these tests. It was somewhat surprising (and disappointing) to learn that ORR activity steadily declines where there are no SU/SD simulations. This is probably due to the Pt loss from the Pt oxidizing and reducing potentials of the CVs, and from contaminants in the air entering the electrolyte.

The Ar CVs from these experiments (Figures 4.22 through 4.24) do show some amount of Pt loss, but the H_{UPD} area loss is not as severe as the ORR loss suggesting contamination is also at work. Figure 4.21 shows, if anything, that the addition of silicone grease seems to improve initial ORR activity and ORR durability.

Another surprise is that the CV to 1.55 V_{RHE} consistently decreased ORR activity within the CV set when there were no SU/SD simulations. Figure 4.25 shows the differences between all intra-CV-characterization-set ORR activities. Recall that during a full AST (including SU/SDs) the CV to 1.55 V_{RHE} usually slightly increased the ORR activity (see Figures 4.14 and 4.15).

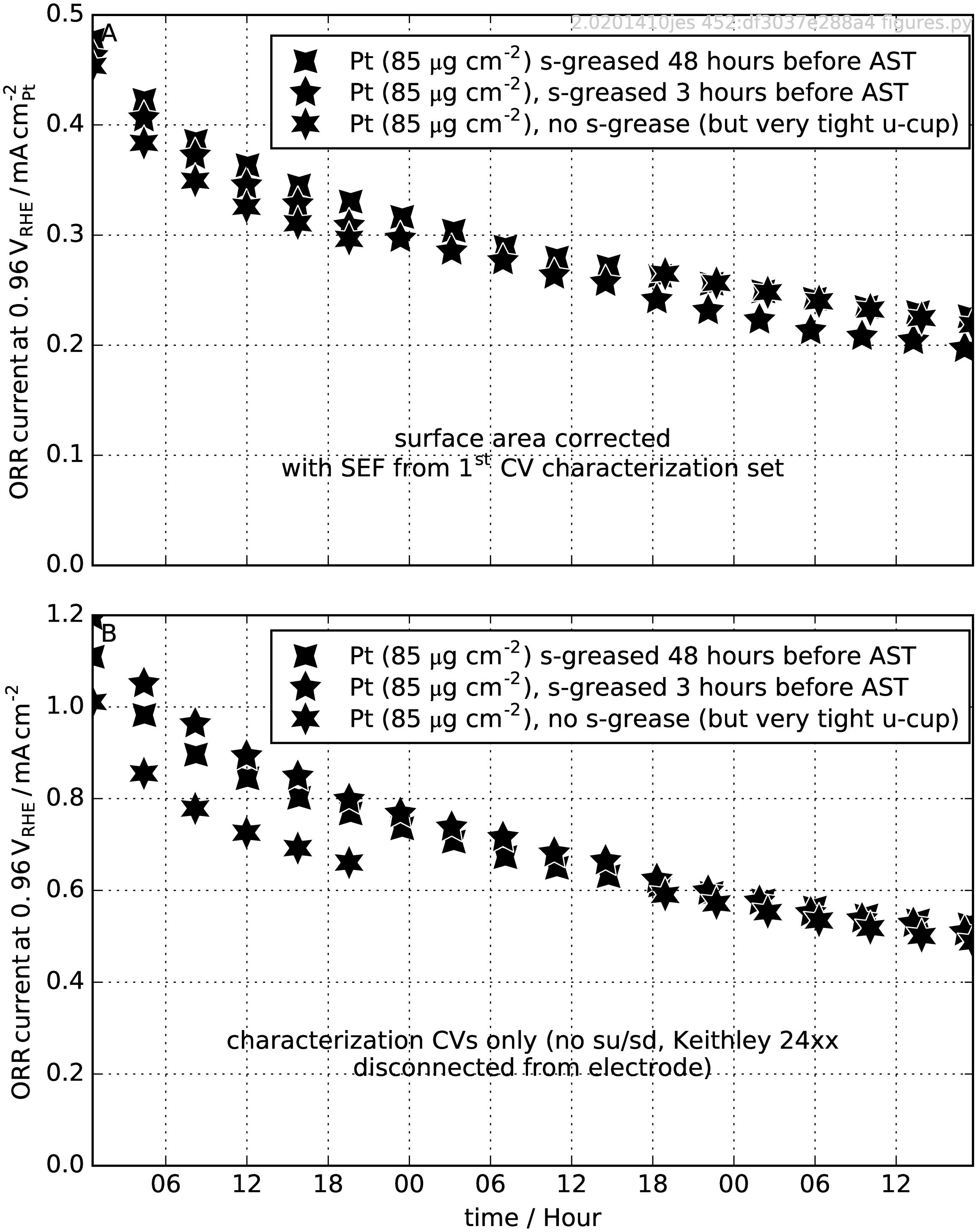


Figure 4.21: ORR activities (background and mass transport (Koutecký-Levich) corrected.) of two silicone greased and one non-greased pure Pt samples subjected to the AST protocol with no SU/SD simulations. **A**: Current densities corrected with the initial SEF, **B**: Geometric current densities. Gas sparging and rotation were maintained as usual between CV characterizations even though no SU/SD simulations were applied. “s-grease” in legends means silicone grease.

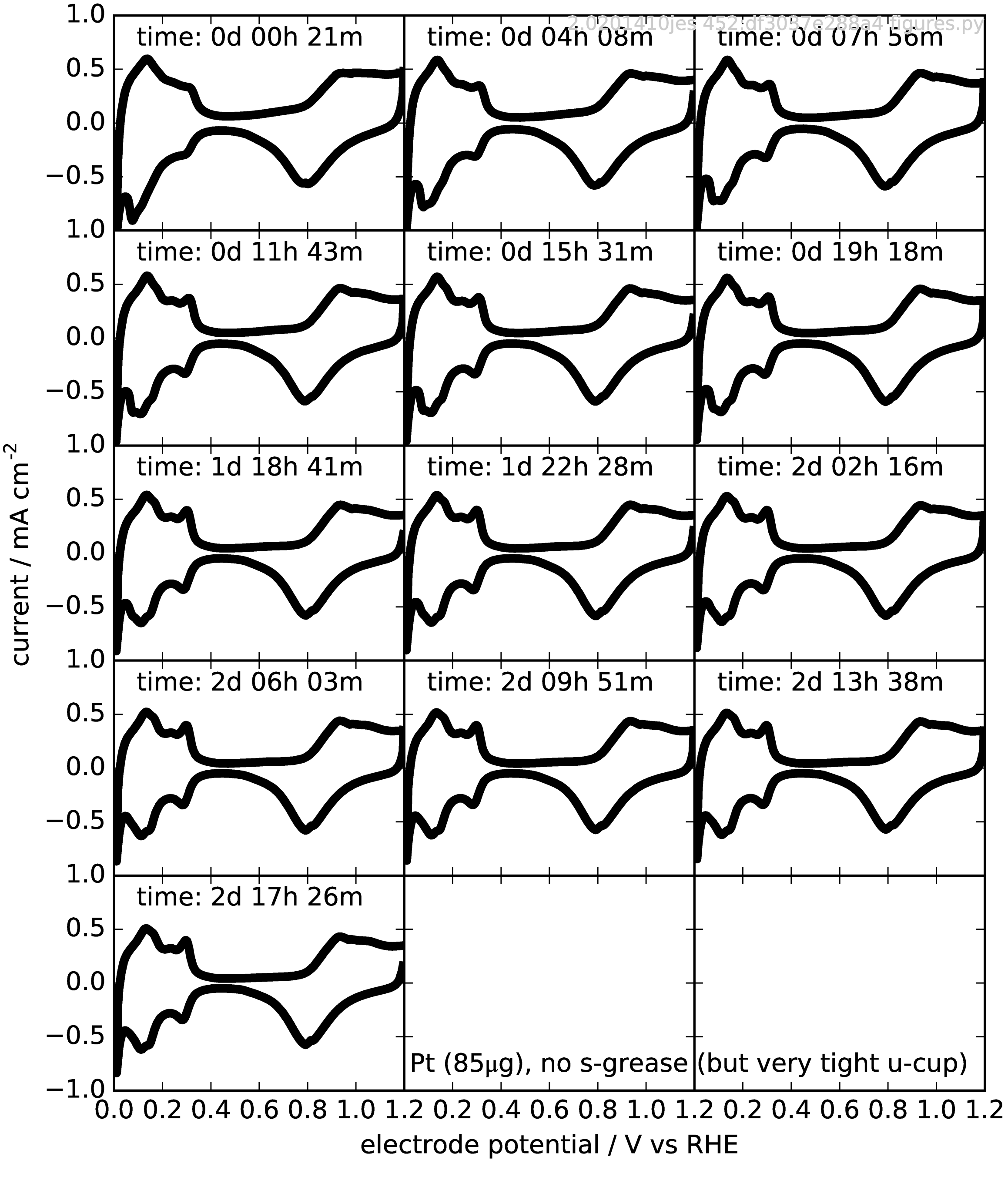


Figure 4.22: Ar CVs of the “no s-grease (but very tight u-cup)” pure Pt sample in Figure 4.21.

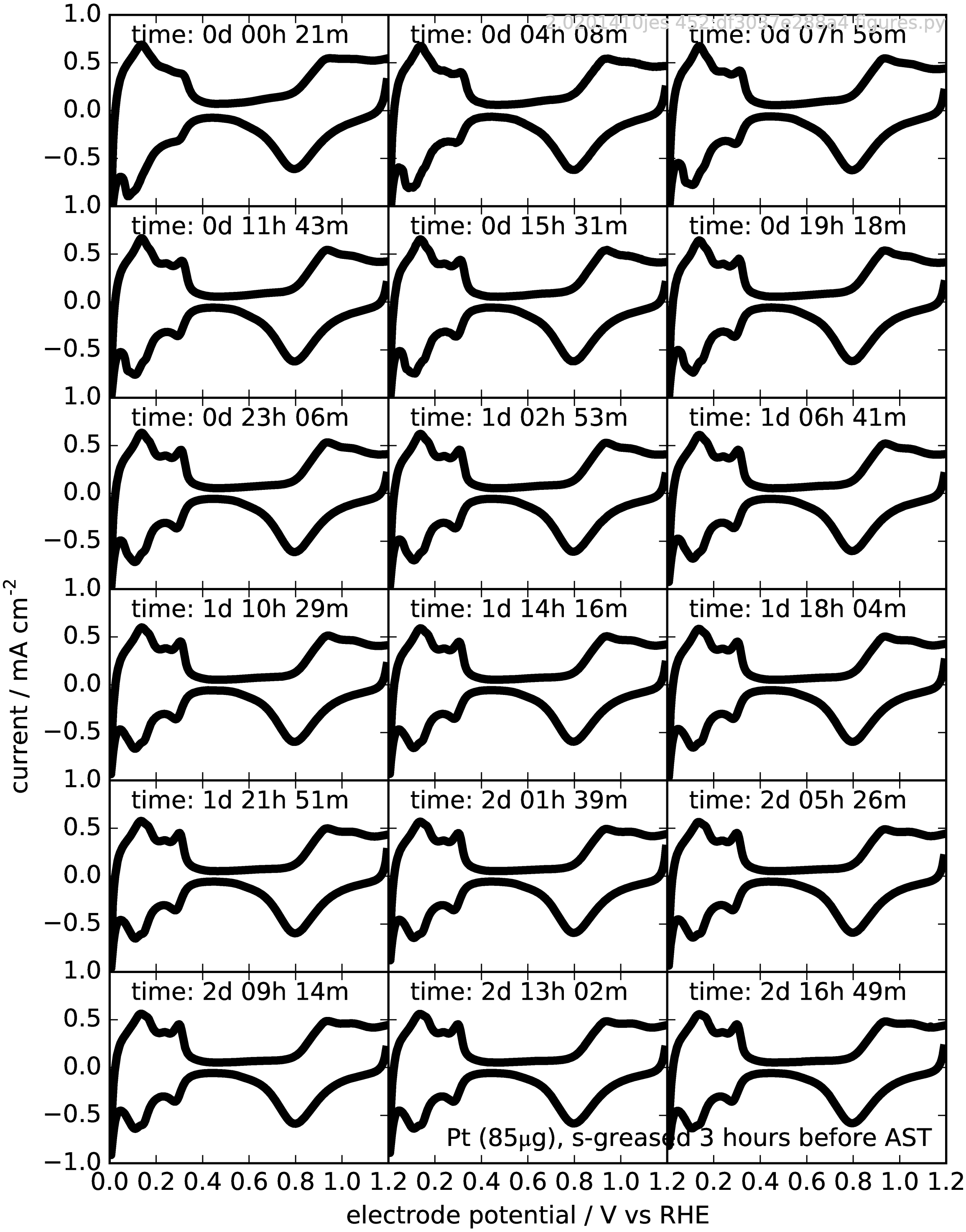


Figure 4.23: Ar CVs of the "s-greased 3 hours before AST" pure Pt sample in Figure 4.21.

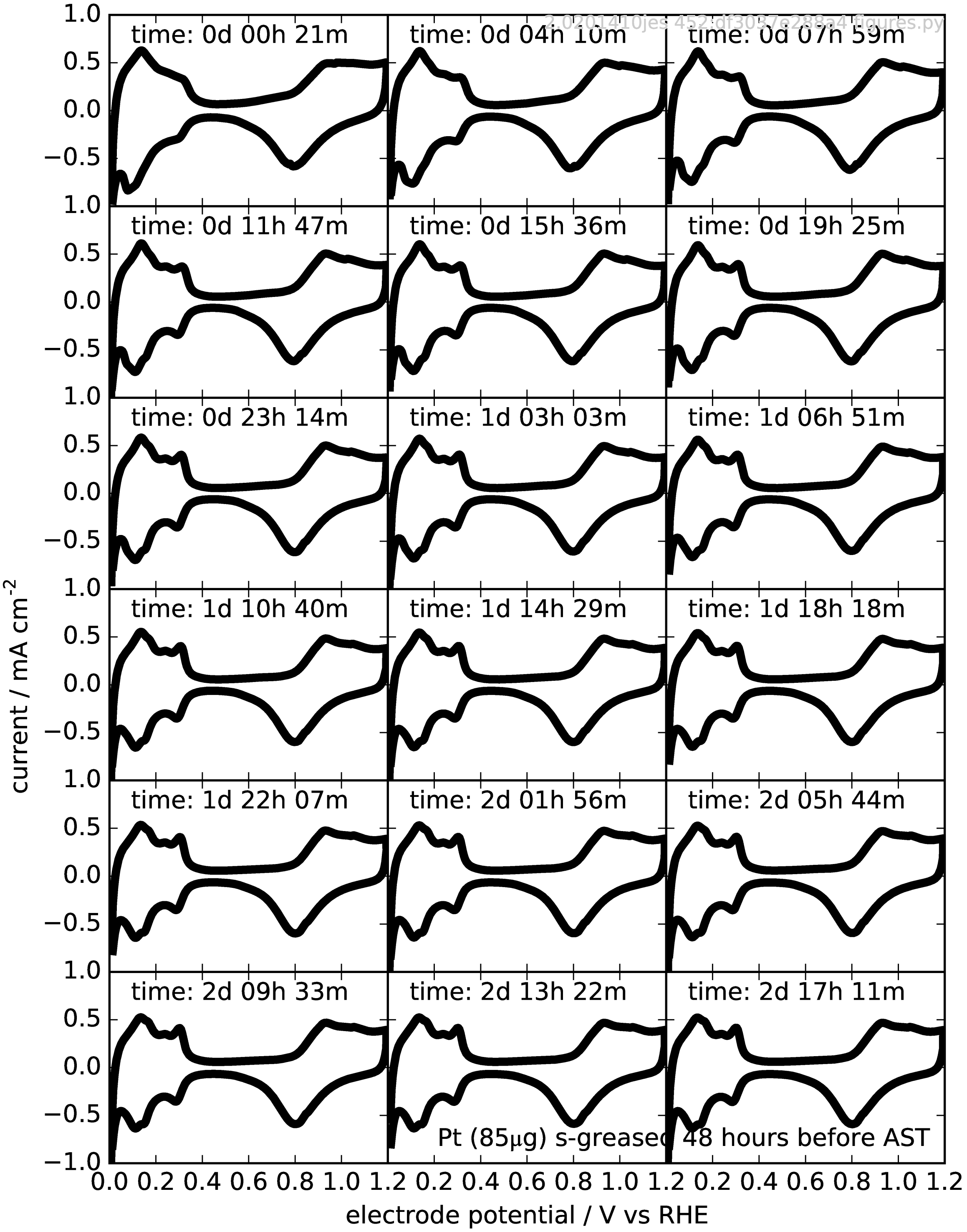


Figure 4.24: Ar CVs of the “s-greased 48 hours before AST” pure Pt sample in Figure 4.21.

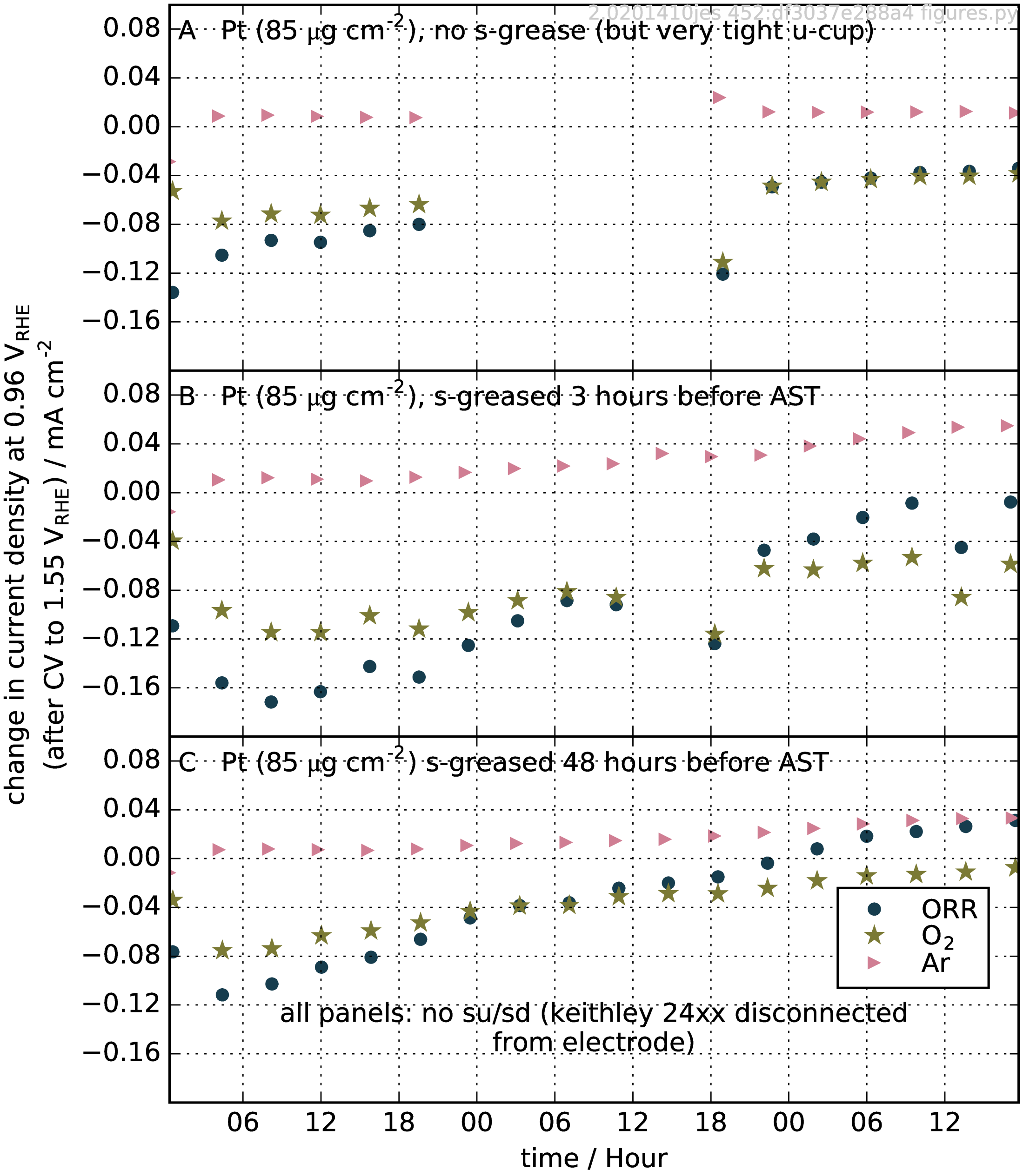


Figure 4.25: The difference between the ORR activity before and after the CV to 1.55 V_{RHE} for silicone greased (**B** and **C**) and non-greased (**A**) pure Pt samples. Currents from the O_2 and Ar CV are also included to help discern the primary cause of ORR change. Note the abscissa is time rather than SU/SDs. The experiment in panel A experienced an accidental pause in measurement, but sparging and rotation were not interrupted. The ORR change is consistently negative (except points after hour 00 in panels B and C), which is opposite to the majority of differences in Figures 4.14 and 4.15. "s-grease" in means panel captions silicone grease.

4.6.2 The Effect of Carbon Corrosion on ORR and OER Decay

Figure 4.26 shows replicate data from different sputtering runs conducted in the next phase of the project (Chapter 5). Both samples start the AST with the same ORR and OER activity, but progress slightly differently. Both samples were silicone greased but experienced different extents of carbon corrosion. Figures 4.27 and 4.28 show the Ar CVs from the experiments in Figure 4.26, which are the best indicators of the extent of carbon corrosion; another indicator is the potential vs. time shape of a start/stop constant current pulse. The sample with less carbon corrosion reached a kinetically limited current, indicated by zero ORR current at 2400 SU/SDs, while the sample with more carbon corrosion did not. The prolonged OER and ORR activity for the sample with more carbon corrosion is quite possibly linked to the greater amount of carbon corrosion. The additional electrochemical pseudocapacitance provided by the corroded carbon would give additional charging capacity during a start/stop constant current pulse. This should result in two things:

1. The potential at the end of the pulse will be lower, and
2. Less current goes to charging (i.e. oxidizing) the Pt, Ir and Ru. Less Pt oxidation should mean less Pt reduction and therefore less Pt loss.

Both of these effects are seen in Figure 4.26, assuming the ORR differences are due to Pt loss, and not some other possible cause like organic contaminants from the air. All the binary samples in this chapter were ran with ungreased u-cups, which means some of them experienced heavy carbon corrosion. The Figures in Appendix B can be used to tell which samples incurred carbon corrosion.

Even though the effect of carbon corrosion is to prolong ORR and OER activity, it is undesirable and should be minimized as much as possible. Recall, the goal of this project is catalyst material screening (pg. 98), and the catalyst material is Pt/Ir/Ru on NSTF. The substrate (i.e. glassy carbon) should not have an influence on the outcome of the test.

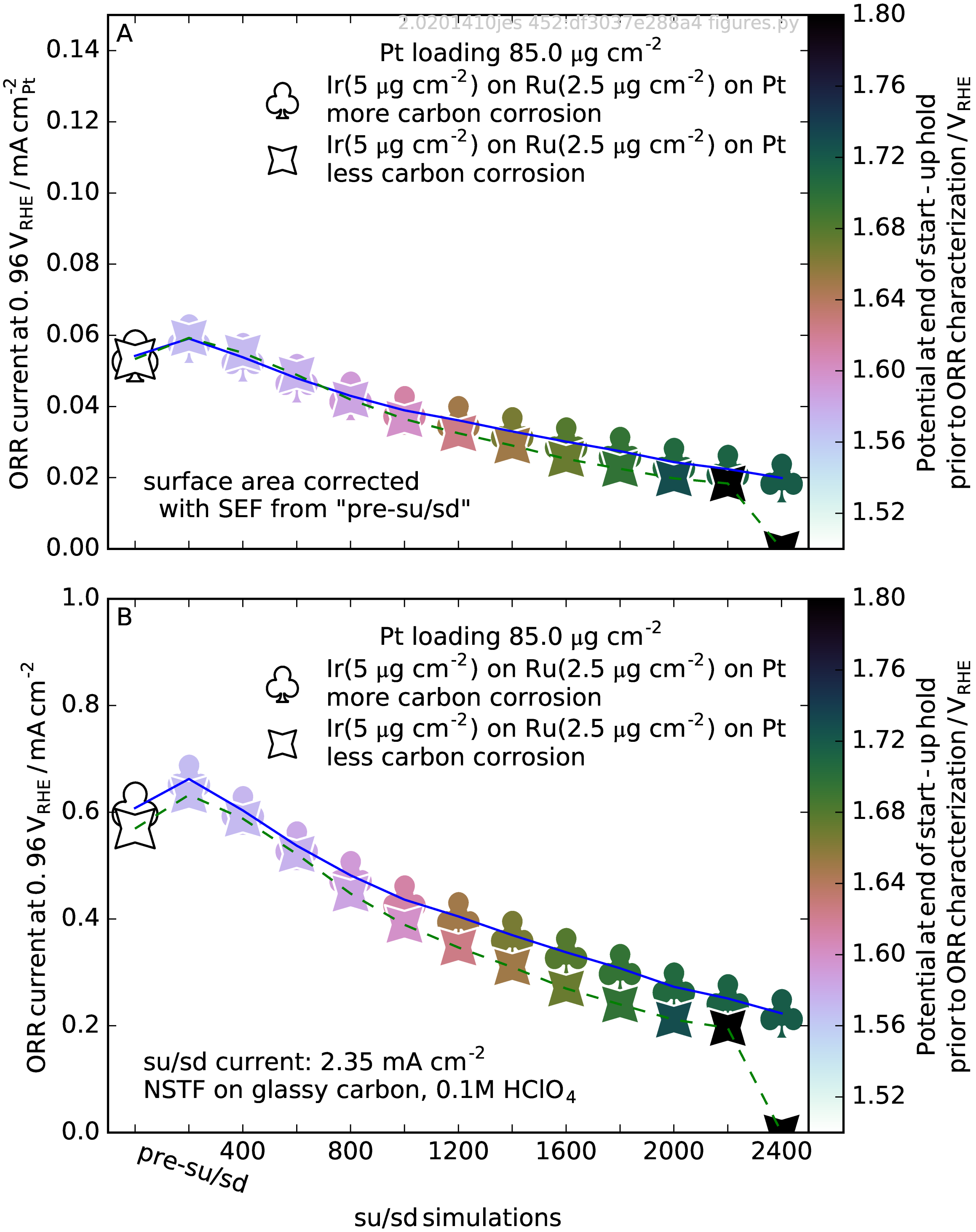


Figure 4.26: The progression of ORR and OER activity for two identical compositions with differing severities of carbon corrosion. **A**: normalized to initial SEF and **B**: geometric current density. (ORR is background and mass transport (Koutecký-Levich) corrected.) The marker colour represents the OER activity and corresponds to highest potential reached by SU/SD cycle prior to ORR characterization. Figures 4.27 and 4.28 show how the carbon corrosion differed.

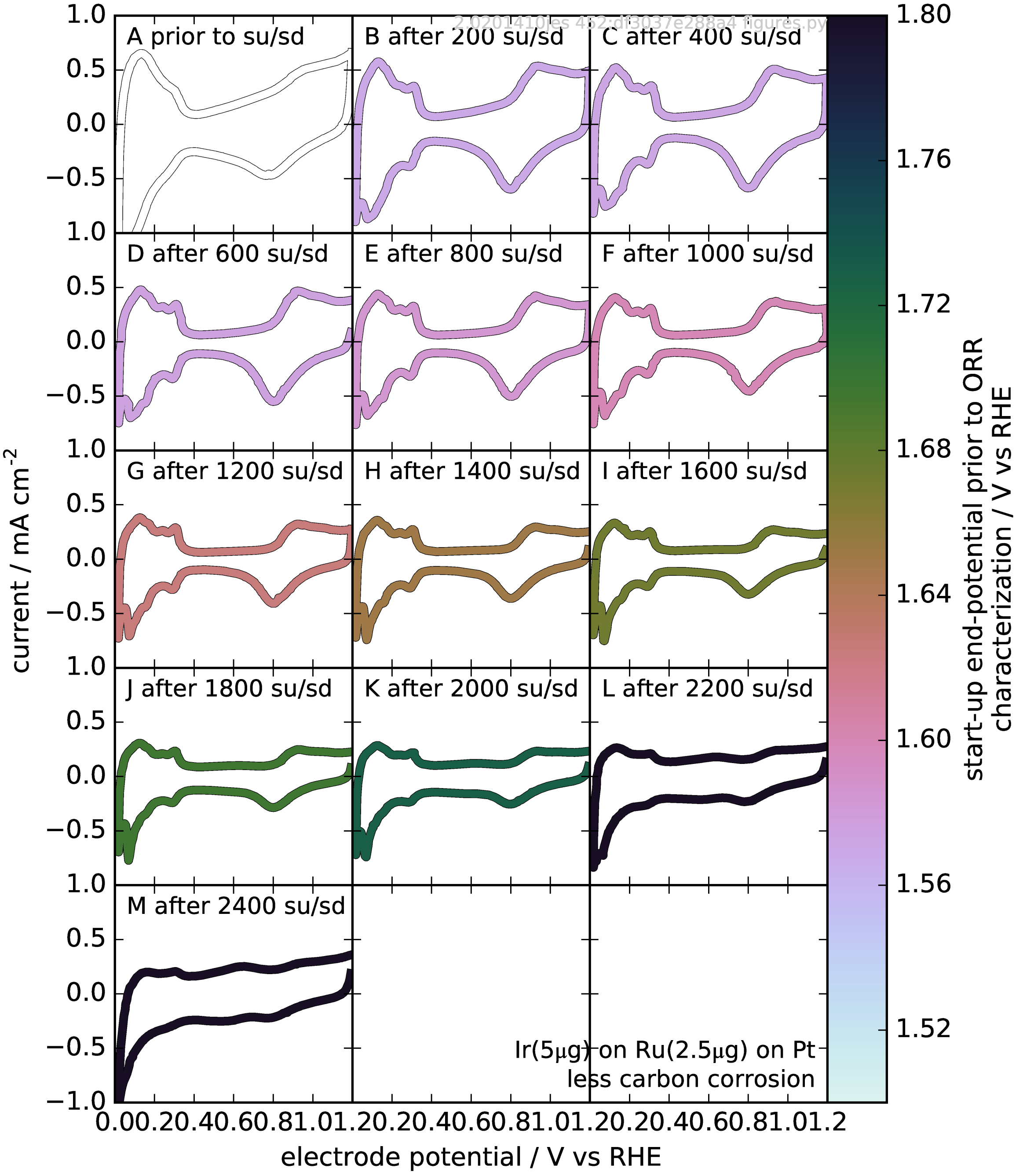


Figure 4.27: Ar CVs of the “less carbon corrosion” sample in Figure 4.26.

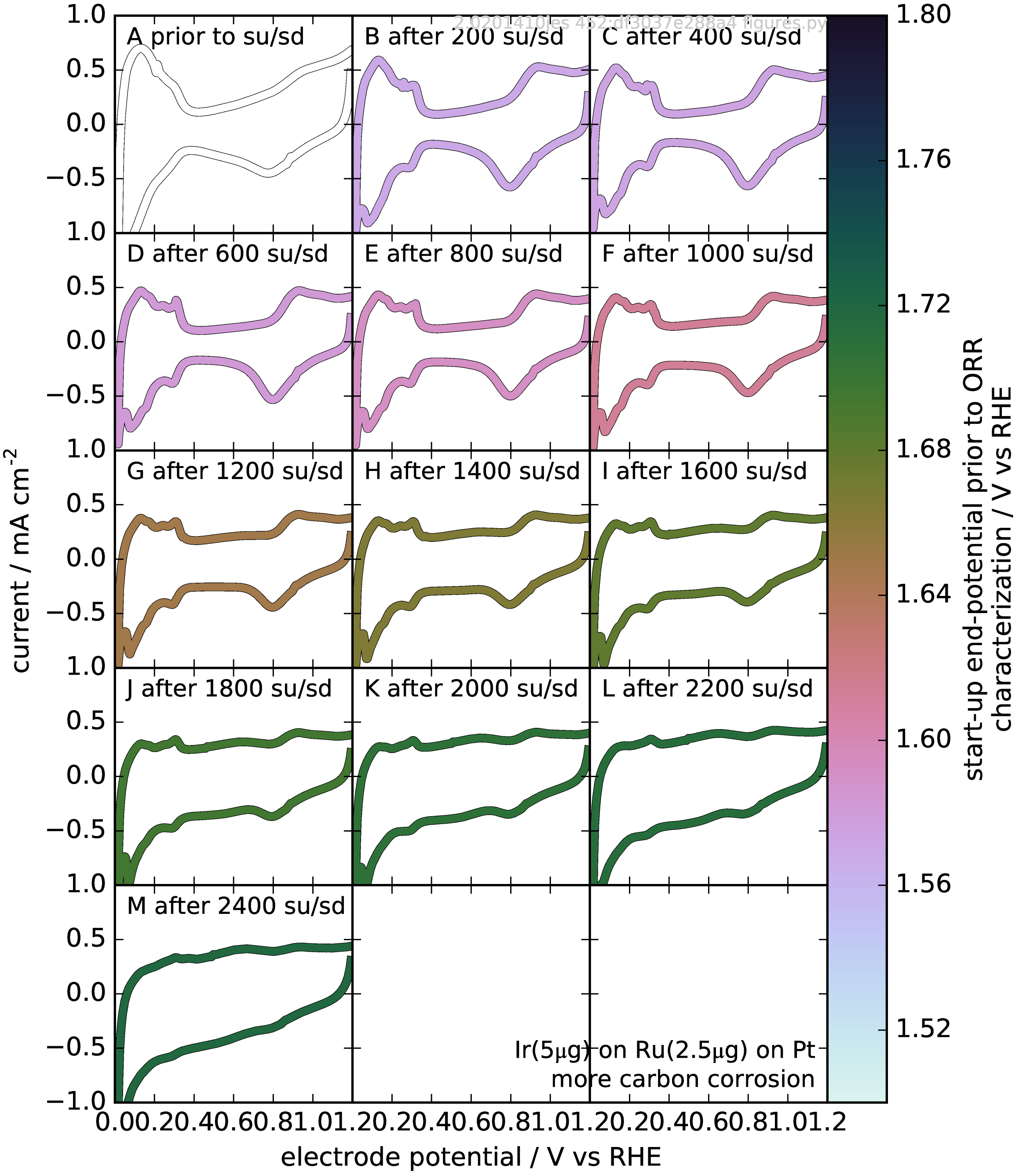


Figure 4.28: Ar CVs of the “more carbon corrosion” sample in Figure 4.26.

4.7 Summary

Conclusions, observations, lessons, and caveats stated throughout this chapter are paraphrased below in point form.

- Addition of Ru or Ir significantly prolongs ORR under repeated (simulated)SU/SD.
- Ru loading positively correlates to ORR activity. The Ru intermix deposition scheme is best for ORR activity.
- Ir overlayer provides the best protection against ORR decay. Furthermore, the ORR stability it provides defies expectations about Pt loss.
- The OER activity of Ru and Ir expectedly decreases during SU/SD with the exception of the two highest (15.3 and $42 \mu g_{Ir}\, cm^{-2}$) Ir overlayer loadings.
- Ru initially blocks ORR but most of it is quickly dissolved, and the Pt's ORR activity is restored. Furthermore, after most of the Ru is lost, the ORR activity is generally higher than pure Pt, probably due to the de-alloying and/or the strain-induced d-band centre shift effect.
- The highest Ir loading ($42 \mu g_{Ir}\, cm^{-2}$) shows curious (i.e. unlike all the other samples) ORR changes within the CV characterization set.
- H_{UPD}-based surface area corrections cannot be applied with confidence on Ru and Ir containing samples (see Figure 4.14 panels C and F).
- The glassy carbon disk current collector corrodes due to the high potentials of the AST if the electrolyte gets between the disk and the u-cup.
- High vacuum silicone grease can seal the u-cup preventing carbon corrosion, and its presence does not significantly affect ORR activity. The visual appearance of silicone grease on the catalyst does not significantly influence ORR activity.
- Carbon corrosion probably affects the progression of the AST, probably prolonging both OER and ORR activity.
- Some amount of carbon corrosion is unavoidable, even with silicone grease, because:
  - There is a small section of disk wall not 'wetted' by silicone grease.
  - Carbon corrosion always occurs under the Pt thin-film ring.
  - Carbon corrosion will eventually occur under the NSTF film if the test is run long enough.

Chapter 5

Screening the Durability of Binary (Ir and Pt) and Ternary (Ir, Ru and Pt) Catalysts

The SU/SD current for the testing protocol used in this chapter was increased from 0.942 $mA\,cm^{-2}$ (used in Chapter 4) to 2.35 $mA\,cm^{-2}$, to make the protocol more aggressive so experiment duration would be shorter. Experiments were allowed to run until the start-up end-potential remained at 1.8 V_{RHE} (the maximum allowed potential) for ~400 SU/SD cycles, or until the total number of SU/SD cycles reached 4000. The intended aim of the study was to assess the benefit Ru could provide to the Pt-Ir system.

Although Chapter 4 established that Ru intermixed with Pt exhibited better ORR activity, the Ru was overlayered on the Pt for this study. This was partially because the ORR analysis had not been fully and properly completed before the planning for this study began; the sub-contractual arrangement with 3M led to the prioritization of sample synthesis and measurement over analysis. Also, it was partially because 3M preferred an overlayer deposition scheme for their roll-to-roll manufacturing process. Ru was deposited before the Ir, because the rational expectation was that an overlayer of Ir would probably better protect the Ru from dissolution.

Figure 5.1 shows all the Ir and Ru compositions and their respective sputtering runs, tested for this next phase of the project. The loadings remain in-line with the USDOE guidelines, as explained in Section 4.2 (pg. 127). Figure 5.1 shows fifty-four unique compositions. One hundred and one samples were tested (most compositions had two replicates).

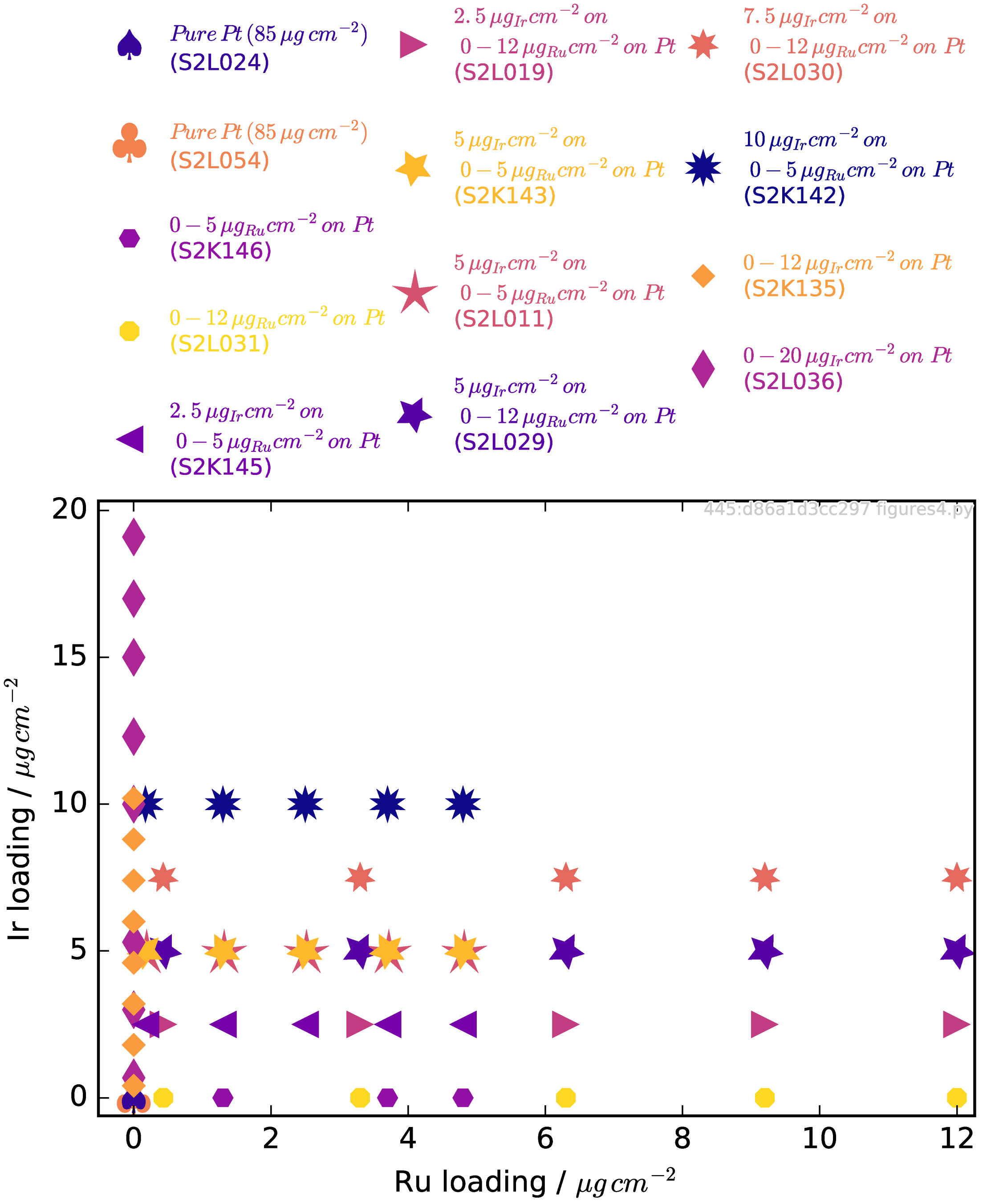


Figure 5.1: Composition space of the samples synthesized for this Chapter. All compositions are Ir on Ru on 85 $\mu g\ cm^{-2}$ on Pt (each element is overlayered). For the Ru-ramp overlayered by Ir compositions, an attempt has been made to correspond the number of points on the marker to the $\mu g\ cm^{-2}$ of Ir for easy recollection, as the marker styles are used throughout the Chapter. The sputtering run codes are included in parenthesis for cross-referencing markers with the figures in Appendix C.

5.1 Analytical Methods for this Chapter

There are a number of differences in the data processing techniques between this Chapter and Chapter 4. The biggest difference is the application of an ohmic drop correction. First, some minor differences in the preliminary CV processing are described.

5.1.1 Preliminary CV Processing

There were some problems with the prior methods of noise removal and sweep cusp[1] determination:

1. Potential data was not original but based on an ordinary least squares regression line. The analogue sweep generator in the Pine AFCBP1 sometimes does not produce perfectly linear potential vs. time data.
2. The number of data points for the moving regression of the sweep cusp determination algorithm was manually chosen, but the polling frequency was not consistent. This led to poor cusp determination, particularly for the noisy OER CVs. The data near the cusp (the highest current) was especially important for the method used to determine resistance for the OER CVs. Inaccuracy in the cusp determination also was problematic for determining the 'saddle' point for H_{UPD} analysis (see Figure 1.8). Adjustments to the moving bin could be made to improve cusp accuracy, but the algorithm was slow and re-determining the cusps for all the CV files (about 8000) was very time consuming.

Therefore improvements were developed.

5.1.1.1 Sweep Cusp Determination

CV data was sorted by potential, and the upper and lower 10% was removed. This left gaps in the data at the cusp locations when the CV was re-sorted according to time. Ordinary least squares regression lines were determined for each potential vs. time segment separated by a time gap. The cusps were located at the intersection of these regression lines. This algorithm was more accurate and much quicker than the previous method, and yielded results independent of the polling frequency of the potentiostat.

---

[1] Cusps are points on the potential vs. time data series for a CV (i.e. the times when the sweep switched direction, from up-sweep to down-sweep, or visa versa).

5.1.1.2 Sweep Monotonicity (Noise Removal)

Instead of substituting measured potential with values from a regression line, the CV data was cleaned of noisy points to yield sweep data where the potential was monotonic with time. first, a potential vs. time linear regression line was determined for the sweep, then the point with the highest squared difference from the regression line was removed and the line was checked for monotonicity in potential. This continued until monotonicity was established. A new regression line was not determined each iteration. Some CVs could have up to 10% of data removed by this method. Figure 5.2A is an example of a CV sweep with a high number of points removed.

5.1.2 Ohmic Drop Correction

In addition to the background and mass transport corrections, the phenomena of ohmic loss should be accounted for. Potential is corrected for ohmic drop according to Ohm's Law:

$$E_{iRcorr} = E_{raw} - i_{raw}R \tag{5.1}$$

where E_{iRcorr} is the electrode potential corrected for ohmic loss, E_{raw} is the measured electrode potential, i_{raw} is the measured current density, and R is the electrical resistance. Unfortunately, conventional experimental techniques for dealing with iR drop (Luggin capillary, current-interrupt technique, frequency response, etc.) were not available. At the time of measurement, it was thought ohmic drop correction was not imperative, but later experience and reading proved otherwise. For example, *van der Vliet et al.* (2010) have published a paper titled "On the importance of correcting for the uncompensated Ohmic resistance in model experiments of the Oxygen Reduction Reaction". A challenge arose: how could the resistance be determined after-the-fact with the existing data?

5.1.3 Ohmic Drop Correction for OER CV: The Derivative Method

The ohmic correction for OER data follows a method given by *Krstajic and Trasatti* (1998). Using Equations 1.11 and 5.1, the Tafel model which accounts for ohmic drop is:

$$\eta = b \log\left(\frac{I}{I_o}\right) + IR \tag{5.2}$$

Differentiating with respect to I gives:

$$\frac{d\eta}{dI} = \frac{b}{I} + R \tag{5.3}$$

R is the ordinate intercept on a plot of I^{-1} versus $\Delta E/\Delta I$. This model, of course, assumes an I-V data set exhibits Tafel behaviour.If current density (i) is used, the intercept is RA_{geo}. Figure 5.2 shows obtaining R with the derivative method improves the fit when applied to an OER CV.

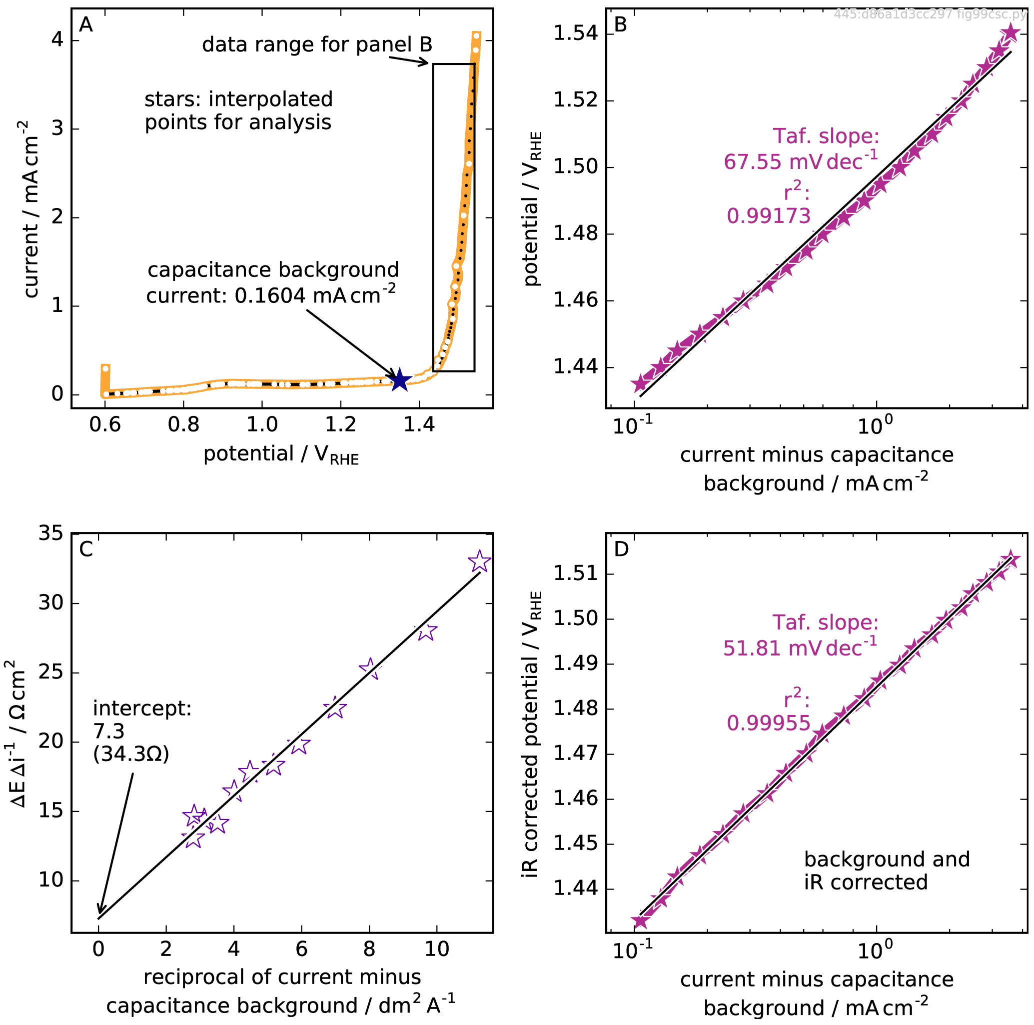


Figure 5.2: Data from the up-sweep of the CV to 1.55 V_{RHE} from the fourth CV characterization set for a sample of 7.5 $\mu g_{Ir}\, cm^{-2}$ on 9.2 $\mu g_{Ru}\, cm^{-2}$ on Pt (sweep rate: 10 $mV\, s^{-1}$). **A**: Dots without colour within the width of the line are points removed to ensure potential monotonicity. **B**: Tafel style plot without iR compensation. r^2 is the linear regression goodness-of-fit parameter. **C**: derivative method used to determine resistance. **D**: Tafel analysis using potential corrected for ohmic drop based on resistance from panel C.

5.1.4 Ohmic Drop Correction for ORR CVs: The H_{UPD} Peak Mis-match Method

A novel 'H_{UPD} peak mis-match' method was used to determine resistance for the ORR data. A different method was used for ORR data because the raw data should be used to determine a resistance. ORR data which is ready to be fitted to the Tafel model has been background and mass-transport corrected so the derivative method cannot be used.

The rationale for the peak mis-match method is as follows: H_{UPD} peaks appear in both the Ar and O_2 CVs but the potentials of the maxima and minima of matching H_{UPD} features do not line up between the two CVs due to ohmic drop. The peaks of the O_2 CV are shifted to the left compared to the Ar CV. This effect can be seen in Figure 4.1. Thus there is a H_{UPD} 'peak mis-match' between the two CVs used for determining the ORR. This effect can be used to determine a resistance. The goal is to find the *iR* correction which best minimizes the peak mis-match.

The area between the up-sweep and down-sweep Faradaic curves in the H_{UPD} region is a way to quantify the H_{UPD} peak mis-match. Figure 5.3 shows the O_2 and Faradaic CV data for multiple resistance corrections. Each panel shows a different *iR* correction. The area between the up and down Faradaic sweeps is shaded. All data above 0.6 V_{RHE} (raw) was excluded for this analysis. The upper limit of 0.6 V_{RHE} meant the potential window of the shaded area shrinks with increasing resistance. Measurement noise will produce an area in addition to mis-match, so a greater potential window will yield a greater proportion of noise-sourced area. Therefore a normalization to potential window was an intuitive action. Each panel in Figure 5.3 shows the numerical value for the mis-match area and the values for the area normalized to the potential window of the mis-match area. The normalization slightly increased the accuracy of the mis-match quantification. For instance, Figure 5.3 panels F and G show *iR* corrections from two different resistances give the same area, but different normalized mis-match values to within three significant digits.

Figure 5.4 shows how the application of an ohmic drop correction can improve the r^2 (goodness-of-fit) parameter and bring the Tafel slope closer to a theoretical value (59.1 $mV\,dec^{-1}$). SEF based corrections were not done on ORR data presented in this chapter because of the SEF inaccuracies explained in Chapter 4.

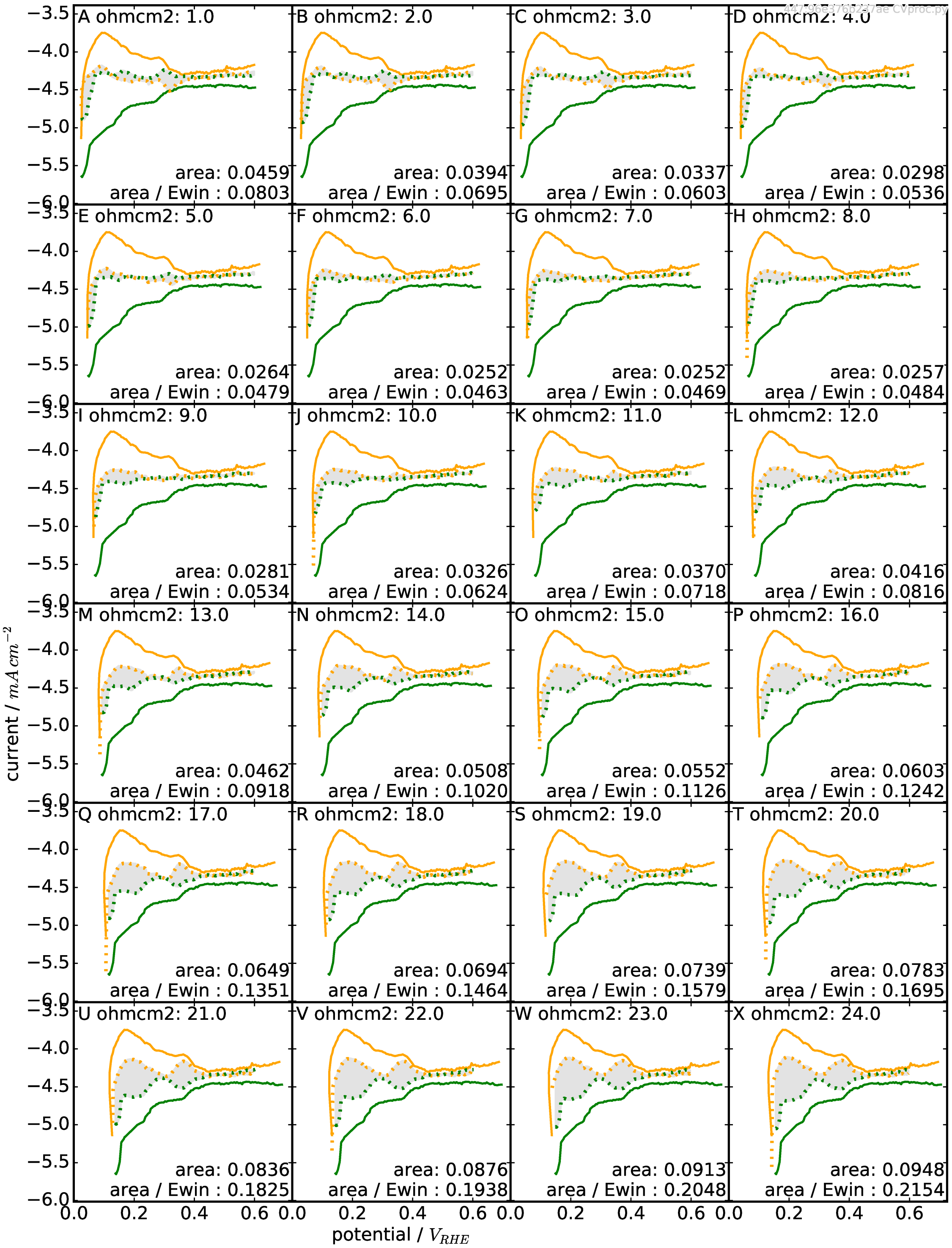


Figure 5.3: The O_2 CV (i_{O_2}) up-sweep (orange/light) and down-sweep (green/dark) in the H_{UPD} region and Faradaic ($i_{O_2} - i_{Ar}$) up and down sweeps (dotted lines) for $\Omega\,cm^2$ values from 1 to 24. The area between the Faradaic up and down-sweep is shaded and is called the 'mis-match' area. The quantity for mis-match area and mis-match area normalized to the potential window over which it occurs are given for each $\Omega\,cm^2$.

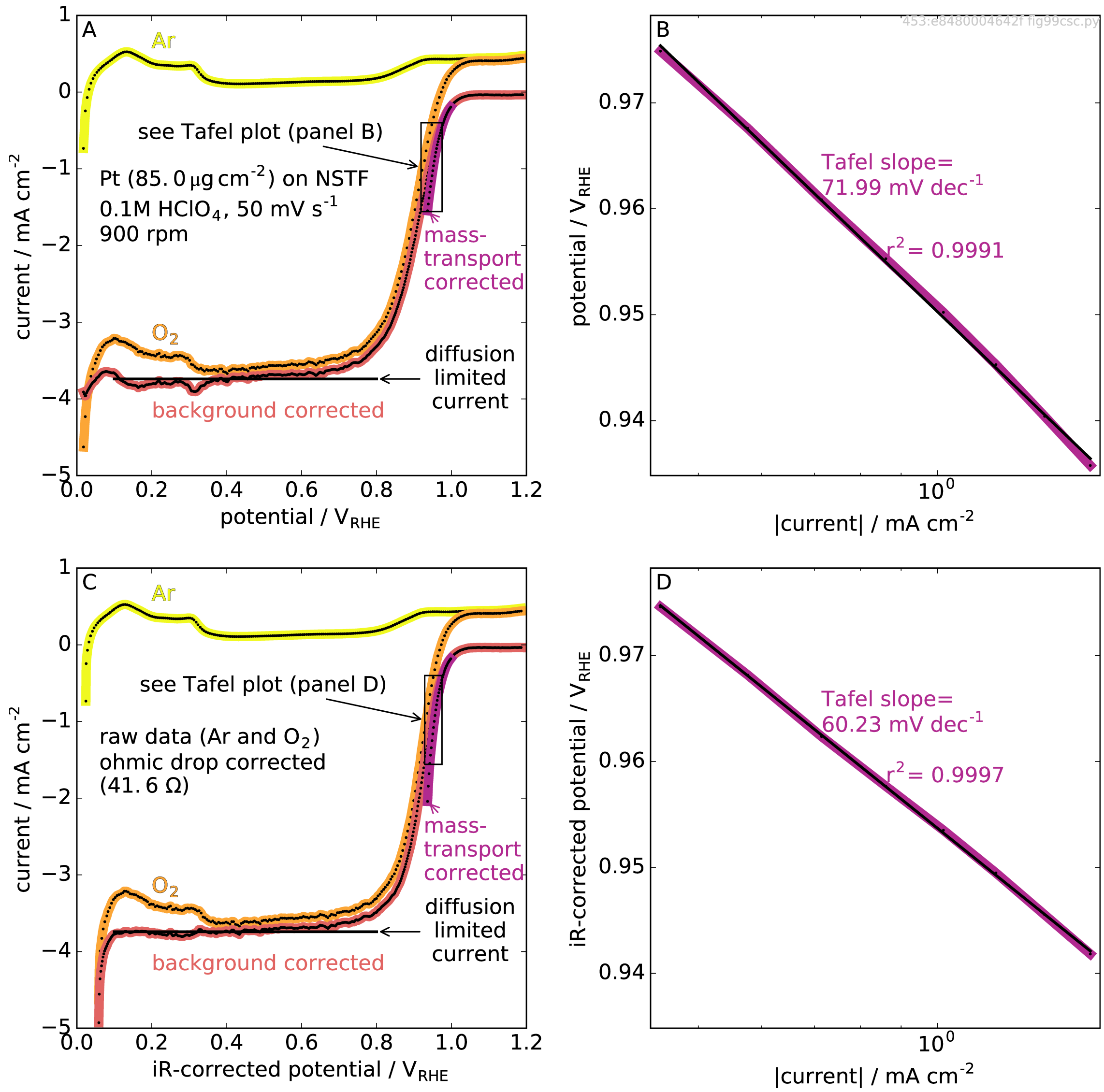


Figure 5.4: **A**: The final up-sweep of an Ar and O$_2$ CV, their resulting background corrected up-sweep, and a small segment of the result of the application of the Koutecký-Levich equation (labelled mass-transport corrected). **B**: A Tafel style plot showing the mass transport corrected data. Panels **C** and **D**: Same as panels A and B but with an ohmic drop correction applied to the Ar and O$_2$ CV data in Panel A.

5.1.5 Post *iR* Correction: Removal of Monotonic Disruptions

Sometimes an ohmic drop correction would introduce monotonic disruptions in what was previously monotonic data. Since the potential vs. time data is no longer linear after the *iR* correction, the previously described noise removal algorithm (pg. 169) could not be applied. Instead, the disruptive points or series of points were simply removed as adjacent potentials, and were compared moving along the sweep in one direction. Probably less than 1% of data was removed from CV sweeps by this method.

5.1.6 Manual Exclusion of Noisy or Bad Data

Experiments were frequently plagued by noise or bad connections. CVs heavily affected by noise or a bad connection are excluded from analysis. If a start-up end-potential point required for analysis falls within a range of SU/SD cycles which were excluded, an interpolation is performed. For some experiments, up to ~30 % of the SU/SD cycles could be excluded.

5.2 Assessing the Durability of OER activity

How long does an OER catalyst last? To answer this question, an end-point activity must be defined at a current and potential, then the number of SU/SD cycles to this point can be called the lifetime. Analysis of both the OER CVs and start-up end-potential, a useful indicator of the OER activity, can answer this question. Once the end-point activity is reached, the number of SU/SD cycles to the end-point can be determined; for the OER CV data, it will have to be interpolated. What is an appropriate end-point activity? The current for the end-point activity should be 2.35 $mA\ cm^{-2}$, the SU/SD current, so the results from one source of OER activity can be checked against the other. Ideally, both should show similar trends. What is an appropriate potential to complete the definition of end-point activity? To answer this question, one should be aware of a problem with this method for defining lifetime; some compositions are not active enough to even start at the defined end-point, and some compositions are so active they do not reach the end-point within the experiment duration; one could say the experiment remains unfinished, even though it may have completed the maximum allowed number of SU/SD cycles (4000) in an AST experiment. An appropriate potential for an end-point using 2.35 $mA\ cm^{-2}$ minimizes the number of experiments that are unfinished and experiments that start above the end-point. The ‘unfinished’ category also contains experiments that are ended prematurely due to equipment problems, power outages, etc. Ideally this potential would be the same for both the CV and start-up end-potential data, but it is not because the CV data is *iR* corrected and the end-potential data is not. Through trial and error, this potential was found to be 1.515 V_{RHR} for the *iR* corrected CV data, and 1.62 V_{RHE} for the non-*iR* corrected start-up end-potential data. For the CV data, the OER activity can be extrapolated outside the range of measured data using the Tafel model. This is required because the OER CVs only go up to $\sim 1.54 V_{RHE}$ and often the current never reaches 2.35 $mA\,cm^{-2}$. Therefore, another criteria for finding an appropriate end-point potential for the OER CV data was minimizing the number of points requiring extrapolation beyond the measured data range.[2]

Figure 5.5 shows the number of SU/SD cycles it takes for an experiment to reach 1.515 V_{RHE} based on the CV data. Lifetimes obtained with an extrapolation based on Tafel analysis are indicated with hollow markers (see legend on Figure for more details). Figure 5.6 shows the number of SU/SD cycles it takes for Ir ramp (no Ru) experiments to reach 1.62 V_{RHE} based on the start-up end-potential data. Figure 5.7 is the analogous figure for the constant Ir on Ru ramp samples. Experiments which are unfinished or ended prematurely are displayed in a small panel above the lifetime vs. loading panel, and those which started above the end-point are displayed in a small panel below the lifetime vs. loading panel

Despite the large amount of scatter in the data, one may see in these Figures that increasing Ir seems to provide an augmenting benefit for lifetime and increasing ruthenium seems to provide a diminishing benefit for lifetime. Some Ir/Ru ramp series display more of a linear relationship, but this effect changes for different end point potential and current values. To show the trends, lines to guide the eye are drawn on the Figures 5.5 to 5.9.

---

[2] *iR* correction also brings a requirement for extrapolation because it shrinks the potential range the measured data falls within.

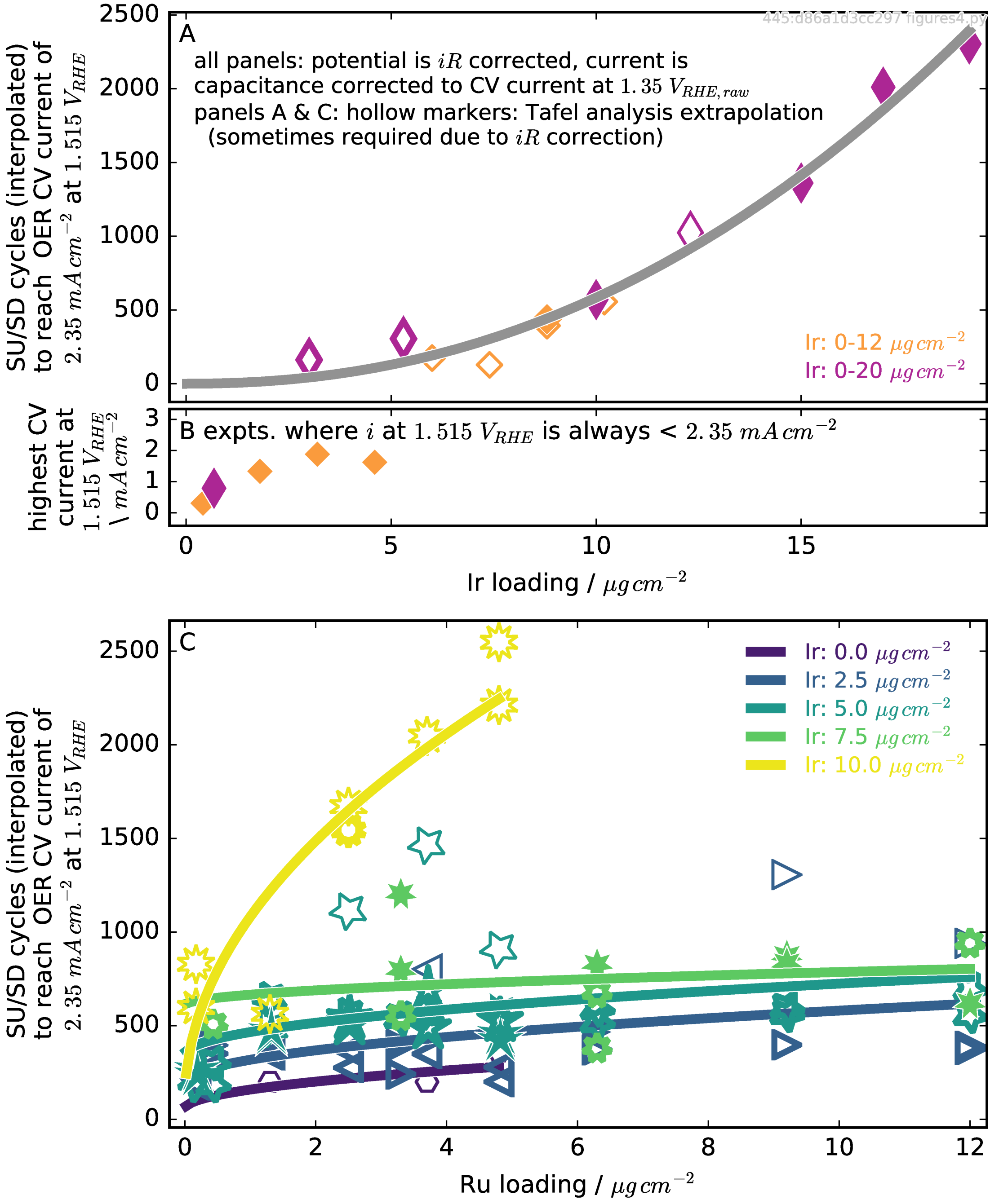


Figure 5.5: The number of SU/SD cycles it takes for the CV OER activity (*iR* corrected) to come down to 2.35 $mA\, cm^{-2}$ at 1.52 V_{RHE}. Each data point represents one AST experiment. Pure Pt samples do not appear because they do not exhibit appreciable OER current). **A & B**: Various loadings of Ir overlayered on Pt (85 $\mu\, cm^{-2}$) on NSTF **C**: Ir overayered on Ru overlayered on Pt (85 $\mu\, cm^{-2}$) on NSTF. The marker styles indicates the nature of the OER activity (extrapolated or not) on each side on the interpolated point. Solid fill: between two points of actual CV data. Thick edge: between one point from a Tafel analysis extrapolation, and one point from actual CV data. Thin edge: between two points, both from a Tafel analysis extrapolation. A legend for the symbols can be found in Figure 5.1

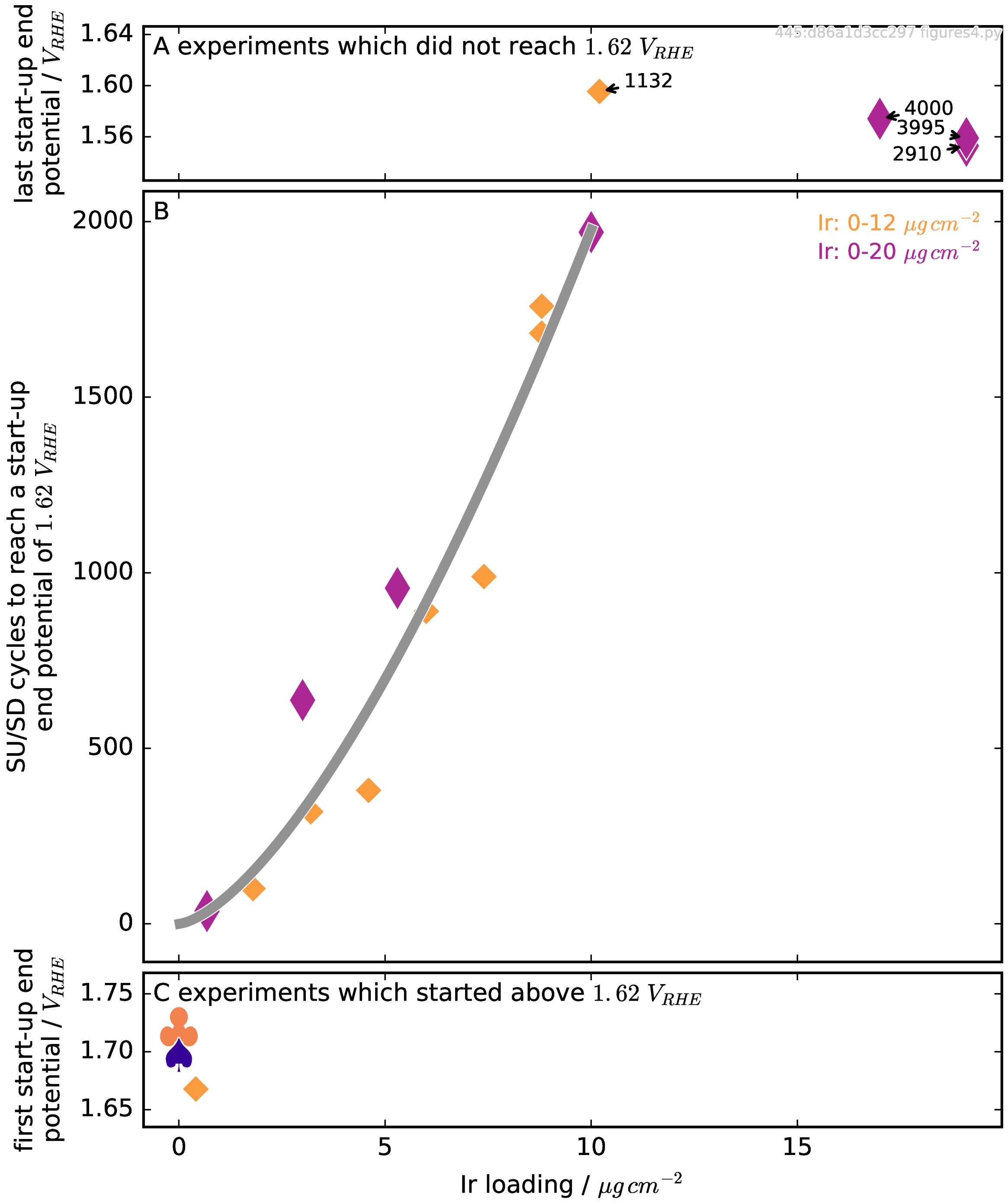


Figure 5.6: The ‘absolute’ OER durability of Ir (various loadings) overlayered on Pt on NSTF. **A**: Samples which were very OER durable and did not climb up to 1.62 V_{RHE} before the end of the experiment (each point is labelled with the total number of SU/SD cycles reached). **B**: The number of SU/SD cycles it takes for the start-up end-potential (an indicator of OER activity) to increase to 1.62 V_{RHE}. **C**: The start-up end-potential of two pure Pt samples and one low-loaded Ir sample started above 1.62 V_{RHE}. A legend for the symbols can be found in Figure 5.1.

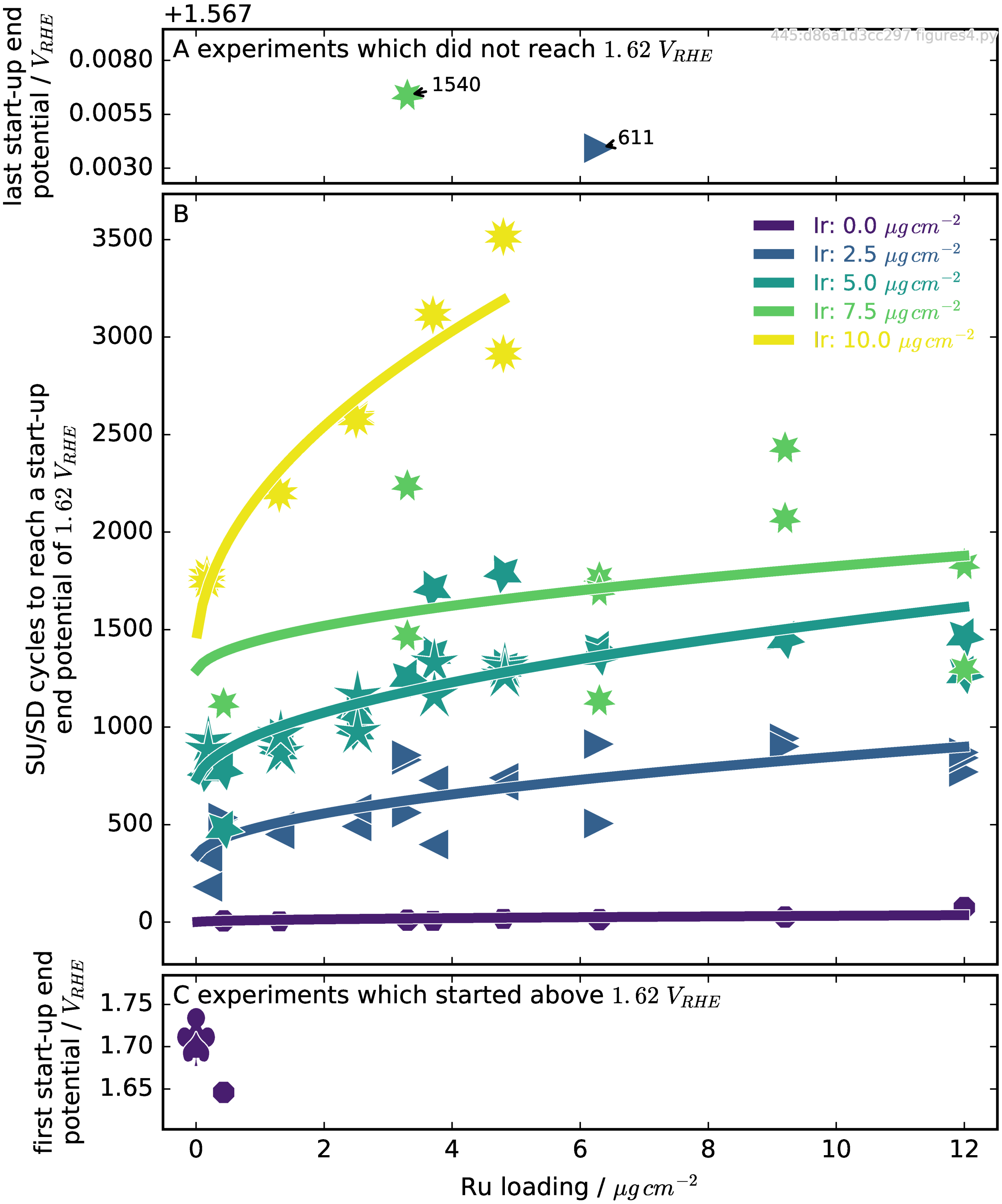


Figure 5.7: The 'absolute' OER durability of Ru (various loadings on abscissa) overlayered on Ir (various loadings in legend) overlayered on Pt on NSTF. **A**: Samples which did not climb up to 1.62 V_{RHE} before the end of the experiment (each point is labelled with the total number of SU/SD cycles reached). **B**: The number of SU/SD cycles it takes for the start-up end-potential (an indicator of OER activity) to increase to 1.62 V_{RHE}. **C**: The start-up end-potential of two pure Pt samples and one low-loaded Ru sample started above 1.62 V_{RHE}. A legend for the symbols can be found in Figure 5.1.

There is a caveat about the assessment of lifetime; the number of SU/SD cycles to reach the end-point would be influenced by the initial activity if the rates of activity degradation are the same. With this in mind, one could distinguish between two types of lifetime definitions, absolute and relative, where relative lifetime is independent of initial activity.

Are the trends seen in Figures 5.5 through 5.7 truly representative of durability, independent of activity? To test this, an end-point which is relative to the initial activity is required. Again, through trial and error to minimize the number of experiments falling within the 'unfinished' and 'not active enough' categories, the relative end-point is defined as a start-up end-potential 0.12 V_{RHE} above the initial start-up end-potential. Experiments with in the 'not active enough' category have an initial start-up end-potential higher than 1.68 V_{RHE}, because start-up end-potential cannot go any higher than 1.8 V_{RHE}. Figures 5.8 and 5.9 show the number of SU/SD cycles required to reach this end-point (based on start-up end-potential data) for the Ir and Ru ramps respectively. The concept of a relative end-point was not be applied to the OER CV data because higher levels of algorithmic processing complexity would have been required to ensure the quality of the Tafel analysis.

Figures 5.8 and 5.9 confirm that for Ir loading, relative durability increases with loading. Ru loading however seems to have no impact on OER durability except when combined with high (10 $\mu g\, cm^{-2}$, and maybe 7.5 $\mu g\, cm^{-2}$) Ir loadings. This concept of durability (something independent of initial activity) is applied to ORR activity later in the chapter. First though, the impact of Ir and Ru on ORR activity is assessed.

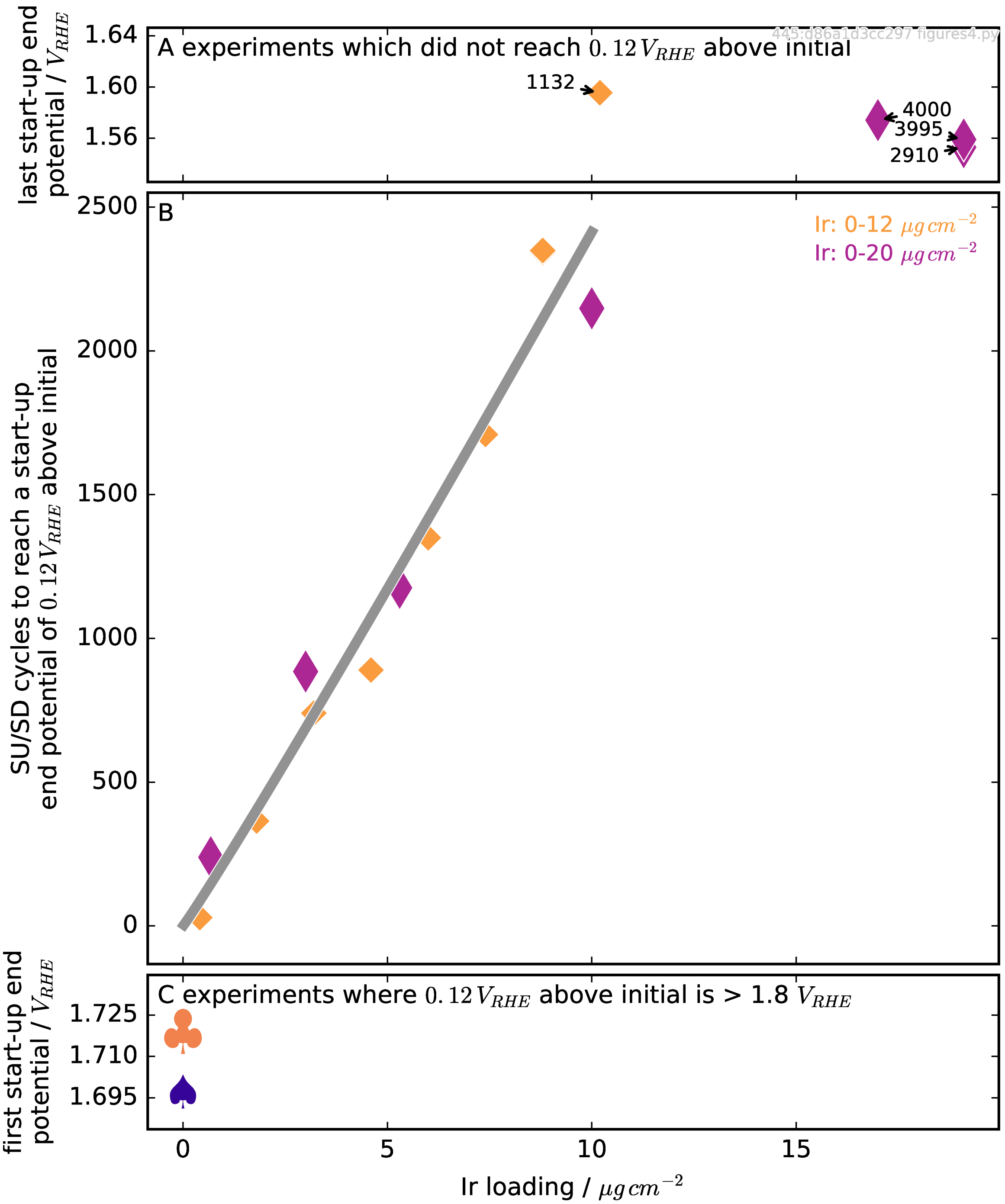


Figure 5.8: The ‘relative’ OER durability of Ir (various loadings) overlayered on Pt on NSTF. **A**: Samples which were very OER durable and did not climb 0.12 V_{RHE} above the initial start-up end-potential before the end of the experiment (each point is labelled with the total number of SU/SD cycles reached). **B**: The number of SU/SD cycles it takes for the start-up end-potential (an indicator of OER activity) to increase 0.12 V_{RHE} above the initial start-up end-potential. **C**: The initial start-up end-potential of two pure Pt samples was less than 0.12 V_{RHE} below 1.8 V_{RHE} (the highest allowable start-up end potential). A legend for the symbols can be found in Figure 5.1.

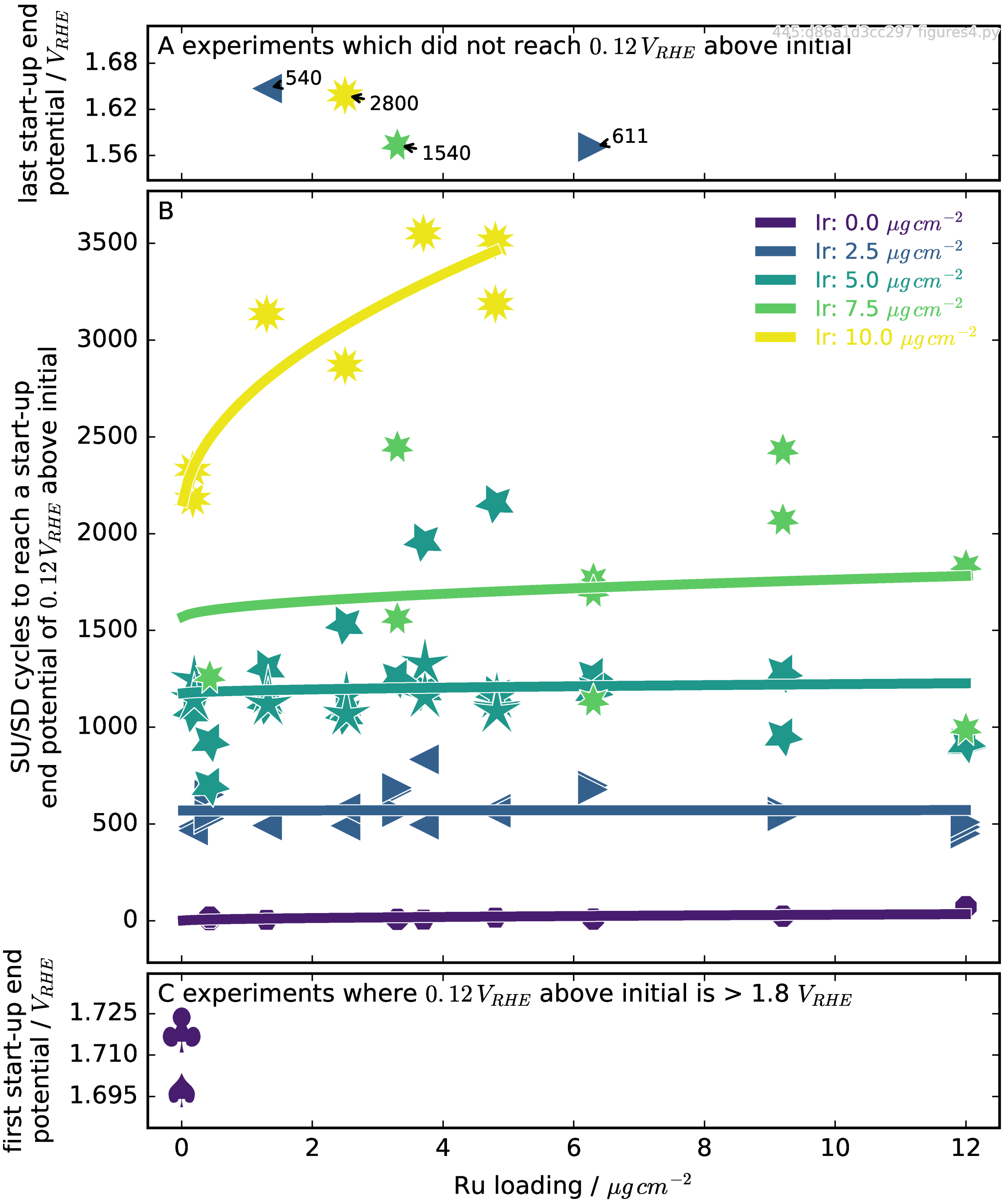


Figure 5.9: The ‘relative’ OER durability of Ru (various loadings on abscissa) overlayered on Ir (various loadings in legend) overlayered on Pt. **A**: Samples which were very OER durable and did not climb 0.12 V_{RHE} above the initial start-up end-potential before the end of the experiment (each point is labelled with the total number of SU/SD cycles reached). **B**: The number of SU/SD cycles it takes for the start-up end-potential to increase 0.12 V_{RHE} above the initial start-up end-potential. **C**: The initial start-up end-potential of two pure Pt samples was less than 0.12 V_{RHE} below 1.8 V_{RHE} (the highest allowable start-up end potential). A legend for the symbols can be found in Figure 5.1.

5.3 The Impact of Ru and Ir on ORR actvity

One of the initial questions at the beginning of this document was: “Will adding Ru and Ir compromise the catalytic activity of the Pt?”. This question was not sufficiently addressed in Chapter 4, so is addressed here. Figure 5.10A shows the maximum ORR activity for all samples tested for this study. In contrast to Chapter 4, the ORR activity for all ORR figures in this Chapter (Figures 5.10, 5.1 and 5.13) were determined with the CVs before the OER CV (the CV to 1.55 V_{RHE}). The two Pt samples clearly have the highest activity. The general trend thereafter is for activity to decrease with increasing molar coverage of OER catalyst. An exception is seen for the Ru on Pt (no Ir) samples, the activities of which are lowered compared to pure Pt, but not dependant on Ru loading. Figures in Appendix C show all ORR activities for every experiment. Figure 5.10B shows the change in ORR activity after the first 200 (usually, sometimes less) SU/SD cycles. Ru plus Ir loading/coverage (in $\mu mol\, cm^{-2}$) clearly has an influence. At coverages greater than about 4 $\mu mol\, cm^{-2}$, 200 SU/SD cycles has a restorative effect on the ORR activity, and at lower coverages, 200 SU/SD cycles decrease ORR activity, as expected. Thus the answer to the first part of the question (will adding Ru and Ir compromise the catalytic activity of the Pt) is a definite yes, but some of that lost ORR activity is restored after 200 SU/SD cycles for Ir plus Ru coverages greater than ~4 $\mu mol\, cm^{-2}$.

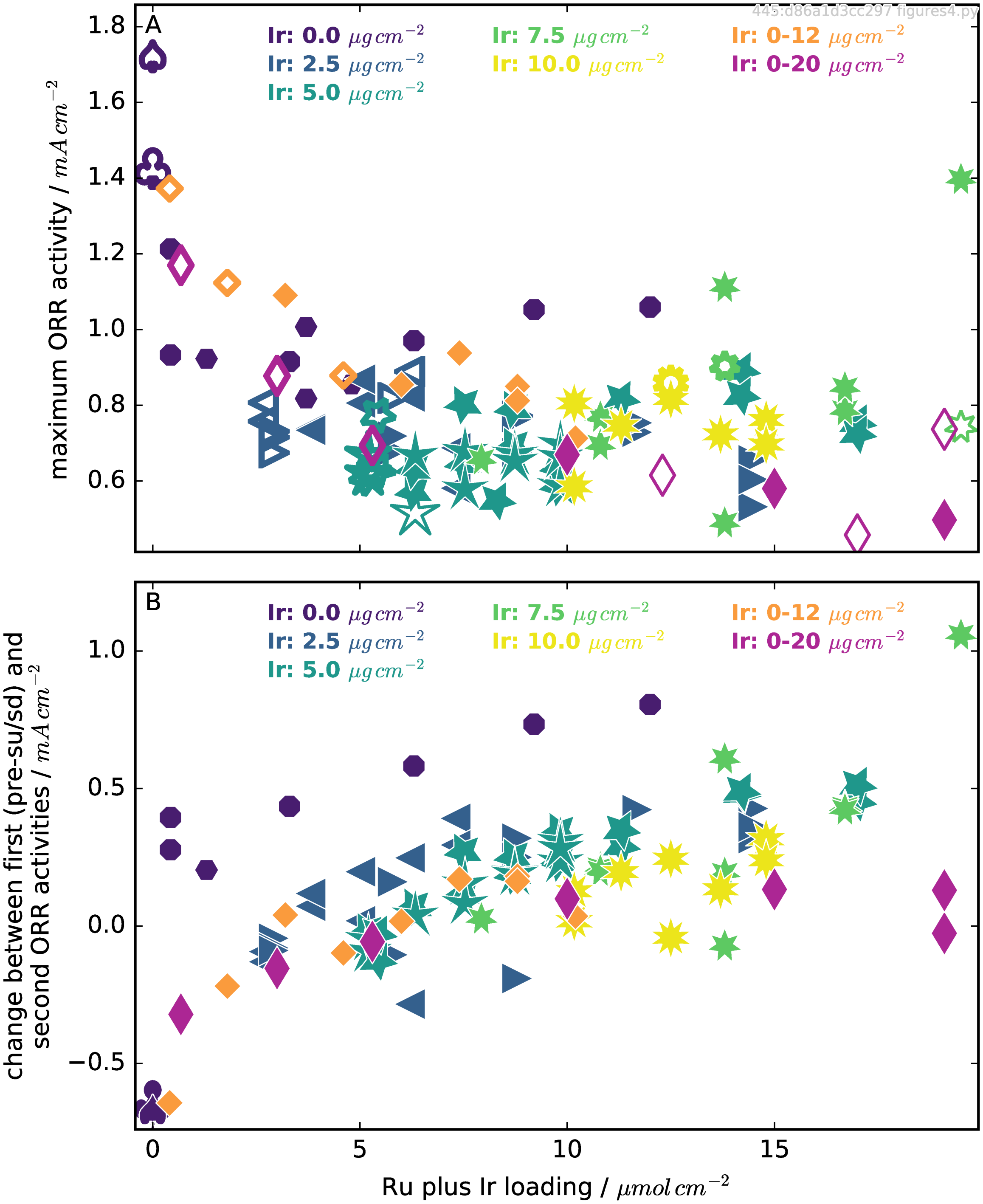


Figure 5.10: **A**: The impact of Ir plus Ru coverage on maximum ORR activity at 0.96 $mA\,cm^{-2}$ (*iR* corrected). Marker edge/fill styles indicate when the maximum occurs. Solid fill: maximum is reached after 200 SU/SD cycles (most common), thick edge: maximum occurs before any SU/SD cycles, thin edge: maximum occurs after 400 or more SU/SD cycles. **B**: Change in ORR activity at 0.96 $mA\,cm^{-2}$ (*iR* corrected) between the initial and at the first 200 SU/SD cycles.

5.4 Assessing the Durability of ORR Activity

To quantify durability for the ORR, end-points for absolute and relative lifetimes need to be defined. Both should be at a potential of 0.96 V_{RHE} to be consistent with the performance metric used in Chapter 4. For the absolute end-point, 0.4 $mA\,cm^{-2}$ is an appropriate current because most samples have an ORR activity below this current before they reach a kinetic limitation. Figure 5.11 shows the number of SU/SD cycles to reach an ORR current of 0.4 $mA\,cm^{-2}$ at 0.96 V_{RHE} for all the experiments in this study.

A kinetic limitation, or turn-over limitation of current is a phenomena which is theoretically predicted by full kinetic models (*Marshall and Vaisson-Béthune* (2015) and *Shinagawa et al.* (2015)) and was perhaps first observed by *Azzam and Bockris* (1950), who demonstrated it for hydrogen evolution on a Pt wire in a stream of rapidly flowing electrolyte. The kinetic limitation phenomena is rarely, if at all, mentioned in ORR-on-Pt literature. Figure 5.12 shows an example of a kinetic limitation emerging in O_2 CV data. At the first sign of a kinetic limitation ORR catalysis is effectively dead. Chapter 4 defined a condition for declaring zero ORR activity ("... if the ORR current at 0.86 V_{RHE} was less than 1.5 $mA\,cm^{-2}$, ORR at 0.96 V_{RHE} was declared to be zero", pg. 132). This condition was based on the emergence of a kinetic limitation in the O_2 CV. Kinetically limited CVs in this chapter were identified with a visual assessment instead of using the numerical identifier used in Chapter 4, because that identifier was not always reliable.

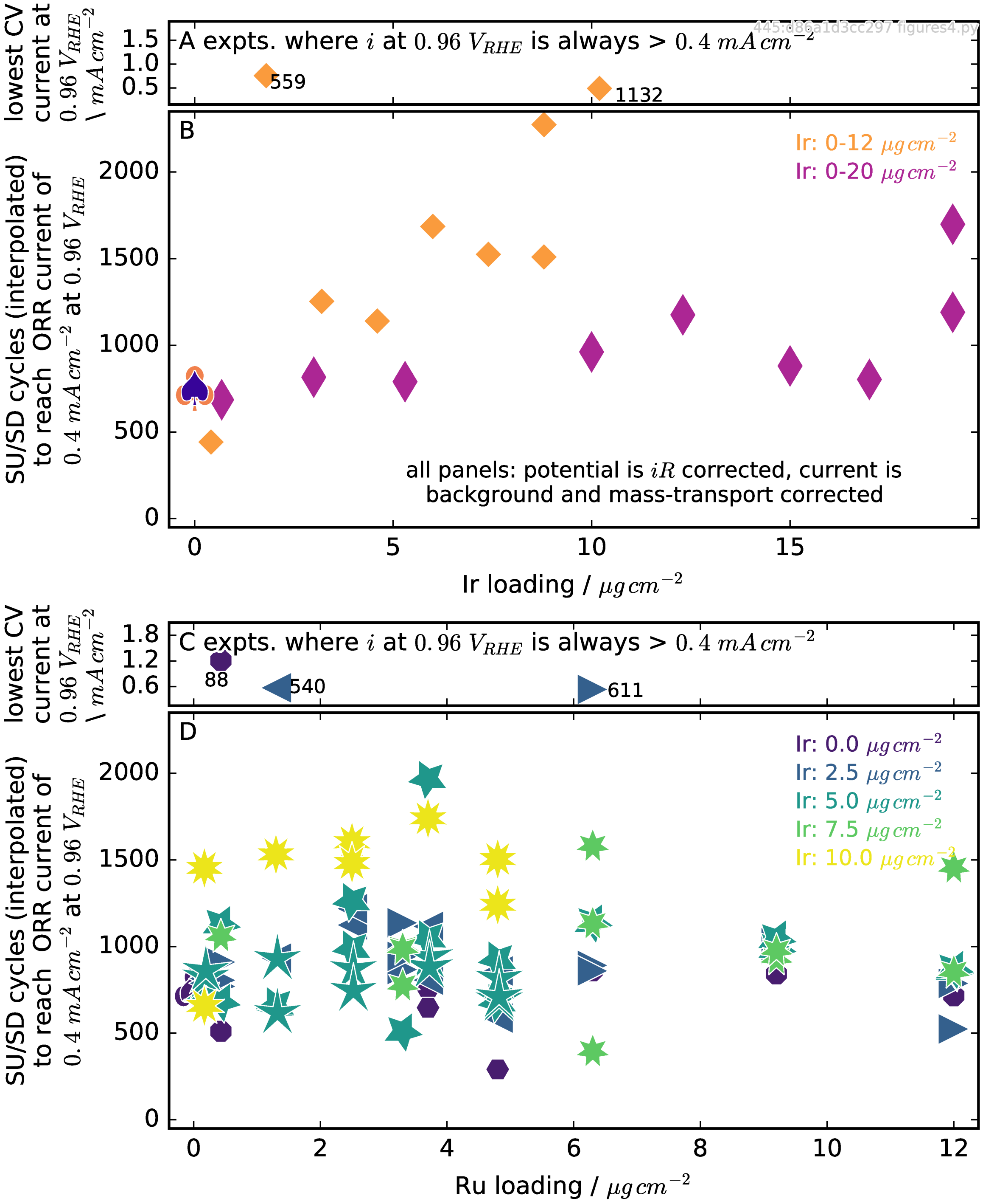


Figure 5.11: The ‘absolute’ ORR durability of **A & B**: Ir (various loadings) overlayered on Pt on NSTF and **C & D**: Ru (various loadings on abscissa) overlayered on Ir (various loadings in legend) overlayered on Pt on NSTF. ORR activity is current at 0.96 V_{RHE} (*iR* corrected). **A & C**: Samples which did not make it down to an ORR activity of 0.4 $mA\ cm^{-2}$. before the end of the experiment (each point is labelled with the total number of SU/SD cycles reached). **B & D**: The number of SU/SD cycles it takes for the ORR activity to come down to 0.4 $mA\ cm^{-2}$. A legend for the symbols can be found in Figure 5.1.

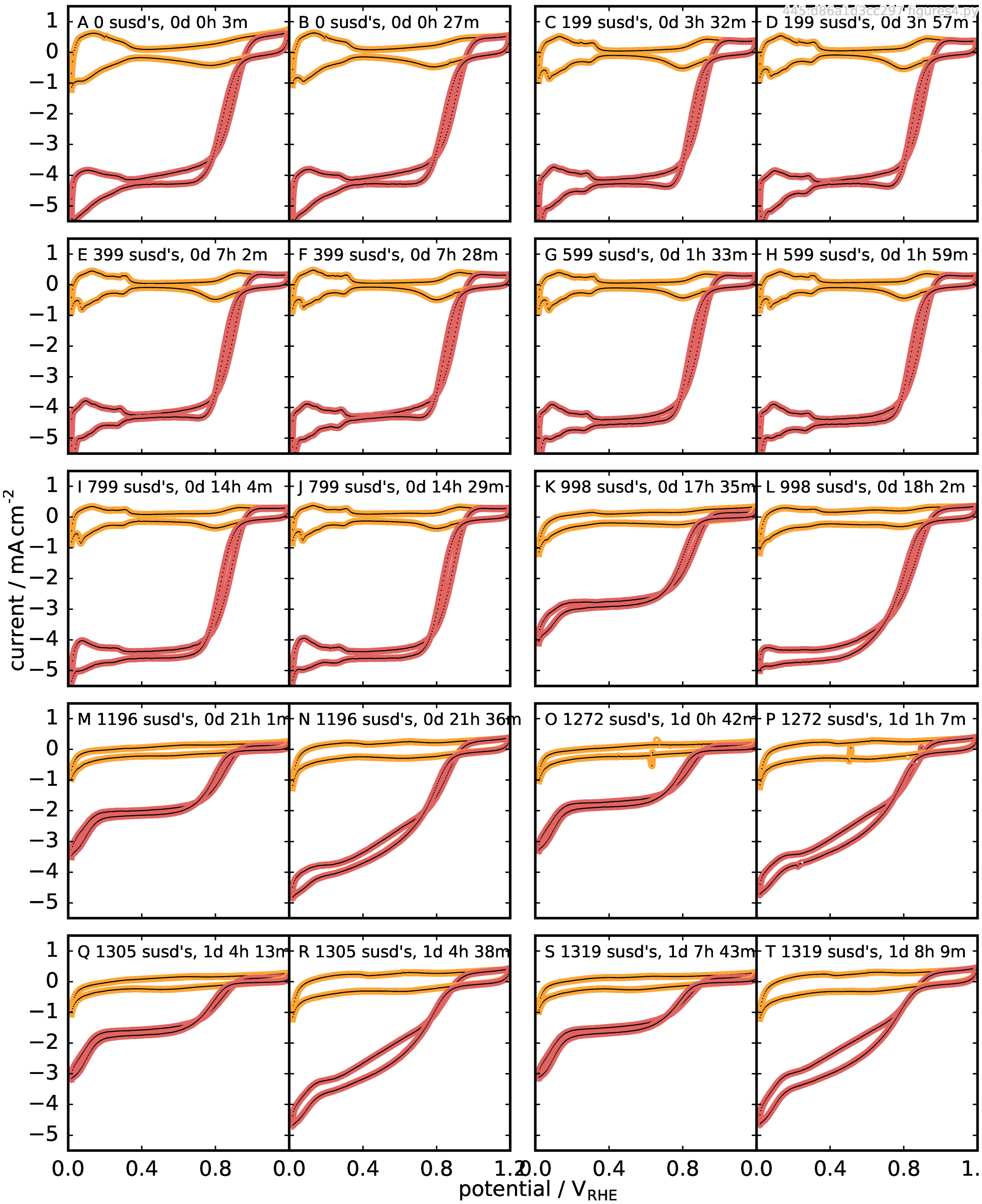


Figure 5.12: Ar (orange) and O_2 (red) CVs of an SU/SD experiment done with a sample of 2.5 $\mu g_{Ir}\,cm^{-2}$ on 0.17 $\mu g_{Ru}\,cm^{-2}$ on Pt which shows a kinetic limitation in the O_2 CVs from panel K onward. Joined panels are from the same CV characterization set.

Fuel cell durability literature typically defines durability targets as some percentage of the initial activity (which is also always the maximum activity) after a certain number catalyst, catalyst support, or membrane degrading cycles. Therefore an appropriate definition for the relative end-point activity could be half of the initial/maximum activity. For the catalysts under study, the initial and maximum are usually not the same, so the end-point must be explicitly defined as the number of cycles it takes to reach half the maximum activity. Figure 5.13 shows the number of SU/SD cycles to reach half of the maximum ORR activity for all the experiments in this study. Both Figure 5.11 and 5.13 show there seems to be no durability dependence on Ru loading. Figure 5.13 shows that increased Ir loading improves ORR durability.

Figure 5.13A shows a point at 19.1 $\mu g_{Ir}\, cm^{-2}$ that reached 3995 SU/SD cycles. This experiment is curious because the ORR activity reached a stable state, similar to the 15.3 $\mu g_{Ir}\, cm^{-2}$ and 42 $\mu g_{Ir}\, cm^{-2}$ compositions in Figure 4.9. The ORR data for this experiment can be seen in Figure C.11H. There are three other experiments in the data set for this chapter which reached a stable ORR activity. They can be seen in Figure C.11G and Figure C.9C and F. This behaviour is completely contrary to expectations for a Pt catalyst subjected to the SU/SD test protocol, and arouses a suspicion that something could be wrong. However it appeared only six times out of ~150 total SU/SD experiments conducted for the project. It is suspected to be the result of a faulty measurement technique rather than a property of the catalyst material. Work began in earnest on solving this mystery of ORR activity stability but was cut short due to the Faculty of Graduate Studies recommended PhD programme time frame. Whatever is causing this disconcerting stability may also be the cause of the wide scatter and outliers seen in all the figures in this Chapter.

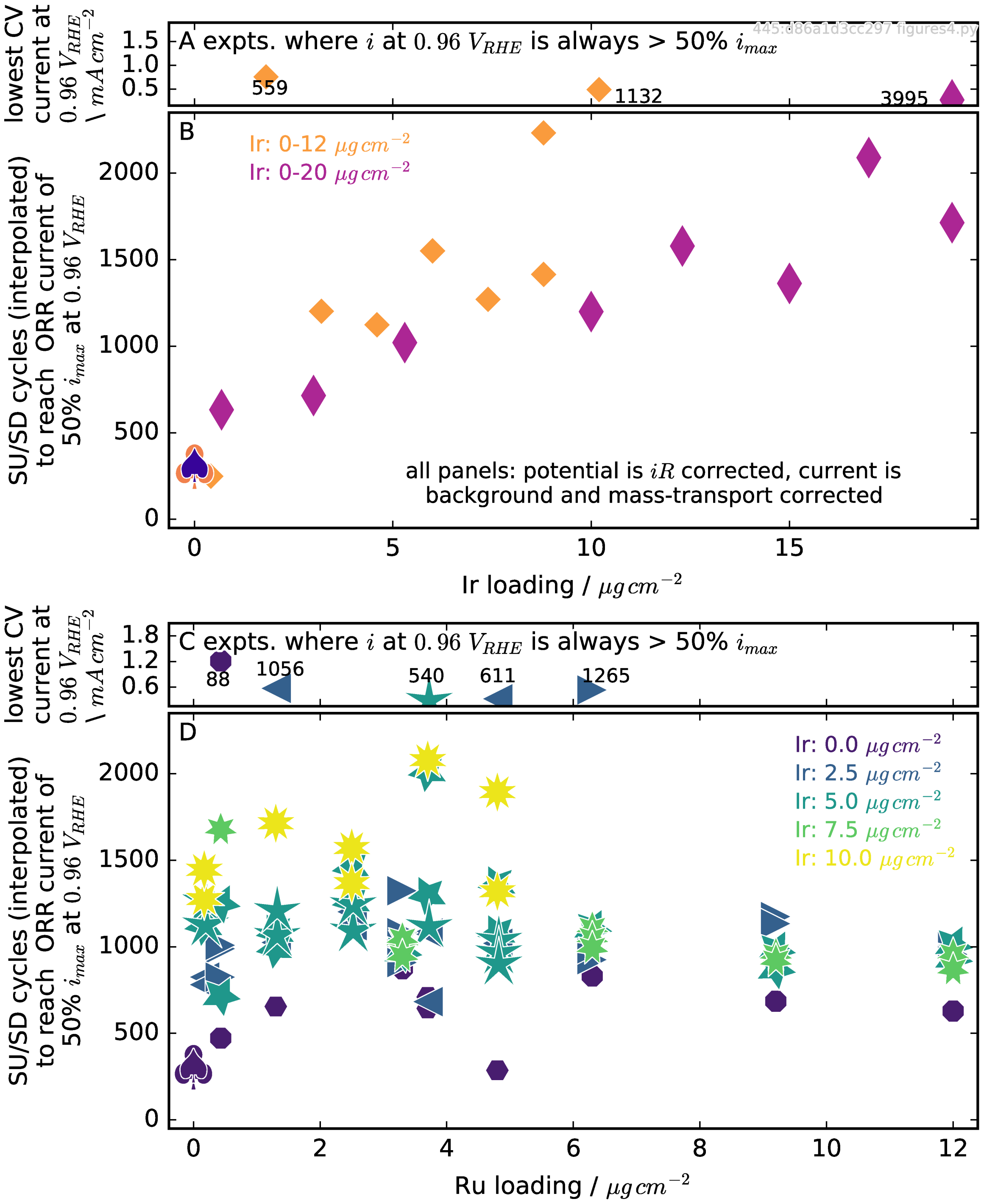


Figure 5.13: The ‘relative’ ORR durability of **A & B**: Ir (various loadings) overlayered on Pt on NSTF and **C & D**: Ru (various loadings on abscissa) overlayered on Ir (various loadings in legend) overlayered on Pt on NSTF. ORR activity is current at 0.96 V_{RHE} (*iR* corrected). **A & C**: Samples which did not make it down to an ORR activity of half the maximum before the end of the experiment (each point is labelled with the total number of SU/SD cycles reached). **B & D**: The number of SU/SD cycles it takes for the ORR activity to come down to half the maximum. A legend for the symbols can be found in Figure 5.1.

5.5 Summary

The large amount of scatter present within the data makes it difficult to make definitive conclusions regarding compositional trends. Nevertheless, the clear observations are summarized below.

- Ir loading increases OER durability (Figures 5.5, 5.6, and 5.8).
- Ru loading only improved the OER durability for the compositions containing 10 $\mu g\, cm^2$ (Figures 5.5, 5.7, and 5.9).
- Ir and Ru coverage deleteriously effects ORR activity but some of the lost activity is restored after the first 200 SU/SD cycles (Figure 5.10).
- Ir loading increases ORR durability (Figure 5.13).
- Ru loading has no influence on the ORR durability (Figures 5.11 and 5.13)

Chapter 6

Conclusion

This thesis project was part of a cooperation between Dalhousie University and 3M Company to enhance the durability of platinum based, NSTF supported, fuel cell cathode catalysts to the degrading effects of fuel cell start-up and shut-down. The durability enhancement was to be achieved by two catalytic modification strategies: 1) reducing the ORR activity of the anode catalyst, and 2) improving the OER activity of the cathode catalyst (*Atanasoski*, 2009). This thesis focused exclusively on the later strategy by adding Ir and Ru, elements known to catalyse the OER in acidic electrolyte, to the ORR-active Pt. This solution to the fuel cell durability problem is distinguished from the many systems-based approaches (e.g. gas purging, and others in *Yu et al.* (2012)) in that it is materials based, and thus “always on” (*Atanasoski et al.*, 2012). In addition, it is distinguished from other materials-based solutions in that it is focused on the catalyst, not the catalyst support or current collector materials.

The mechanism that causes degradation during fuel cell SU/SD (the RCDM) was first described, modelled, and experimentally verified by *Reiser et al.* (2005). A simpler concept for modelling the mechanism was introduced by *Sidik* (2009), who also claimed *Reiser et al.’s* (2005) model was incorrect. This simpler concept, based only on a system of Tafel equations, was used in this thesis for the first time (to the best of the author’s knowledge), to quantitatively demonstrate the effectiveness of using either, or both catalytic modification strategies to lower the potential on the fuel cell cathode in the fuel starved region during SU/SD events (Figure 2.14). Lowering the potential during SU/SD is key to lessening the damage caused to carbon current collector materials and the platinum catalyst.

6.1 Project Goals

There were three goals of this PhD Project. These goals can be construed from the questions posed at the end of the *Project Motivation* Section on pg. 1. Determining the best, or optimal sputtering deposition scheme techniques and compositions was the primary goal of this project. The work in Chapter 4 and 5 was done to achieve the primary goal, and will be summarized in the next section.

A secondary goal of the project was to characterize the behaviour of Ru and Ir supported on NSTF, and to compare that with the behaviour of Ru and Ir as flat film electrodes under similar conditions. Supplemental to this was a tertiary goal which was not anticipated at the beginning of the project, which was to learn about the durability issues associated with Ru and Ir electrodes in acid to be able to better interpret the results. The secondary goal was addressed by original research in Section 2.3.4.2. There were indeed some differences between the behaviour of Ir and Ru on NSTF compared to flat films. For Ru, the upper potentials for various stages in the development of the anodic oxides generally start sooner when supported by NSTF. For example pseudocapacitance, peaks at 1.495 V_{RHE} (1.53 V_{RHE} for flat film) and the maximum OER current occurs at 1.56 V_{RHE} (1.64 V_{RHE} for flat film). An exception is when the irreversible Ru oxide starts to grow; 1.39 V_{RHE} for flat film Ru and 1.44 V_{RHE} for Ru on NSTF. All these potantials are above the potential at which Ru becomes thermodynamically unstable (1.383 V_{RHE}). The lower potential for maximum OER current of Ru on NSTF may lead one to conclude that it is less stable than a Ru flat film. More careful experiments, or other techniques, such as using an in-line ICP-MS flow cell would be required to determine the nature of Ru stability on NSTF.

For Ir, the CVs of Ir on NSTF showed a curious shrinking prior to irreversible anodic oxidation which was probably Ir dissolution by the dynamic/transient/cathodic mechanism. Ir on NSTF also showed relatively more growth of pseudocapacitance after the complete disappearance of the H_{UPD} peaks. This could be due to either a greater ability of anodically formed Ir oxides on NSTF to gain porosity, or some remaining unconverted metallic Ir which cannot adsorb/desorb H_{UPD}, possibly because of a path of high electrical resistance to the remaining metallic Ir. This scenario is conceivable for Ir deposited on NSTF because more material deposits on the tip of an NSTF whisker, and the NSTF itself is not an electrical conductor.

The tertiary project goal (the nature of Ru and Ir instability) was addressed with a review of literature published after research for this PhD project was complete (Section 2.3.5). Ir and Ru are susceptible to two dissolution mechanisms: 1) anodic dissolution which occurs in conjunction with the OER, and 2) dynamic/transient/cathodic dissolution which occurs when Ru or Ir oxide is electrochemically reduced. The second mechanism was surprising because the analogous mechanism for dynamic Pt dissolution occurs when the Pt is reduced back to the metallic phase, and it was always thought that anodically oxidized Ru and Ir displaying pseudocapacitance cannot be reduced back to the metallic phase. Figures 2.37 and 2.40 show the nature of the instability is not simple. The mechanism responsible for most of the dissolution is strongly dependant on the upper potential (when the electrode is cycled).

6.2 The Best Deposition Scheme and Compositions for Durable Pt-Ru-Ir Catalysts

Ru is a less expensive and more active OER catalyst than Ir, but is very unstable at potentials above ~1.4 V_{RHE}, which are to be expected from the RCDM. The RDE technique was used to screen many NSTF supported Pt-Ir-Ru catalyst samples differing in deposition method and composition for the durability of their ORR activity. A consequence of using the RDE technique to assess the durability of NSTF supported fuel cell catalysts is that it will characterize only the catalyst degradation, not the degradation of the various carbonaceous materials of the fuel cell current collector, which will also have a significant impact on fuel cell performance.

The screening of two catalyst sputter deposition schemes (intermix and overlayer) and compositions for durability was accomplished with a carefully designed testing protocol (using both constant potential and constant current holds), interspersed with CVs to characterize the ORR activity. The constant current holds distinguish this protocol from all other fuel cell ASTs in the literature. A constant current hold does not fix the highest potential reached during a simulated start-up or shut-down; it is free to increase as the catalyst degrades as would occur in an actual fuel cell.

All catalyst samples were sputtered on NSTF whiskers (grown by 3M) on polished glassy carbon disks. Various amounts of Ir, or Ru, or both Ir and Ru were added to a base Pt amount of 85 $\mu g\, cm^{-2}$. The loadings were selected based on 3M's experience with NSTF fuel cells, and precious metal loading targets set by the US Department of Energy.

6.2.1 Sputtering Deposition Scheme: Overlayer vs. Intermix (Chapter 4)

While performing the work to determine the best sputtering deposition scheme (intermixed or overlayered) some other important lessons were learned and these are discussed prior to summarizing the main results.

6.2.1.1 Carbon Corrosion and Surface Area Normalization

An unexpected consequence of using the Pine-manufactured ChangeDisk electrodes for durability testing was corrosion of the glassy carbon disk electrode, which is undesirable because it will prolong the duration of the accelerated stress test. This problem was caused by electrolyte creeping between the disk electrode and the u-cup, and partially fixed by sealing this crevice with silicone grease, which did not adversely affect the ORR activity. Some amount of carbon corrosion seemed to be unavoidable, even with the application of silicone grease, because the corrosion would get under a ring of flat platinum thin film left on every sample by the NSTF growth and subsequent sputtering step.

It is common in fuel cell catalyst work to normalize activity to catalytic surface area based on the H_{UPD} desorption area. The presence of Ir and Ru creates problems for this type of surface area normalization because of an increase in H_{UPD} desorption current while there is still some metallic Ru or Ir, and pseudocapacitance in the double-layer region (especially for Ru). Determining the Pt catalytic surface area with a technique known as CO stripping is the best way to deal with this challenge (*Binninger et al.*, 2014).

6.2.1.2 Main Conclusions from Chapter 4

Ir was better at improving ORR durability than Ru. This was expected because Ru is unstable above ~1.4 V_{RHE}. However Ru containing samples were more ORR durable compared to pure Pt. Overlayer was deemed to be the best deposition technique for Ir because of a more prolonged ORR activity and higher OER activity. The higher OER activity for the overlayer samples was expected. Ru containing samples had a higher ORR activity than pure Pt.

6.2.2 Compositions: The Effect of Overlayer Ru and Ir on Durability (Chapter 5)

This study was carried out to determine 1) how the Ir loading of an Ir overlayered on Pt deposition scheme affects the ORR and OER durability, and 2) if various loadings of Ru (0 to 12 $\mu g\, cm^{-2}$) could improve the OER and ORR durability of various loadings of Ir (2.5 to 10 $\mu g\, cm^{-2}$) on Pt. Higher Ir loadings provided a clear benefit for both ORR and

OER durability. Higher Ru loadings increased the OER durability. Higher Ru loadings increased the ORR durability only when combined with 10 $\mu g\, cm^{-2}$ Ir. Compared to a pure Pt benchmark, beginning-of-test ORR activity was negatively affected by Ir plus Ru coverages. For Ir plus Ru coverages greater than $\sim$4 $\mu mol\, cm^{-2}$, ORR activity improved after the first 200 SU/SD cycles, indicating some of the ORR activity lost due to the Ir plus Ru overlayer coverage was partially restored by the SU/SD cycles.

6.3 Future Work

Recommendations for future work are split into two sections focused on proposed changes to sample synthesis and measurement techniques, and questions that remain unanswered.

6.3.1 Measurement Techniques

The following are recommendations for changes to the synthesis and measurement of catalyst samples:

- Hundreds of glassy carbon disks were prepared for NSTF coating with the intent that they would fix the problem of the strangely shaped CVs (the carbon corrosion problem). However, silicone grease turned out to be the solution to the problem. Pyrolytically coated graphite disks (much quicker to make and far less expensive) could probably be used in the future in conjunction with the silicone grease to mitigate carbon corrosion.
- The dynamic dissolution behaviour of PGMs was completely unknown at the beginning of the project. Had this been known, the experimental protocol would have been designed differently. The potential at the end of the shut-down hold (see Figure 3.15) should be swept down gradually (linearly would be fine) to the rest potential. Not only is this a more accurate imitation of reality (see Figure 3.18), it should be more aggressive (a slow down-sweep dissolves more Pt than a fast one (see Figure 2.7)), which is a good thing for an an AST.
- The ORR characterizations ought to be changed to minimize the risk of dynamic dissolution of Ir and Ru. This type of dissolution would probably never occur in a fuel cell cathode because a fuel cell usually is not operated much below 0.6 V (i.e. the potential on the cathode stays above 0.6 V_{RHE}). Based on Figure 2.36, the

onset potential for Ir dissolution is about 0.5 V_{RHE} and based on Figure 2.40, the onset potential for Ru dissolution is about 0.3 V_{RHE} for Ru. Keeping the potential above these values during the ORR characterization is possible, but excludes the possibility of using the H_{UPD} desorption area for Pt surface area normalization. This lends further support for applying *Binninger et al.'s* (2014) CO stripping technique.

- Noisy data caused problems with the analysis. Electrical noise should be fixed at the source, not after the fact. Placing the RDE in a Faraday cage is recommended.
- A potentiostat with automatic *iR* compensation capabilities is highly recommended. A potentiostat with a capability to auto-range the current is also highly recommended. The Pine AFCBP1 potentiostat possessed neither of these features.

6.3.2 Remaining Problems and Questions

There was a remarkable ORR stability in some experiments in both Chapter 4 and 5 (described on pgs. 142 and 187). ORR activity should not stabilize because Pt should not be stable under the conditions of the accelerated stress test. The cause of this ORR stability should be identified before any further catalyst durability studies are performed. This cause of the ORR stability may also be prolonging the duration of other experiments which do not exhibit the stabilized ORR.

Figure 4.21 showed ORR activity declines even when there were no SU/SD simulations. This was suspected to be due to contamination from the air entering the electrolyte, and due to the Pt degrading effect of the ORR and OER characterization CVs. Needless to say, the ORR activity decline due to either of these two causes should be minimized.

A question posed in *Project Motivation* but never addressed in this thesis was: "What are the best sputtering conditions for Ru and Ir on NSTF?" Sputtering conditions like pressure, target power, or table temperature probably do not have a large influence. Rather, this question had a view toward a synthesis technique known as reactive sputtering, where the material ejected from the target reacts with the sputtering gas. This is usually done to create nitrides and oxides. Therefore a more focused version of the question would be: Should Ru and Ir be sputtered as metals, or as oxides via reactive sputtering? In other words, how does the as-synthesized phase affect electrochemical activity and durability? This question is similar to a question asked on pg. 81: "What is the influence of various pre-oxidizing methods (i.e. thermal, reactive sputtering, etc.) on dissolution behaviour?" It is also somewhat similar to the question which immediately follows ("What is the relationship between anodically oxidized Ir stoichiometry and activity?") because oxide stoichiometry of reactively stuttered metals can be controlled with the oxygen partial pressure in the sputtering chamber.

For Ir plus Ru coverages greater than ~4 $\mu mol\,cm^{-2}$, ORR activity lost due to coverage was partially restored after the first 200 SU/SD cycles. If this restoration effect was due to the high potentials of the SU/SD cycles, perhaps a quicker, more effective electrochemical pretreatment could be designed to maximize ORR activity as soon an possible.

Finally, why does silicone grease not decrease the ORR activity of Pt? Recall that silicone grease even seemed to have a minor benefit for ORR durability. Perhaps it could be investigated as an additive for fuel cell electrodes.

6.4 The Big Picture

It is prudent to ask if the work should even be continued at all due to the following points:

- The need for a more durable NSTF based catalyst is questionable when so little is known about the actual performance of NSTF in fuel cell vehicles.
- The fuel cell community will probably abandon NSTF for vehicle applications. In 2015, an annual USDOE cost analysis for a state-of-the-art fuel cell system dropped 3M's "best-in-class" NSTF supported catalyst in favour of a Johnson Matthey Pt\C material using $PtNi_3$ as the catalyst
- The need for an electric vehicular drive train powered by a hydrogen fuel cell stack is in jeopardy due to the ongoing rapid commercial success of Li-ion battery powered all-electric cars.

These concerns ought to be seriously considered before making research on the durability of NSTF fuel cell catalyst materials a priority. However, even if never used in automotive applications, all hope is not lost for Pt, Ru, and Ir catalyst materials supported by NSTF; they could have application in perfluorosulfonic acid (PFSA) electrolyzers and as bi-functional catalysts in regenerative fuel cells.

References

Adzic, R. R., J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio, and F. Uribe, Platinum Monolayer Fuel Cell Electrocatalysts, *Topics in Catalysis*, *46*, 249–262, 2007.

Amend, J., GM Says FCEVs Developing Too Quickly for Production Engines content from WardsAuto, `http://wardsauto.com/engines/gm-says-fcevs-developing-too-quickly-production` (Accessed: 2016-03-15), 2016.

Antolini, E., Carbon supports for low-temperature fuel cell catalysts, *Applied Catalysis B: Environmental*, *88*, 1–24, 2009.

Atanasoski, R., Durable Catalysts for Fuel Cell Protection during Transient Conditions (Topic 1c), Kickoff meeting for new DOE Fuel Cell projects from solicitation DE - PS36 - 08GO98009 and lab call DE - PS36 - 08GO98010, `http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/atanasoski_kickoff.pdf` (Accessed: 2016-02-26), 2009.

Atanasoski, R., D. van der Vliet, D. Cullen, and L. Atanasoska, Final Report - Durable Catalysts for Fuel Cell Protection During Transient Conditions, *Tech. Rep. DOE-3M-0000456-1*, 3M Company, 2015.

Atanasoski, R. T., L. L. Atanasoska, D. A. Cullen, G. M. Haugen, K. L. More, and G. D. Vernstrom, Fuel Cells Catalyst for Start-Up and Shutdown Conditions: Electrochemical, XPS, and STEM Evaluation of Sputter-Deposited Ru, Ir, and Ti on Pt-Coated Nanostructured Thin Film Supports, *Electrocatalysis*, *3*, 284–297, 2012.

Atanasoski, R. T., D. A. Cullen, G. D. Vernstrom, G. M. Haugen, and L. L. Atanasoska, A Materials-Based Mitigation Strategy for SU/SD in PEM Fuel Cells: Properties and Performance-Specific Testing of IrRu OER Catalysts, *ECS Electrochemistry Letters*, *2*, F25–F28, 2013.

Azzam, A. M., and J. O. Bockris, Cathodic Evolution of Hydrogen at Very High Current Densities, *Nature*, *165*, 403–404, 1950.

Bacon, F. T., Research into the Properties of the Hydrogen-Oxygen Cell, *Tech. Rep. no. Z/T 94*, British Electrical and Allied Industries Research Association, 1953.

Barbir, F., Chapter 3 - 3. Fuel Cell Electrochemistry, in *PEM Fuel Cells*, edited by F. Barbir, pp. 33–72, Academic Press, Burlington, 2005.

Bard, A. J., and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, 2000.

Bard, A. J., M. Stratmann, and G. S. Frankel, *Encyclopedia of Electrochemistry, Corrosion and Oxide Films*, Wiley, 2003.

Barkhouse, D. A. R., A. Bonakdarpour, M. Fleischauer, T. D. Hatchard, and J. R. Dahn, A combinatorial sputtering method to prepare a wide range of A/B artificial superlattice structures on a single substrate, *Journal of Magnetism and Magnetic Materials*, *261*, 399–409, 2003.

Beck, W. H., J. V. Dobson, and W. F. K. Wynne-Jones, The potentials of the mercurous sulphate/mercury electrode, *Transactions of the Faraday Society*, *56*, 1172, 1960.

Beer, H. B., The Invention and Industrial Development of Metal Anodes, *Journal of The Electrochemical Society*, *127*, 303C–307C, 1980.

Belanger, G., and A. K. Vijh, Anodic oxides on noble metals, in *Oxides and Oxide Films*, vol. 5 of *Anodic behavior of metals and semiconductors series*, M. Dekker, New York, 1977.

Benke, G., and W. Gnot, The electrochemical dissolution of platinum, *Hydrometallurgy*, *64*, 205–218, 2002.

Bett, J., K. Kinoshita, K. Routsis, and P. Stonehart, A comparison of gas-phase and electrochemical measurements for chemisorbed carbon monoxide and hydrogen on platinum crystallites, *Journal of Catalysis*, *29*, 160–168, 1973.

Binninger, T., E. Fabbri, R. Kötz, and T. J. Schmidt, Iridium-Titanium Oxide as Support for Pt Catalyst in PEFC Cathodes, *ECS Transactions*, *58*, 1835–1841, 2013.

Binninger, T., E. Fabbri, R. Kötz, and T. J. Schmidt, Determination of the Electrochemically Active Surface Area of Metal-Oxide Supported Platinum Catalyst, *Journal of The Electrochemical Society*, *161*, H121–H128, 2014.

Bock, C., A. Smith, and B. MacDougall, Anodic oxidation of oxalic acid using WO_x based anodes, *Electrochimica Acta*, *48*, 57–67, 2002.

Bockris, J. O., Kinetics of Activation Controlled Consecutive Electrochemical Reactions: Anodic Evolution of Oxygen, *The Journal of Chemical Physics*, *24*, 817–827, 1956.

Bockris, J. O., The Founding of the International Society for Electrochemistry, *Electrochimica Acta*, *36*, 1–4, 1991.

Bockris, J. O., and Z. Nagy, Symmetry factor and transfer coefficient. A source of confusion in electrode kinetics, *Journal of Chemical Education*, *50*, 839, 1973.

Boeriu, H., BMW plans fuel-cell sedan after 2020, `http://www.bmwblog.com/2015/10/29/report-bmw-plans-fuel-cell-sedan-after-2020/` (Accessed: 2015-12-10), 2015.

Bonakdarpour, A., A combinatorial study of platinum-based oxygen reduction electrocatalysts for hydrogen fuel cells, Ph.d., Dalhousie University (Canada), Canada, 2007.

Bonakdarpour, A., K. C. Hewitt, T. D. Hatchard, M. D. Fleischauer, and J. R. Dahn, Combinatorial synthesis and rapid characterization of $Mo_{1-x}Sn_x$ ($0 \leq x \leq 1$) thin films, *Thin Solid Films*, *440*, 11–18, 2003.

Bonakdarpour, A., R. Lobel, S. Sheng, T. L. Monchesky, and J. R. Dahn, Acid Stability and Oxygen Reduction Activity of Magnetron-Sputtered Pt[sub 1 - x]Ta[sub x] (0 <= x <= 1) Films, *Journal of The Electrochemical Society*, *153*, A2304–A2313, 2006.

Bratsch, S. G., Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K, *Journal of Physical and Chemical Reference Data*, *18*, 1–21, 1989.

Breitwieser, M., M. Klingele, B. Britton, S. Holdcroft, R. Zengerle, and S. Thiele, Improved Pt-utilization efficiency of low Pt-loading PEM fuel cell electrodes using direct membrane deposition, *Electrochemistry Communications*, *60*, 168–171, 2015.

Brett, C. M. A., and A. M. O. Brett, Hydronamic Electrodes (Chapter 8), in *Electrochemistry: Principles, Methods, and Applications*, Oxford University Press, Oxford ; New York, 1993a.

Brett, C. M. A., and A. M. O. Brett, Mass Transport (Chapter 5), in *Electrochemistry: Principles, Methods, and Applications*, Oxford University Press, Oxford ; New York, 1993b.

Buckley, D. N., and L. D. Burke, The oxygen electrode. Part 5.—Enhancement of charge capacity of an iridium surface in the anodic region, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, *71*, 1447–1459, 1975.

Buckley, D. N., and L. D. Burke, The oxygen electrode. Part 6.—Oxygen evolution and corrosion at iridium anodes, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, *72*, 2431–2440, 1976.

Burke, L. D., Oxide growth and oxygen evolution on noble metals, in *Electrodes of Conductive Metal Oxides, Part A*, Studies in Physical and Theoretical Chemistry, pp. 141–181, Elsevier Scientific Publishing Co., 1980.

Burke, L. D., and M. E. G. Lyons, Electrochemistry of Hydrous Oxide Films, in *Modern Aspects of Electrochemistry*, edited by R. E. White, J. O. Bockris, and B. E. Conway, no. 18 in Modern Aspects of Electrochemistry, pp. 169–248, Springer US, 1986.

Burke, L. D., and J. K. Mulcahy, The formation and reduction of anodic films on electrodeposited ruthenium, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *73*, 207–218, 1976.

Burke, L. D., and T. O. O'Meara, Oxygen electrode reaction. Part 2.—Behaviour at ruthenium black electrodes, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, *68*, 839–848, 1972.

Burke, L. D., and E. J. M. O'Sullivan, Selective oxide growth at a rhodium-platinum alloy under potential cycling conditions in base, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *112*, 247–252, 1980.

Burke, L. D., and E. J. M. O'Sullivan, Oxygen gas evolution on hydrous oxides — An example of three-dimensional electrocatalysis?, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *117*, 155–160, 1981.

Cao, M., D. Wu, and R. Cao, Recent Advances in the Stabilization of Platinum Electrocatalysts for Fuel-Cell Reactions, *ChemCatChem*, *6*, 26–45, 2014.

Cardarelli, F., Miscellaneous Electrical Materials, in *Materials Handbook*, 2nd ed., pp. 543–591, Springer London, 2008.

Chen, C., Y. Kang, Z. Huo, Z. Zhu, W. Huang, H. L. Xin, J. D. Snyder, D. Li, J. A. Herron, M. Mavrikakis, M. Chi, K. L. More, Y. Li, N. M. Markovic, G. A. Somorjai, P. Yang, and V. R. Stamenkovic, Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces, *Science*, *343*, 1339–1343, 2014.

Chen, E., History, in *Fuel Cell Technology Handbook*, Handbook Series for Mechanical Engineering, CRC Press, 2002.

Chen, G., D. A. Delafuente, S. Sarangapani, and T. E. Mallouk, Combinatorial discovery of bifunctional oxygen reduction – water oxidation electrocatalysts for regenerative fuel cells, *Catalysis Today*, *67*, 341–355, 2001.

Cheng, J., H. Zhang, G. Chen, and Y. Zhang, Study of $Ir_xRu_{1-x}O_2$ oxides as anodic electrocatalysts for solid polymer electrolyte water electrolysis, *Electrochimica Acta*, *54*, 6250–6256, 2009.

Cherevko, S., A. R. Zeradjanin, A. A. Topalov, N. Kulyk, I. Katsounaros, and K. J. J. Mayrhofer, Dissolution of Noble Metals during Oxygen Evolution in Acidic Media, *ChemCatChem*, *6*, 2219–2223, 2014.

Cherevko, S., S. Geiger, O. Kasian, A. Mingers, and K. J. J. Mayrhofer, Oxygen evolution activity and stability of iridium in acidic media. Part 1. – Metallic iridium, *Journal of Electroanalytical Chemistry*, *773*, 69–78, 2016a.

Cherevko, S., S. Geiger, O. Kasian, A. Mingers, and K. J. J. Mayrhofer, Oxygen evolution activity and stability of iridium in acidic media. Part 2. – Electrochemically grown hydrous iridium oxide, *Journal of Electroanalytical Chemistry*, *774*, 102–110, 2016b.

Cherevko, S., G. P. Keeley, N. Kulyk, and K. J. J. Mayrhofer, Pt Sub-Monolayer on Au: System Stability and Insights into Platinum Electrochemical Dissolution, *Journal of The Electrochemical Society*, *163*, H228–H233, 2016c.

Cherevko, S., N. Kulyk, and K. J. Mayrhofer, Durability of platinum-based fuel cell electrocatalysts: Dissolution of bulk and nanoscale platinum, *Nano Energy*, *29*, 275–298, 2016d.

Cherevko, S., S. Geiger, O. Kasian, N. Kulyk, J.-P. Grote, A. Savan, B. R. Shrestha, S. Merzlikin, B. Breitbach, A. Ludwig, and K. J. J. Mayrhofer, Oxygen and hydrogen evolution reactions on Ru, RuO_2, Ir, and IrO_2 thin film electrodes in acidic and alkaline electrolytes: A comparative study on activity and stability, *Catalysis Today*, *262*, 170–180, 2016e.

Chevrier, V., and J. R. Dahn, Production and visualization of quaternary combinatorial thin films, *Measurement Science and Technology*, *17*, 1399, 2006.

Chevrier, V. L., Production, characterization and visualization of quaternary combinatorial thin films, M.sc., Dalhousie University (Canada), Ann Arbor, 2006.

Choi, K.-S., E. McFarland, and G. Stucky, Electrocatalytic Properties of Thin Mesoporous Platinum Films Synthesized Utilizing Potential-Controlled Surfactant Assembly, *Advanced Materials*, *15*, 2018–2021, 2003.

Conway, B., Electrochemical oxide film formation at noble metals as a surface-chemical process, *Progress in Surface Science*, *49*, 331–452, 1995.

Conway, B. E., V. Birss, and J. Wojtowicz, The role and utilization of pseudocapacitance for energy storage by supercapacitors, *Journal of Power Sources*, *66*, 1–14, 1997.

Cordfunke, E. H. P., and G. Meyer, The system iridium - oxygen I. Measurements on the volatile oxide of iridium, *Recueil des Travaux Chimiques des Pays-Bas*, *81*, 495–504, 1962.

Cowley, A., Johnson Matthey Platinum 2013 Interim Review, `http://www.platinum.matthey.com/services/market-research/market-review-archive/platinum-2013-interim-review` (Accessed: 2015-12-09), 2013.

Crowtz, T. C., D. A. Stevens, R. J. Sanderson, J. E. Harlow, G. D. Vernstrom, L. L. Atanasoska, G. M. Haugen, R. T. Atanasoski, and J. R. Dahn, The Effect of Ru or Ir Addition on Nano-Structured-Thin-Film Supported Pt Fuel Cell Catalysts under Rotating Disk Electrode Simulated Start-up Shut-down, *Journal of The Electrochemical Society*, *161*, F961–F968, 2014.

Cullen, D. A., K. L. More, K. S. Reeves, G. D. Vernstrom, L. L. Atanasoska, G. M. Haugen, and R. Atanasoski, Characterization of Durable Nanostructured Thin Film Catalysts Tested under Transient Conditions Using Analytical Aberration-Corrected Electron Microscopy, *ECS Transactions*, *41*, 1099–1103, 2011.

Cullen, D. A., K. L. More, L. L. Atanasoska, and R. T. Atanasoski, Impact of IrRu oxygen evolution reaction catalysts on Pt nanostructured thin films under start-up/shutdown cycling, *Journal of Power Sources*, *269*, 671–681, 2014.

Dahn, J. R., S. Trussler, T. D. Hatchard, A. Bonakdarpour, J. R. Mueller-Neuhaus, K. C. Hewitt, and M. Fleischauer, Economical Sputtering System To Produce Large-Size Composition-Spread Libraries Having Linear and Orthogonal Stoichiometry Variations, *Chemistry of Materials*, *14*, 3519–3523, 2002.

Damjanovic, A., A. Dey, and J. O. Bockris, Electrode Kinetics of Oxygen Evolution and Dissolution on Rh, Ir, and Pt-Rh Alloy Electrodes, *Journal of The Electrochemical Society*, *113*, 739–746, 1966.

Danilovic, N., R. Subbaraman, K. C. Chang, S. H. Chang, Y. Kang, J. Snyder, A. P. Paulikas, D. Strmcnik, Y. T. Kim, D. Myers, V. R. Stamenkovic, and N. M. Markovic, Using Surface Segregation To Design Stable Ru-Ir Oxides for the Oxygen Evolution Reaction in Acidic Environments, *Angewandte Chemie*, *126*, 14240–14245, 2014.

de Grotthius, C. I. T., Memoir upon the decomposition of water, and of the bodies which it holds in solution, by means of galvanic electricity, *Philosophical Magazine Series 1*, *25*, 330–339, 1806.

de Levie, R., What's in a Name?, *Journal of Chemical Education*, *77*, 610, 2000.

Debe, M. K., Article having surface layer of uniformly oriented, crystalline, organic microstructures, United States, *Patent US4812352 A*, 1989.

Debe, M. K., Novel catalysts, catalysts support and catalysts coated membrane methods, in *Handbook of Fuel Cells*, John Wiley & Sons, Ltd, 2003.

Debe, M. K., Electrocatalyst approaches and challenges for automotive fuel cells, *Nature*, *486*, 43–51, 2012.

Debe, M. K., Tutorial on the Fundamental Characteristics and Practical Properties of Nanostructured Thin Film (NSTF) Catalysts, *Journal of The Electrochemical Society*, *160*, F522–F534, 2013.

Debe, M. K., and A. R. Drube, Structural characteristics of a uniquely nanostructured organic thin film, *Journal of Vacuum Science & Technology B*, *13*, 1236–1241, 1995.

Debe, M. K., and R. J. Poirier, Postdeposition growth of a uniquely nanostructured organic film by vacuum annealing, *Journal of Vacuum Science & Technology A*, *12*, 2017–2022, 1994.

Debe, M. K., A. Schmoeckel, S. Hendricks, G. Vernstrom, G. Haugen, and R. Atanasoski, Durability Aspects of Nanostructured Thin Film Catalysts for PEM Fuel Cells, *ECS Transactions*, *1*, 51–66, 2006.

Delahay, P., and C. W. Tobias, *Advances in Electrochemistry and Electrochemical Engineering*, Wiley, 1963.

Dokoutchaev, A. G., F. Abdelrazzaq, M. E. Thompson, J. Willson, C. Chang, and A. Bocarsly, Multicomponent Electrodes for Water Oxidation: From Combinatorial to Individual Electrode Study, *Chemistry of Materials*, *14*, 3343–3348, 2002.

Dross, R., and B. Maynard, In-Situ Reference Electrode Testing for Cathode Carbon Corrosion, *ECS Transactions*, *11*, 1059–1068, 2007.

Durst, J., A. Orfanidi, P. J. Rheinländer, F. Hasché, C. Eickes, P. Suchsland, M. Binder, and H. A. Gasteiger, Selective Hydrogen Oxidation Catalyst for Reduced Startup/Shutdown Degradation in Low Temperature Fuel Cells, *ECS Transactions*, *69*, 67–76, 2015.

El Kadiri, F., R. Faure, and R. Durand, Electrochemical reduction of molecular oxygen on platinum single crystals, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *301*, 177–188, 1991.

Engstrom, R. C., and V. A. Strasser, Characterization of electrochemically pretreated glassy carbon electrodes, *Analytical Chemistry*, *56*, 136–141, 1984.

Evans, J. F., T. Kuwana, M. T. Henne, and G. P. Royer, Electrocatalysis of solution species using modified electrodes, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *80*, 409–416, 1977.

Fabbri, E., A. Habereder, K. Waltar, R. Kötz, and T. J. Schmidt, Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction, *Catalysis Science & Technology*, *4*, 3800–3821, 2014.

Ferreira, P. J., G. J. la O', Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, and H. A. Gasteiger, Instability of Pt/C Electrocatalysts in Proton Exchange Membrane Fuel Cells A Mechanistic Investigation, *Journal of The Electrochemical Society*, *152*, A2256–A2271, 2005.

Fournier, J., G. Faubert, J. Y. Tilquin, R. Côté, D. Guay, and J. P. Dodelet, High-Performance, Low Pt Content Catalysts for the Electroreduction of Oxygen in Polymer-Electrolyte Fuel Cells, *Journal of The Electrochemical Society*, *144*, 145–154, 1997.

Gabe, D. R., Oxide films on anodes during electrodeposition, in *Oxides and Oxide Films*, vol. 6 of *Anodic behavior of metals and semiconductors series*, pp. 147–250, M. Dekker, New York, 1981.

Garsany, Y., O. A. Baturina, K. E. Swider-Lyons, and S. S. Kocha, Experimental Methods for Quantifying the Activity of Platinum Electrocatalysts for the Oxygen Reduction Reaction, *Analytical Chemistry*, *82*, 6321–6328, 2010.

Garsany, Y., I. L. Singer, and K. E. Swider-Lyons, Impact of film drying procedures on RDE characterization of Pt/VC electrocatalysts, *Journal of Electroanalytical Chemistry*, *662*, 396–406, 2011.

Gasteiger, H. A., W. Gu, R. Makharia, M. F. Mathias, and B. Sompalli, Beginning-of-life MEA performance — efficiency loss contributions, in *Handbook of Fuel Cells: Fundamentals, Technology, Applications*, edited by W. Vielstich, A. Lamm, and H. A. Gasteiger, vol. Volume 3, 1st edition ed., Wiley, Chichester, England ; Hoboken, N.J, 2003.

Gasteiger, H. A., S. S. Kocha, B. Sompalli, and F. T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, *Applied Catalysis B: Environmental*, *56*, 9–35, 2005.

Genorio, B., D. Strmcnik, R. Subbaraman, D. Tripkovic, G. Karapetrov, V. R. Stamenkovic, S. Pejovnik, and N. M. Marković, Selective catalysts for the hydrogen oxidation and oxygen reduction reactions by patterning of platinum with calix[4]arene molecules, *Nat Mater*, *9*, 998–1003, 2010.

Gewirth, A. A., and M. S. Thorum, Electroreduction of Dioxygen for Fuel-Cell Applications: Materials and Challenges, *Inorganic Chemistry*, *49*, 3557–3566, 2010.

Godwin, I. J., R. L. Doyle, and M. E. G. Lyons, The Mechanism of Oxygen Reactions at Porous Oxide Electrodes III. Water Oxidation Catalysis at RuO_2/NiO Mixed Oxide Electrodes, *Journal of The Electrochemical Society*, *161*, F906–F917, 2014.

Gostick, J. T., M. A. Ioannidis, M. W. Fowler, and M. D. Pritzker, On the role of the microporous layer in PEMFC operation, *Electrochemistry Communications*, *11*, 576–579, 2009.

Gröger, O., H. A. Gasteiger, and J.-P. Suchsland, Review Electromobility: Batteries or Fuel Cells?, *Journal of The Electrochemical Society*, *162*, A2605–A2622, 2015.

Grove, W. E. M. F., On a gaseous voltaic battery (LXXII), *Philosophical Magazine Series 3*, *21*, 417–420, 1842.

Guerrini, E., and S. Trasatti, Electrocatalysis in Water Electrolysis, in *Catalysis for Sustainable Energy Production*, edited by P. Barbaro and C. Bianchini, pp. 235–269, Wiley-VCH Verlag GmbH & Co. KGaA, 2009.

Hadzi-Jordanov, S., H. Angerstein-Kozlowska, M. Vukovic, and B. E. Conway, Reversibility and Growth Behavior of Surface Oxide Films at Ruthenium Electrodes, *Journal of The Electrochemical Society*, *125*, 1471–1480, 1978.

Hadzi Jordanov, S., P. Paunovic, A. Dimitrov, D. Slavkov, and O. Popovski, Electrocatalysts in the last 30 years–from precious metals to cheaper but sophisticated complex systems, *Bulletin of the Chemists and Technologists of Macedonia*, *23*, 101–112, 2004.

Hale, A. J., *The Manufacture of Chemicals by Electrolysis*, D. Van Nostrand Co., New York, 1919.

Harlow, J. E., D. A. Stevens, R. J. Sanderson, C. W. Watson, T. C. Crowtz, J. R. Dahn, G. M. Haugen, L. L. Atanasoska, G. D. Vernstrom, and R. T. Atanasoski, Durable, OER-Active Compositions of Pt, Ir, and Ru for PEM Fuel Cell Start-Stop Protection, *ECS Transactions*, *50*, 1575–1582, 2013.

Hatchard, T., J. Harlow, D. Stevens, G. C.-K. Liu, R. Sanderson, N. van der Bosch, J. Dahn, G. Haugen, G. Vernstrom, and R. Atanasoski, Rapid rotating-disk-electrode evaluation of catalyst performance and durability during transient conditions: The Pt–Hf binary system, *Electrochimica Acta*, *56*, 10436–10442, 2011.

Hatchard, T. D., J. R. Dahn, S. Trussler, M. Fleischauer, A. Bonakdarpour, J. R. Mueller-Neuhaus, and K. C. Hewitt, The amorphous range in sputtered Si–Al–Sn films, *Thin Solid Films*, *443*, 144–150, 2003.

Healy, J., C. Hayden, T. Xie, K. Olson, R. Waldo, M. Brundage, H. Gasteiger, and J. Abbott, Aspects of the Chemical Degradation of PFSA Ionomers used in PEM Fuel Cells, *Fuel Cells*, *5*, 302–308, 2005.

Helmholtz, H., Studien über electrische Grenzschichten, *Annalen der Physik*, *243*, 337–382, 1879.

Hickling, A., Studies in electrode polarisation. Part IV.—The automatic control of the potential of a working electrode, *Transactions of the Faraday Society (1905 - 1971)*, *38*, 27–33, 1942.

Higgins, D., M. A. Hoque, M. H. Seo, R. Wang, F. Hassan, J.-Y. Choi, M. Pritzker, A. Yu, J. Zhang, and Z. Chen, Development and Simulation of Sulfur-doped Graphene Supported Platinum with Exemplary Stability and Activity Towards Oxygen Reduction, *Advanced Functional Materials*, *24*, 4325–4336, 2014.

Hoare, J. P., Rest Potentials in the Platinum-Oxygen-Acid System, *Journal of The Electrochemical Society*, *109*, 858–865, 1962.

Hoare, J. P., On the Mixed Potentials Observed in the Iridium-Oxygen-Acid System, *Journal of The Electrochemical Society*, *111*, 988–992, 1964.

Hodnik, N., P. Jovanovi*v*c, A. Pavli*v*si*v*c, B. Jozinović, M. Zorko, M. Bele, V. S. *v*Selih, M. *v*Sala, S. Ho*v*cevar, and M. Gaber*v*s*v*cek, New Insights into Corrosion of Ruthenium and Ruthenium Oxide Nanoparticles in Acidic Media, *The Journal of Physical Chemistry C*, *119*, 10140–10147, 2015.

Hoffmann, P., *Tomorrow's Energy: Hydrogen, Fuel Cells, and the Prospects for a Cleaner Planet*, MIT Press, 2002.

Huang, S.-Y., P. Ganesan, and B. N. Popov, Titania supported platinum catalyst with high electrocatalytic activity and stability for polymer electrolyte membrane fuel cell, *Applied Catalysis B: Environmental*, *102*, 71–77, 2011.

Hunt, L. B., A History of Iridium, *Platinum Metals Review*, *31*, 32–41, 1987.

Inzelt, G., Milestones of the development of kinetics of electrode reactions, *Journal of Solid State Electrochemistry*, *15*, 1373–1389, 2011.

Jovanovivc, P., A. Pavlivsivc, V. S. vSelih, M. vSala, N. Hodnik, M. Bele, S. Hovcevar, and M. Gabervsvcek, New Insight into Platinum Dissolution from Nanoparticulate Platinum-Based Electrocatalysts Using Highly Sensitive In Situ Concentration Measurements, *ChemCatChem*, *6*, 449–453, 2014.

Kepley, L. J., and A. J. Bard, Ellipsometric, electrochemical, and elemental characterization of the surface phase produced on glassy carbon electrodes by electrochemical activation, *Analytical Chemistry*, *60*, 1459–1467, 1988.

Kim, J., J. Lee, and Y. Tak, Relationship between carbon corrosion and positive electrode potential in a proton-exchange membrane fuel cell during start/stop operation, *Journal of Power Sources*, *192*, 674–678, 2009.

Kinoshita, K., *Electrochemical Oxygen Technology*, Wiley-Interscience, 1992.

Klemm, S. O., A. A. Topalov, C. A. Laska, and K. J. Mayrhofer, Coupling of a high throughput microelectrochemical cell with online multielemental trace analysis by ICP-MS, *Electrochemistry Communications*, *13*, 1533–1535, 2011.

Kocha, S., Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique, `https://www.hydrogen.energy.gov/pdfs/review14/fc111_kocha_2014_o.pdf` (Accessed: 2015-03-24), 2014.

Kocha, S., Y. Garsany, and D. Myers, Testing Oxygen Reduction Reaction Activity with the Rotating Disc Electrode Technique, `http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/webinarslides_rde_technique_031213.pdf` (Accessed: 2014-03-24), 2013.

Kongkanand, A., Z. Liu, I. Dutta, and F. T. Wagner, Electrochemical and Microstructural Evaluation of Aged Nanostructured Thin Film Fuel Cell Electrocatalyst, *Journal of The Electrochemical Society*, *158*, B1286–B1291, 2011.

Kongkanand, A., J. Zhang, Z. Liu, Y.-H. Lai, P. Sinha, E. L. Thompson, and R. Makharia, Degradation of PEMFC Observed on NSTF Electrodes, *Journal of The Electrochemical Society*, *161*, F744–F753, 2014.

Kötz, R., and S. Stucki, Stabilization of RuO_2 by IrO_2 for anodic oxygen evolution in acid media, *Electrochimica Acta*, *31*, 1311–1316, 1986.

Kötz, R., H. J. Lewerenz, and S. Stucki, XPS Studies of Oxygen Evolution on Ru and RuO2 Anodes, *Journal of The Electrochemical Society*, *130*, 825–829, 1983.

Kötz, R., H. Neff, and S. Stucki, Anodic Iridium Oxide Films XPS-Studies of Oxidation State Changes and, *Journal of the Electrochemical Society*, *131*, 72–77, 1984a.

Kötz, R., S. Stucki, D. Scherson, and D. M. Kolb, In-situ identification of RuO_4 as the corrosion product during oxygen evolution on ruthenium in acid media, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *172*, 211–219, 1984b.

Koutecký, J., and B. Levich, The Application of the Rotating Disc Electrode to Studies of Kinetic and Catalytic Processes, *Zhurnal Fizicheskoi Khimii*, *32*, 1565–1575, 1958.

Krstajic, N., and S. Trasatti, Cathodic behaviour of RuO2-doped Ni/Co3O4 electrodes in alkaline solutions: Hydrogen evolution, *Journal of Applied Electrochemistry*, *28*, 1291–1297, 1998.

Kucernak, A. R., and E. Toyoda, Studying the oxygen reduction and hydrogen oxidation reactions under realistic fuel cell conditions, *Electrochemistry Communications*, *10*, 1728–1731, 2008.

Larminie, J., and A. Dicks, *Fuel Cell Systems Explained*, 2 ed., Wiley, 2003.

Latimer, W. M., *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, Prentice-Hall chemistry series, 2nd ed ed., Prentice-Hall, New York, 1952.

Lee, J. B., Elevated Temperature Potential-pH Diagrams for the Cr-H_2O, Ti-H_2O, Mo-H_2O, and Pt-H_2O Systems, *Corrosion*, *37*, 467–481, 1981.

Levich, V. G., *Physicochemical Hydrodynamics*, Prentice-Hall international series in the physical and chemical engineering sciences, Prentice-Hall, Englewood Cliffs, N.J, 1962.

Li, J., Catalyst Layer Degradation, Diagnosis and Failure Mitigation, in *PEM Fuel Cell Electrocatalysts and Catalyst Layers*, edited by J. Zhang, pp. 1041–1094, Springer London, 2008.

Liu, G. C.-K., Studies of Oxygen Reduction Electrocatalysts Enhanced by Dealloying, Ph.D. thesis, Dalhousie University, Halifax, NS, Canada, 2011.

Liu, G. C.-K., R. J. Sanderson, G. Vernstrom, D. A. Stevens, R. T. Atanasoski, M. K. Debe, and J. R. Dahn, RDE Measurements of ORR Activity of $Pt_{1-x}Ir_x$ ($0<x<0.3$) on High Surface Area NSTF-Coated Glassy Carbon Disks, *Journal of The Electrochemical Society*, *157*, B207, 2010.

Loferski, P. J., 2013 Minerals Yearbook Platinum Group Metals [Advance Release], *Annual publication*, United States Geological Survey, 2015.

Lopes, P. P., D. Strmcnik, D. Tripkovic, J. G. Connell, V. Stamenkovic, and N. M. Markovic, Relationships between Atomic Level Surface Structure and Stability/Activity of Platinum Surface Atoms in Aqueous Environments, *ACS Catalysis*, *6*, 2536–2544, 2016.

Maass, S., F. Finsterwalder, G. Frank, R. Hartmann, and C. Merten, Carbon support oxidation in PEM fuel cell cathodes, *Journal of Power Sources*, *176*, 444–451, 2008.

Marshall, A. T., and L. Vaisson-Béthune, Avoid the quasi-equilibrium assumption when evaluating the electrocatalytic oxygen evolution reaction mechanism by Tafel slope analysis, *Electrochemistry Communications*, *61*, 23–26, 2015.

Matsumoto, M., T. Miyazaki, and H. Imai, Oxygen-Enhanced Dissolution of Platinum in Acidic Electrochemical Environments, *J. Phys. Chem. C*, *115*, 11163–11169, 2011.

Mayrhofer, K. J. J., B. B. Blizanac, M. Arenz, V. R. Stamenkovic, P. N. Ross, and N. M. Markovic, The Impact of Geometric and Surface Electronic Properties of Pt-Catalysts on the Particle Size Effect in Electrocatalysis, *The Journal of Physical Chemistry B*, *109*, 14433–14440, 2005.

Meites, L., P. Zuman, and H. W. Nurnberg, Recommended terms, symbols, and definitions for electroanalytical chemistry (Recommendations 1985), *Pure and Applied Chemistry*, *57*, 1985.

Miles, M. H., and M. A. Thomason, Periodic Variations of Overvoltages for Water Electrolysis in Acid Solutions from Cyclic Voltammetric Studies, *Journal of The Electrochemical Society*, *123*, 1459–1461, 1976.

Miles, M. H., E. A. Klaus, B. P. Gunn, J. R. Locker, W. E. Serafin, and S. Srinivasan, The oxygen evolution reaction on platinum, iridium, ruthenium and their alloys at 80°C in acid solutions, *Electrochimica Acta*, *23*, 521–526, 1978.

Min, M., N.-w. Kong, E. You, T.-y. Kim, and C. Pak, Application of Oxygen Evolution Reaction Catalyst to Polymer Electrolyte Membrane Fuel Cells for Protection of Carbon Corrosion during Transient Conditions in Fuel Cell Vehicle, *Meeting Abstracts*, *MA2014-02*, 1072–1072, 2014.

Minguzzi, A., O. Lugaresi, E. Achilli, C. Locatelli, A. Vertova, P. Ghigna, and S. Rondinini, Observing the oxidation state turnover in heterogeneous iridium-based water oxidation catalysts, *Chemical Science*, *5*, 3591–3597, 2014.

Minguzzi, A., C. Locatelli, O. Lugaresi, E. Achilli, G. Cappelletti, M. Scavini, M. Coduri, P. Masala, B. Sacchi, A. Vertova, P. Ghigna, and S. Rondinini, Easy Accommodation of Different Oxidation States in Iridium Oxide Nanoparticles with Different Hydration Degree as Water Oxidation Electrocatalysts, *ACS Catalysis*, *5*, 5104–5115, 2015.

More, K. L., D. A. Cullen, J. C. Idrobo, K. A. Perry, and K. S. Reeves, Correlating Catalyst and Catalyst-Support Structures with Observed Degradation in PEM Fuel Cell, *Electrochemical Society Meeting Abstracts*, *MA2012-02*, 1313–1313, 2012.

Nagaoka, T., and T. Yoshino, Surface properties of electrochemically pretreated glassy carbon, *Analytical Chemistry*, *58*, 1037–1042, 1986.

Nidola, A., Technological impact of metallic oxides as anodes, in *Electrodes of Conductive Metallic Oxides Part B*, Studies in Physical and Theoretical Chemistry, pp. 627–659, Elsevier Scientific Publishing Co., 1981.

Nørskov, J. K., J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, and H. Jónsson, Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode, *The Journal of Physical Chemistry B*, *108*, 17886–17892, 2004.

Nørskov, J. K., T. Bligaard, J. Rossmeisl, and C. H. Christensen, Towards the computational design of solid catalysts, *Nature Chemistry*, *1*, 37–46, 2009.

Oh, J.-G., W. H. Lee, and H. Kim, The inhibition of electrochemical carbon corrosion in polymer electrolyte membrane fuel cells using iridium nanodendrites, *International Journal of Hydrogen Energy*, *37*, 2455–2461, 2012.

O'Hayre, R., W. Colella, S.-W. Cha, and F. B. Prinz, Fuel Cell Thermodyanmics (Chapter 2), in *Fuel Cell Fundamentals*, 3rd ed., John Wiley & Sons, 2009.

Ohma, A., K. Shinohara, A. Iiyama, T. Yoshida, and A. Daimaru, Membrane and Catalyst Performance Targets for Automotive Fuel Cells by FCCJ Membrane, Catalyst, MEA WG, *ECS Transactions*, *41*, 775–784, 2011.

OICA, Organization of Motor Vehicle Manufacturers 2010 Production Statistics, `http://www.oica.net/category/production-statistics/2013-statistics/` (Accessed: 2015-12-09), 2013.

Okamoto, H., The Ir-Ru (iridium-ruthenium) system, *Journal of Phase Equilibria*, *13*, 565–567, 1992.

Opekar, F., and P. Beran, Rotating disk electrodes, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *69*, 1–105, 1976.

Park, S., Y. Shao, J. Liu, and Y. Wang, Oxygen electrocatalysts for water electrolyzers and reversible fuel cells: Status and perspective, *Energy & Environmental Science*, *5*, 9331, 2012.

Parrondo, J., T. Han, E. Niangar, C. Wang, N. Dale, K. Adjemian, and V. Ramani, Platinum supported on titanium–ruthenium oxide is a remarkably stable electrocatayst for hydrogen fuel cell vehicles, *Proceedings of the National Academy of Sciences*, *111*, 45–50, 2014.

Parsonage, E. E., and M. K. Debe, Nanostructured electrode membranes, United States, *Patent US5338430 A*, 1994.

Paulus, U. A., T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, Oxygen reduction on a high-surface area Pt/Vulcan carbon catalyst: A thin-film rotating ring-disk electrode study, *Journal of Electroanalytical Chemistry*, *495*, 134–145, 2001.

Peuckert, M., XPS study on thermally and electrochemically prepared oxidic adlayers on iridium, *Surface Science*, *144*, 451–464, 1984.

Peuckert, M., On the electrosorption of oxygen species and adlayer growth on noble metal surfaces, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *185*, 379–391, 1985.

Pfeifer, V., T. E. Jones, J. J. V. Vélez, C. Massué, M. T. Greiner, R. Arrigo, D. Teschner, F. Girgsdies, M. Scherzer, J. Allan, M. Hashagen, G. Weinberg, S. Piccinin, M. Hävecker, A. Knop-Gericke, and R. Schlögl, The electronic structure of iridium oxide electrodes active in water splitting, *Physical Chemistry Chemical Physics*, *18*, 2292–2296, 2016.

Pickup, P. G., and V. I. Birss, A model for anodic hydrous oxide growth at iridium, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *220*, 83–100, 1987.

Pine Research Instrumentation, Working with ChangeDisk RRDE Tips (Document LMEC003), `https://www.pineresearch.com/echem/files/LMEC003.pdf` (Accessed: 2016-12-31), 2005.

Pine Research Instrumentation, E6TQ ChangeDisk RDE Tips, PEEK, `https://www.pineresearch.com/shop/products/electrodes/rde/e6tq-changedisk/` (Accessed: 2016-12-31), 2016.

Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford; New York, 1966.

Pourbaix, M. J. N., Thermodynamique des solutions aqueuses diluées: représentation graphique du rôle du pH et du potentiel, Dissertation, TU Delft, Delft University of Technology, 1945.

Pourbaix, M. J. N., J. Van Muylde, and N. de Zoubov, Electrochemical Properties of the Platinum Metals, *Platinum Metals Review*, *3*, 100–106, 1959a.

Pourbaix, M. J. N., J. Van Muylder, and N. de Zoubov, Electrochemical Properties of the Platinum Metals A New Approach to Studies of Corrosion Resistance and Cathodic Protection, *Platinum Metals Review*, *3*, 47–53, 1959b.

Ragone, D. V., Review of Battery Systems for Electrically Powered Vehicles, *SAE Technical Paper 680453*, SAE Technical Paper, Warrendale, PA, 1968.

Raistrick, I. D., Modified gas diffusion electrode for proton exchange membrane fuel cells, in *Proceedings of the Symposium on Diaphragms, Separation, and Ion-Exchange Membranes.*, vol. 86-13, p. 172, Electrochemical Society, Pennington (NJ), Boston, Mass., 1986.

Rakhtsaum, G., Platinum Alloys: A Selective Review of the Available Literature, *Platinum Metals Review*, *57*, 202–213, 2013.

Rand, D., and R. Woods, Cyclic voltammetric studies on iridium electrodes in sulphuric acid solutions: Nature of oxygen layer and metal dissolution, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *55*, 375–381, 1974.

Reiser, C. A., L. Bregoli, T. W. Patterson, J. S. Yi, J. D. Yang, M. L. Perry, and T. D. Jarvi, A Reverse-Current Decay Mechanism for Fuel Cells, *Electrochemical and Solid-State Letters*, *8*, A273–A276, 2005.

Rifkin, J., *The Hydrogen Economy: The Creation of the Worldwide Energy Web and the Redistribution of Power on Earth*, Penguin, 2003.

Roen, L. M., C. H. Paik, and T. D. Jarvi, Electrocatalytic Corrosion of Carbon Support in PEMFC Cathodes, *Electrochemical and Solid-State Letters*, *7*, A19–A22, 2004.

Romm, J. J., *The Hype About Hydrogen: Fact and Fiction in the Race to Save the Climate*, new edition edition ed., Island Press, Washington, DC, 2005.

Russell, J. H., L. J. Nuttall, and A. P. Fickett, Hydrogen generation by solid polymer electrolyte water electrolysis, *American Chemical Society Division of Fuel Chemistry Preprints*, *18*, 24e40, 1973.

Santana, M. H., L. M. Da Silva, and L. A. De Faria, Investigation of surface properties of Ru-based oxide electrodes containing Ti, Ce and Nb, *Electrochimica Acta*, *48*, 1885–1891, 2003.

Satyapal, S., DOE Hydrogen Program: 2010 Annual Merit Review and Peer Evaluation Report, *Tech. Rep. DOE/GO-102010-3144*, National Renewable Energy Laboratory (NREL), Golden, CO., 2010.

Schmickler, W., In Search of Lost Platinum, *ChemPhysChem*, *14*, 881–883, 2013.

Schmidt, T. J., and H. A. Gasteiger, Rotating thin-film method for supported catalysts, in *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, edited by W. Vielstich, A. Lamm, and H. A. Gasteiger, vol. 2, John Wiley & Sons, Ltd, 2003.

Schmidt, T. J., H. A. Gasteiger, G. D. Stäb, P. M. Urban, D. M. Kolb, and R. J. Behm, Characterization of High-Surface-Area Electrocatalysts Using a Rotating Disk Electrode Configuration, *Journal of The Electrochemical Society*, *145*, 2354–2358, 1998.

Shao, Y., G. Yin, and Y. Gao, Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell, *Journal of Power Sources*, *171*, 558–566, 2007.

Sheng, W., H. A. Gasteiger, and Y. Shao-Horn, Hydrogen Oxidation and Evolution Reaction Kinetics on Platinum: Acid vs Alkaline Electrolytes, *Journal of The Electrochemical Society*, *157*, B1529, 2010.

Shimoi, R., T. Aoyama, and A. Iiyama, Development of Fuel Cell Stack Durability based on Actual Vehicle Test Data: Current Status and Future Work, *SAE International Journal of Engines*, *2*, 960–970, 2009.

Shinagawa, T., A. T. Garcia-Esparza, and K. Takanabe, Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion, *Scientific Reports*, *5*, 2015.

Shinozaki, K., J. W. Zack, S. Pylypenko, B. S. Pivovar, and S. S. Kocha, Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique II. Influence of Ink Formulation, Catalyst Layer Uniformity and Thickness, *Journal of The Electrochemical Society*, *162*, F1384–F1396, 2015a.

Shinozaki, K., J. W. Zack, S. Pylypenko, R. M. Richards, B. S. Pivovar, and S. S. Kocha, Benchmarking the oxygen reduction reaction activity of Pt-based catalysts using standardized rotating disk electrode methods, *International Journal of Hydrogen Energy*, *40*, 16820–16830, 2015b.

Shinozaki, K., J. W. Zack, R. M. Richards, B. S. Pivovar, and S. S. Kocha, Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique I. Impact of Impurities, Measurement Protocols and Applied Corrections, *Journal of The Electrochemical Society*, *162*, F1144–F1158, 2015c.

Shirouzu, N., P. Lienert, and Y. Kubota, Insight : In green car race, Toyota adds muscle with fuel-cell launch (Reuters), `http://www.reuters.com/article/us-autos-hydrogen-toyota-motor-insight-idUSBREA3F1UN20140417` (Accessed: 2015-12-09), 2014.

Sidik, R. A., The maximum potential a PEM fuel cell cathode experiences due to the formation of air/fuel boundary at the anode, *Journal of Solid State Electrochemistry*, *13*, 1123–1126, 2009.

Sidik, R. A., A. B. Anderson, N. P. Subramanian, S. P. Kumaraguru, and B. N. Popov, O2 Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory, *The Journal of Physical Chemistry B*, *110*, 1787–1793, 2006.

Sinha, P. K., W. Gu, A. Kongkanand, and E. Thompson, Performance of Nano Structured Thin Film (NSTF) Electrodes under Partially-Humidified Conditions, *Journal of The Electrochemical Society*, *158*, B831–B840, 2011.

Siracusano, S., V. Baglio, E. Moukheiber, L. Merlo, and A. S. Aricò, Performance of a PEM water electrolyser combining an IrRu-oxide anode electrocatalyst and a short-side chain Aquivion membrane, *International Journal of Hydrogen Energy*, *40*, 14430–14435, 2015.

Snyder, J., T. Fujita, M. W. Chen, and J. Erlebacher, Oxygen reduction in nanoporous metal–ionic liquid composite electrocatalysts, *Nature Materials*, *9*, 904–907, 2010.

Solla-Gullón, J., V. Montiel, A. Aldaz, and J. Clavilier, Electrochemical characterisation of platinum nanoparticles prepared by microemulsion: How to clean them without loss of crystalline surface structure, *Journal of Electroanalytical Chemistry*, *491*, 69–77, 2000.

Solla-Gullón, J., F. Vidal-Iglesias, E. Herrero, J. Feliu, A. Aldaz, and F. José, Electrocatalysis on Shape-Controlled Pt Nanoparticles, in *Polymer Electrolyte Fuel Cells: Science, Applications, and Challenges*, edited by A. A. Franco, CRC Press, 2013.

Spendelow, J., and J. Marcinkoski, Fuel Cell System Cost - 2014, *Tech. Rep. 14014*, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office, 2014.

Springer, T. E., Polymer Electrolyte Fuel Cell Model, *Journal of The Electrochemical Society*, *138*, 2334, 1991.

Srinivasan, V., Batteries for Vehicular Applications, in *AIP Conference Proceedings*, vol. 1044, pp. 283–296, AIP Publishing, 2008.

Stamenkovic, V., N. M. Markovic, and P. N. Ross Jr., Structure-relationships in electrocatalysis: Oxygen reduction and hydrogen oxidation reactions on Pt(111) and Pt(100) in solutions containing chloride ions, *Journal of Electroanalytical Chemistry*, *500*, 44–51, 2001.

Stamenkovic, V., B. S. Mun, J. Mayrhofer, Karl J. P. N. Ross, N. M. Markovic, J. Rossmeisl, J. Greeley, and J. K. Nørskov, Changing the Activity of Electrocatalysts for Oxygen Reduction by Tuning the Surface Electronic Structure, *Angewandte Chemie*, *118*, 2963–2967, 2006.

Steegstra, P., M. Busch, I. Panas, and E. Ahlberg, Revisiting the Redox Properties of Hydrous Iridium Oxide Films in the Context of Oxygen Evolution, *The Journal of Physical Chemistry C*, *117*, 20975–20981, 2013.

Steinbach, A., High-Performance, Durable, Low-Cost Membrane Electrode Assemblies for Transportation Applications, Department of Energy Hydrogen and Fuel Cells Program 2016 Annual Merit Review Proceedings, `https://energy.gov/sites/prod/files/2016/08/f33/fcto_cwg_july2016_steinbach.pdf` (Accessed: 2017-01-31), 2016.

Stevens, D., R. Sanderson, T. Hatchard, T. Crowtz, J. R. Dahn, G. D. Vernstrom, G. M. Haugen, T. Watschke, L. L. Atanasoska, and R. T. Atanasoski, Development of Catalysts with Enhanced Tolerance to Fuel Cell Transient Conditions, *ECS Transactions*, *33*, 419–423, 2010.

Stevens, D. A., and J. R. Dahn, Thermal degradation of the support in carbon-supported platinum electrocatalysts for PEM fuel cells, *Carbon*, *43*, 179–188, 2005.

Stevens, D. A., M. T. Hicks, G. M. Haugen, and J. R. Dahn, Ex Situ and In Situ Stability Studies of PEMFC Catalysts Effect of Carbon Type and Humidification on Degradation of the Carbon, *Journal of The Electrochemical Society*, *152*, A2309–A2315, 2005.

Stevens, D. A., J. Harlow, R. J. Sanderson, C. W. Watson, T. J. Crowtz, J. R. Dahn, G. D. Vernstrom, L. L. Atanasoska, G. M. Haugen, and R. T. Atanasoski, Rotating Disk Electrode Techniques Designed to Simulate Fuel Cell Startup/Shut-Down Transient Conditions, *ECS Transactions*, *50*, 1533–1538, 2013.

Strasser, P., S. Koh, T. Anniyev, J. Greeley, K. More, C. Yu, Z. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney, and A. Nilsson, Lattice-strain control of the activity in dealloyed core–shell fuel cell catalysts, *Nature Chemistry*, *2*, 454–460, 2010.

Subramanian, V., H. Zhu, R. Vajtai, P. M. Ajayan, and B. Wei, Hydrothermal Synthesis and Pseudocapacitance Properties of MnO_2 Nanostructures, *The Journal of Physical Chemistry B*, *109*, 20207–20214, 2005.

Tang, H., Z. Qi, M. Ramani, and J. F. Elter, PEM fuel cell cathode carbon corrosion due to the formation of air/fuel boundary at the anode, *Journal of Power Sources*, *158*, 1306–1312, 2006.

Thuv, H., The Oxygen Evolution Reaction at Iridium-Ruthenium Oxide Catalysts for PEM Water Electrolysis, Master thesis, Norges teknisk-naturvitenskapelige universitet, 2015.

Tilak, B. V., P. W. T. Lu, J. E. Colman, and S. Srinivasan, Electrolytic Production of Hydrogen, in *Comprehensive Treatise of Electrochemistry*, edited by J. O. Bockris, B. E. Conway, E. Yeager, and R. E. White, no. 2 in Comprehensive Treatise of Electrochemistry, pp. 1–104, Springer US, 1981.

Topalov, A. A., Design and implementation of an automated electrochemical flow system coupled with mass spectrometry for investigation of the dissolution behavior of platinum, Ph.D. thesis, Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, Bochum, Germany, 2014.

Topalov, A. A., I. Katsounaros, M. Auinger, S. Cherevko, J. C. Meier, S. O. Klemm, and K. J. J. Mayrhofer, Dissolution of Platinum: Limits for the Deployment of Electrochemical Energy Conversion?, *Angewandte Chemie International Edition*, *51*, 12613–12615, 2012.

Topalov, A. A., S. Cherevko, A. R. Zeradjanin, J. C. Meier, I. Katsounaros, and K. J. J. Mayrhofer, Towards a comprehensive understanding of platinum dissolution in acidic media, *Chemical Science*, 2013.

Trasatti, S., Electrocatalysis: Understanding the success of DSA®, *Electrochimica Acta*, *45*, 2377–2385, 2000.

Trasatti, S., and G. Lodi, Properties of Conductive Transition Metal Oxides with Rutile-type Structure, in *Electrodes of Conductive Metal Oxides, Part A*, Studies in Physical and Theoretical Chemistry, pp. 301–358, Elsevier Scientific Publishing Co., 1980.

Trasatti, S., and G. Lodi, Oxygen and chlorine evolution reactions on conductive metallic oxide anodes, in *Electrodes of Conductive Metallic Oxides Part B*, Studies in Physical and Theoretical Chemistry, pp. 521–626, Elsevier Scientific Publishing Co., 1981.

Trasatti, S., and W. O'Grady, Properties and applications of RuO_2-based electrodes, in *Advances in Electrochemical and Electrochemical Engineering*, edited by H. Gerischer, vol. 12, John Wiley & Sons Canada, Limited, 1981.

Trasatti, S., P. N. Ross, and J. Lipkowski, Transition metal oxides: Versatile materials for electrocatalasis, in *The Electrochemistry of Novel Materials*, vol. 3 of *Frontiers of Electrochemistry*, VCH, 1994.

Treimer, S., A. Tang, and D. Johnson, A Consideration of the Application of Koutecký-Levich Plots in the Diagnoses of Charge-Transfer Mechanisms at Rotated Disk Electrodes, *Electroanalysis*, *14*, 165–171, 2002.

United States DOE, RFI - Rotating Disk Electrode Experiments for PEMFC Electrocatalyst Screening, *Request for Information DE-FOA-0000926*, USDOE Office of Energy Efficiency and Renewable Energy, 2013.

United States DOE, Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan Sec. 3.4 Fuel Cells, `http://energy.gov/node/994171` (Accessed: 2016-09-01), 2016.

van der Vliet, D., D. S. Strmcnik, C. Wang, V. R. Stamenkovic, N. M. Markovic, and M. T. Koper, On the importance of correcting for the uncompensated Ohmic resistance in model experiments of the Oxygen Reduction Reaction, *Journal of Electroanalytical Chemistry*, *647*, 29–34, 2010.

van der Vliet, D. F., C. Wang, D. Tripkovic, D. Strmcnik, X. F. Zhang, M. K. Debe, R. T. Atanasoski, N. M. Markovic, and V. R. Stamenkovic, Mesostructured thin films as electrocatalysts with tunable composition and surface morphology, *Nature Materials*, *11*, 1051–1058, 2012.

Vidal-Iglesias, F. J., J. Solla-Gullón, V. Montiel, and A. Aldaz, Errors in the use of the Koutecky–Levich plots, *Electrochemistry Communications*, *15*, 42–45, 2012.

Villars, P., A. Prince, and H. Okamoto, *Handbook of Ternary Alloy Phase Diagrams*, vol. 9, ASM International, 1995.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Selected Values of Chemical Thermodynamic Properties [Part 4] Tables for Elements 35-53 in the Standard Order of Arrangement, *Tech. Rep. 270-4*, Institute for Materials Research National Bureau of Standards, Washington, DC, 1969.

Wagner, F. T., B. Lakshmanan, and M. F. Mathias, Electrochemistry and the Future of the Automobile, *The Journal of Physical Chemistry Letters*, *1*, 2204–2219, 2010.

Wang, C., D. van der Vliet, K. L. More, N. J. Zaluzec, S. Peng, S. Sun, H. Daimon, G. Wang, J. Greeley, J. Pearson, A. P. Paulikas, G. Karapetrov, D. Strmcnik, N. M. Markovic, and V. R. Stamenkovic, Multimetallic Au/$FePt_3$ Nanoparticles as Highly Durable Electrocatalyst, *Nano Letters*, *11*, 919–926, 2011.

Wilson, M. S., and S. Gottesfeld, Thin-film catalyst layers for polymer electrolyte fuel cell electrodes, *Journal of Applied Electrochemistry*, *22*, 1–7, 1992.

Winter, M., and R. J. Brodd, What Are Batteries, Fuel Cells, and Supercapacitors?, *Chem. Rev.*, *104*, 4245–4270, 2004.

Wöhler, L., and W. Witzmann, Die Oxyde des Iridiums, *Zeitschrift für anorganische Chemie*, *57*, 323–352, 1908.

Wood, D., P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, R. Borup, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.-i. Kimijima, N. Iwashita, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, and F. Garzon, Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation, *Chemical Reviews*, *107*, 3904–3951, 2007.

Woods, R., Hydrogen adsorption on platinum, iridium and rhodium electrodes at reduced temperatures and the determination of real surface area, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *49*, 217–226, 1974.

Woods, R., The Properties of Oxide Layers Formed on Iridium, Rhodium and Ruthenium Electrodes During Potential Cycling, *Israel Journal of Chemistry*, *18*, 118–124, 1979.

Xing, Y., Y. Cai, M. B. Vukmirovic, W.-P. Zhou, H. Karan, J. X. Wang, and R. R. Adzic, Enhancing Oxygen Reduction Reaction Activity via Pd-Au Alloy Sublayer Mediation of Pt Monolayer Electrocatalysts, *The Journal of Physical Chemistry Letters*, *1*, 3238–3242, 2010.

Yu, P. T., W. Gu, R. Makharia, F. T. Wagner, and H. A. Gasteiger, The Impact of Carbon Stability on PEM Fuel Cell Startup and Shutdown Voltage Degradation, *ECS Transactions*, *3*, 797–809, 2006.

Yu, X., and S. Ye, Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC: Part II: Degradation mechanism and durability enhancement of carbon supported platinum catalyst, *Journal of Power Sources*, *172*, 145–154, 2007.

Yu, Y., H. Li, H. Wang, X.-Z. Yuan, G. Wang, and M. Pan, A review on performance degradation of proton exchange membrane fuel cells during startup and shutdown processes: Causes, consequences, and mitigation strategies, *Journal of Power Sources*, *205*, 10–23, 2012.

Zalitis, C. M., D. Kramer, and A. R. Kucernak, Electrocatalytic performance of fuel cell reactions at low catalyst loading and high mass transport, *Physical Chemistry Chemical Physics*, *15*, 4329–4340, 2013.

Zenyuk, I. V., and S. Litster, Modeling ion conduction and electrochemical reactions in water films on thin-film metal electrodes with application to low temperature fuel cells, *Electrochimica Acta*, *146*, 194–206, 2014.

Appendix A

OER-in-Acid Catalyst Alternatives

Pourbaix (1966) predicts several elements, other than Ru, Ir and Pt will be stable in the pH and potential range for OER catalysis in acid. These elements are Rh, W, Pd, Ti, Sn, Ta, and Nb. Figure A.1 shows the Pourbaix diagrams for these elements, including Ir and Ru for reference. Some non-Ru/Ir OER in acid studies are briefly addressed below:

Rh *Damjanovic et al.* (1966) tested Ir, Rh Pt, and a Rh-Pt alloy for OER activity in $HClO_4$, with Rh coming in second place. Other studies on the OER activity of Rh in acid are *Miles and Thomason* (1976), *Chen et al.* (2001), and *Dokoutchaev et al.* (2002).

W: The OER on W in acid has seldom been reported, though *Bock et al.* (2002) report that WO_x with “Pt micro-centers” has better OER activity than pure Pt. W is also discussed in Chapter 3 of *Bard et al.* (2003).

Pd: The Pourbaix diagram of Pd looks very similar to Pt, and Pd, like Pt, is a poor OER catalyst. Still, it is worthy of investigation as a stabilizing agent for Ru.

Nb: Discussed in Chapter 3 of *Bard et al.* (2003).

Ta: Discussed in Chapter 3 of *Bard et al.* (2003).

Metalloids such as Si, Ga, Ge, and Sb are other possible candidates which may be practically (though probably not thermodynamically) stable during OER-in-acid catalysis. Other elements may also be good candidates. For example, Ce has been investigated by (*Santana et al.*, 2003).

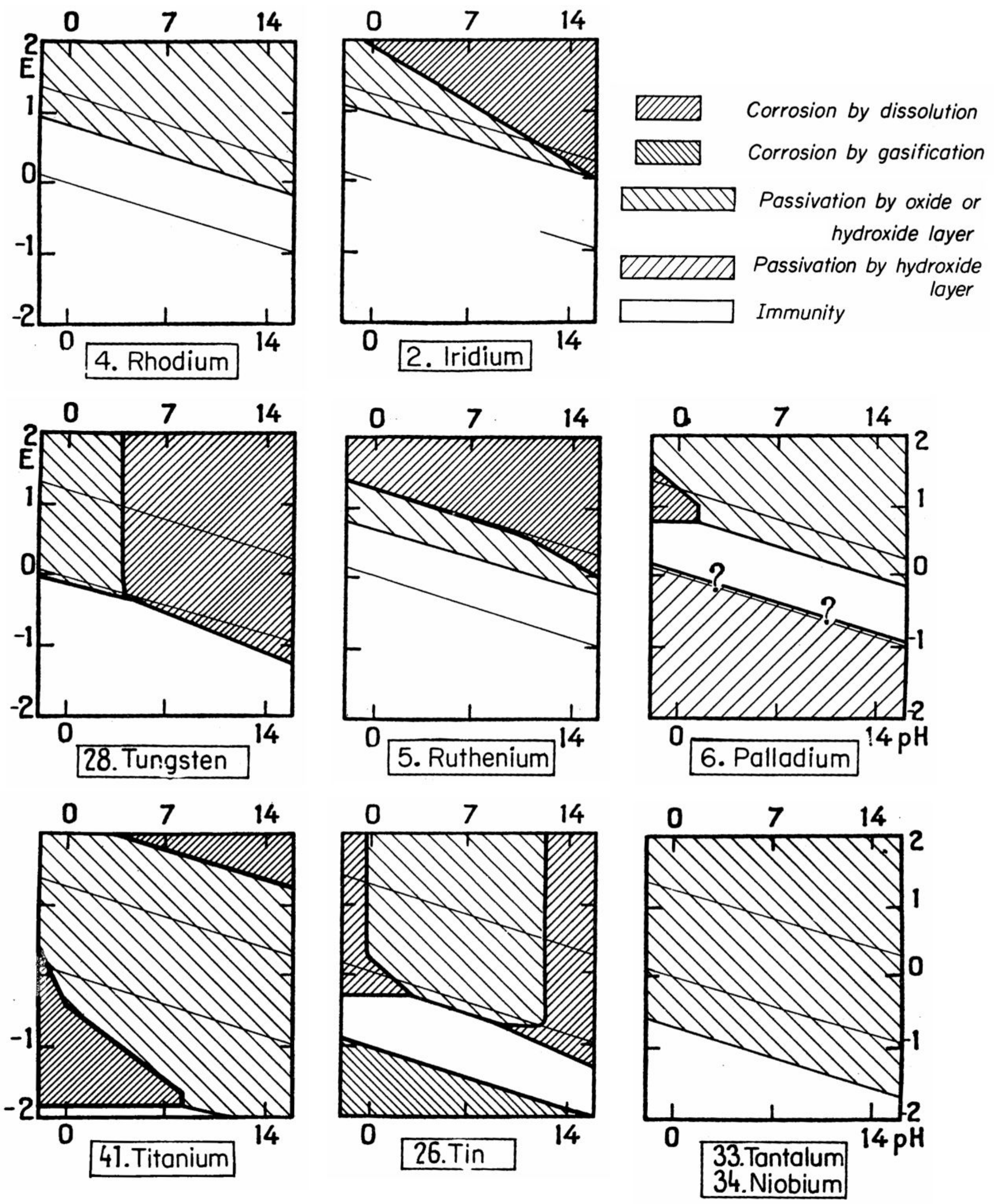


Figure A.1: Pourbaix diagrams of elements with stability in low pH (0 to 4) and at high (1.2 to 1.7 V_{SHE}) potential, which could serve as candidates for OER catalysis materials in acid.

Appendix B

Ar CVs for Binary Compositions in Chapter 4

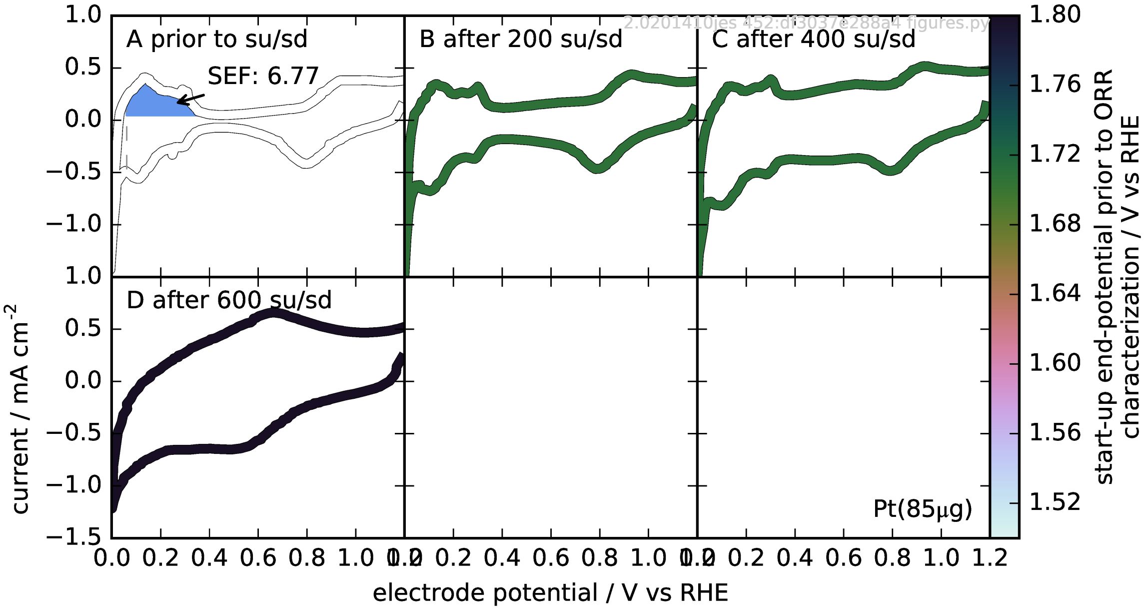


Figure B.1: Ar CVs from the pure Pt (85 $\mu g\, cm^{-2}$) sample in Figures 4.8 through 4.11 .

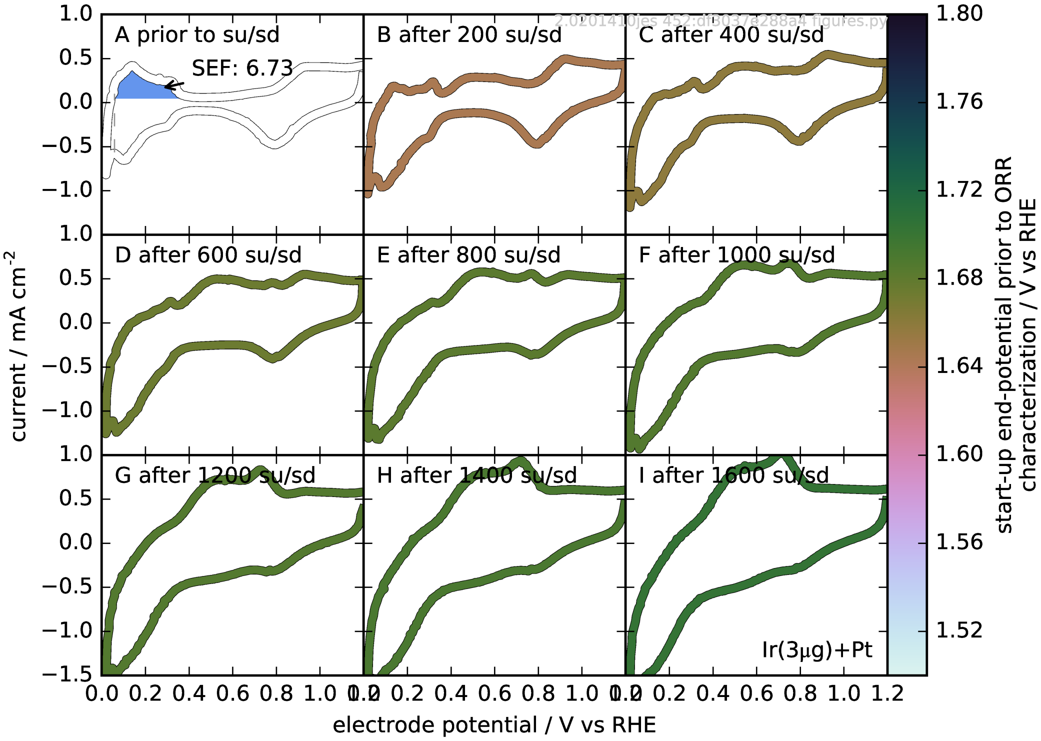


Figure B.2: Ar CVs from the intermix $\mathrm{Pt}_{1-x}\mathrm{Ir}_{x,x=0.035}$ ($3\ \mu g_{Ir}\ cm^{-2}$, $85\ \mu g_{Pt}\ cm^{-2}$) sample in Figure 4.8.

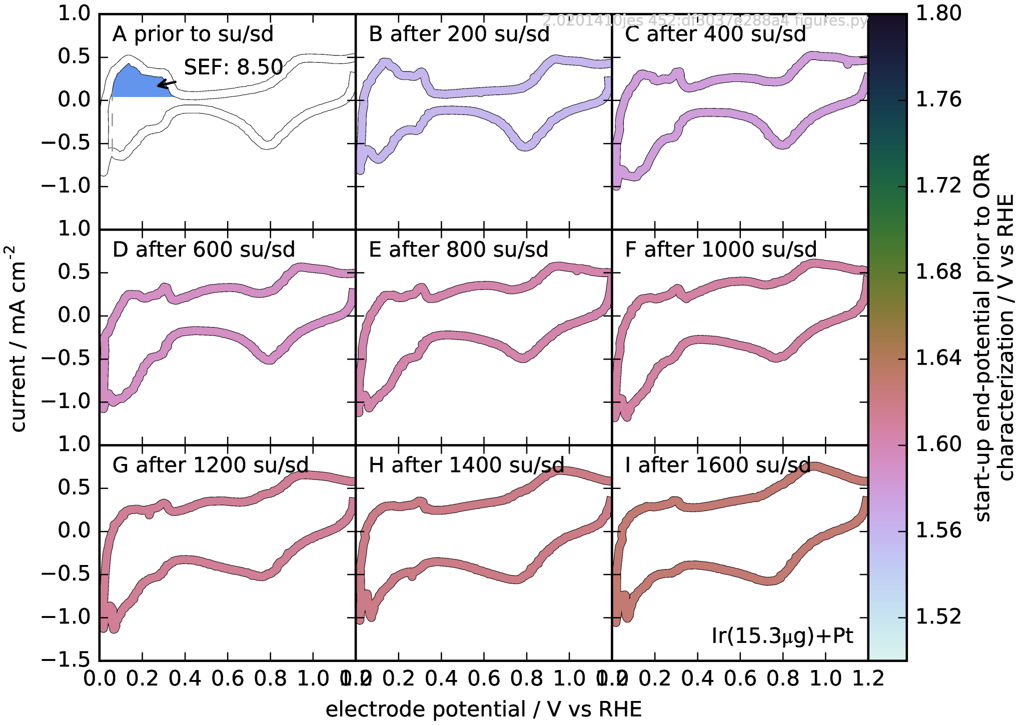


Figure B.3: Ar CVs from the intermix $\mathrm{Pt}_{1-x}\mathrm{Ir}_{x,x=0.15}$ ($15.3\ \mu g_{Ir}\ cm^{-2}$, $85\ \mu g_{Pt}\ cm^{-2}$) sample in Figure 4.8.

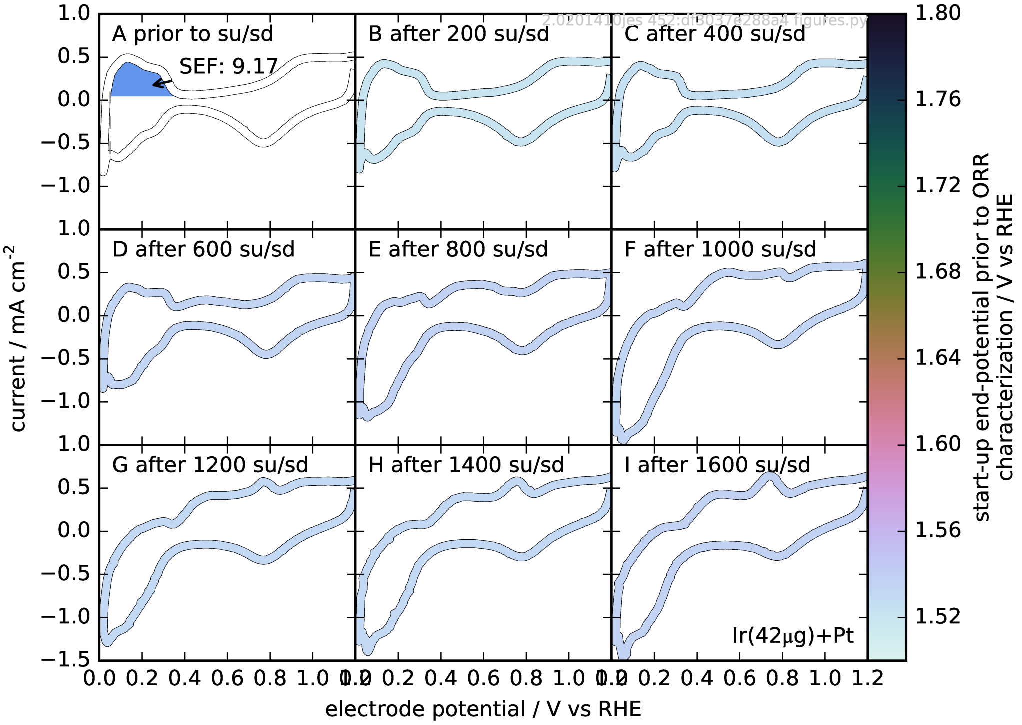


Figure B.4: Ar CVs from the intermix $\text{Pt}_{1-x}\text{Ir}_{x,x=0.33}$ ($42\ \mu g_{Ir}\ cm^{-2}$, $85\ \mu g_{Pt}\ cm^{-2}$) sample in Figure 4.8.

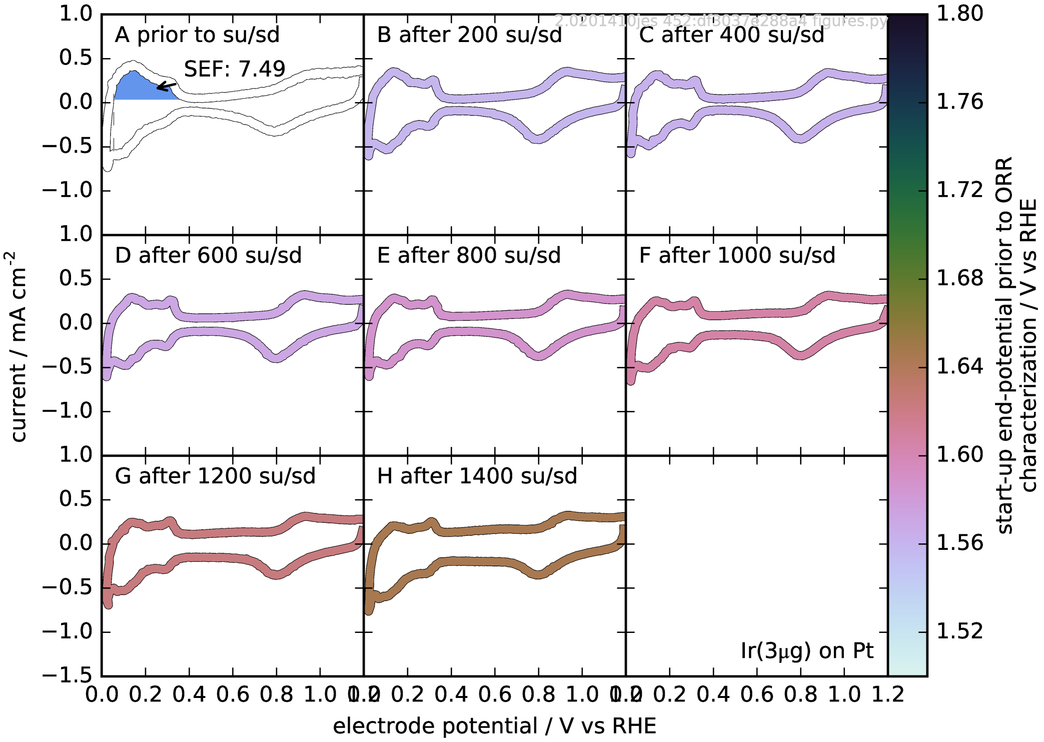


Figure B.5: Ar CVs from the overlayer $\text{Pt}_{1-x}\text{Ir}_{x,x=0.035}$ ($3\ \mu g_{Ir}\ cm^{-2}$, $85\ \mu g_{Pt}\ cm^{-2}$) sample in Figure 4.9.

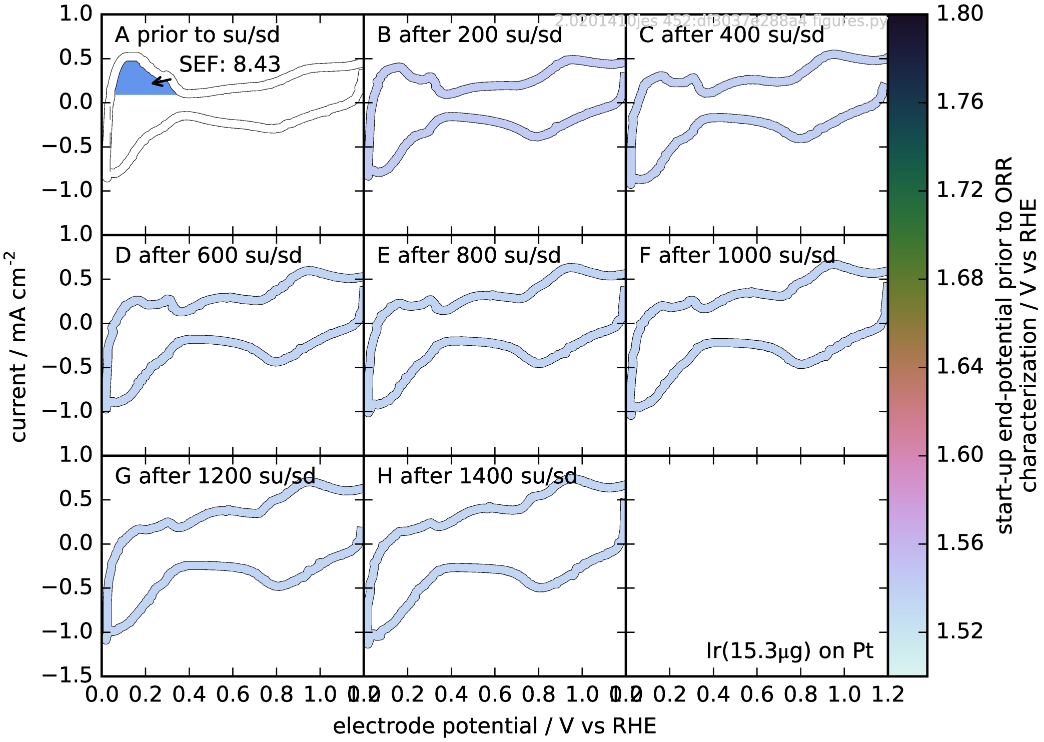


Figure B.6: Ar CVs from the overlayer $\mathrm{Pt}_{1-x}\mathrm{Ir}_{x,x=0.15}$ (15.3 $\mu g_{Ir}\ cm^{-2}$, 85 $\mu g_{Pt}\ cm^{-2}$) sample in Figure 4.9.

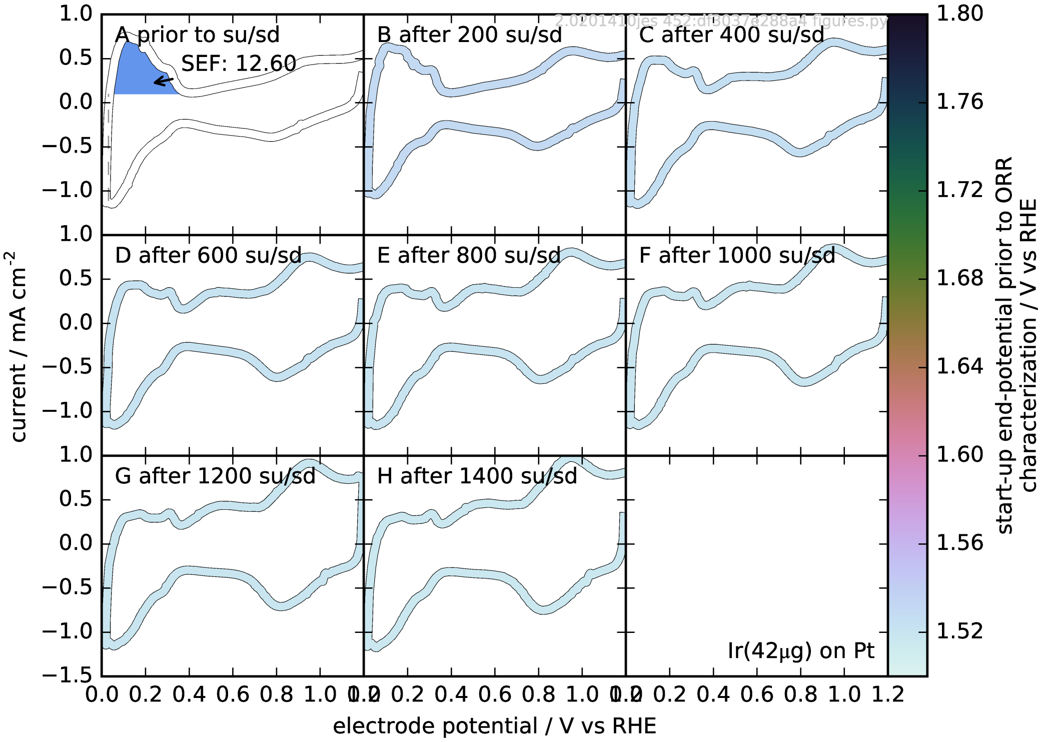


Figure B.7: Ar CVs from the overlayer $\mathrm{Pt}_{1-x}\mathrm{Ir}_{x,x=0.33}$ (42 $\mu g_{Ir}\ cm^{-2}$, 85 $\mu g_{Pt}\ cm^{-2}$) sample in Figure 4.9.

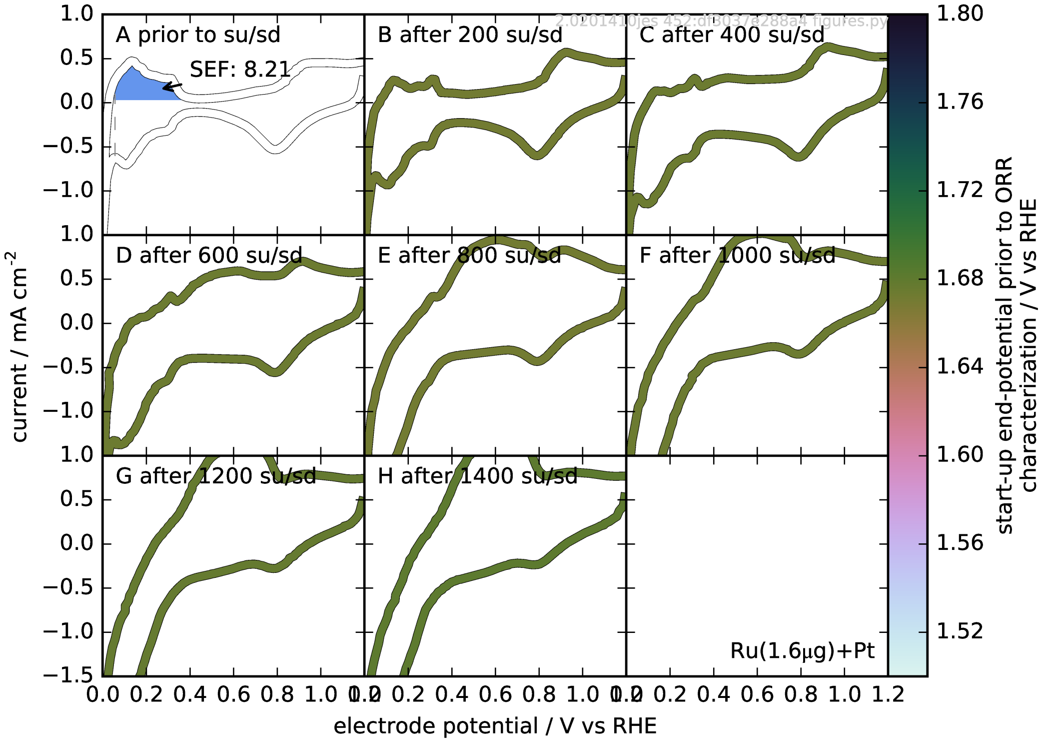


Figure B.8: Ar CVs from the intermix $Pt_{1-x}Ru_{x,x=0.035}$ (1.6 $\mu g_{Ru}\ cm^{-2}$, 85 $\mu g_{Pt}\ cm^{-2}$) sample in Figure 4.10.

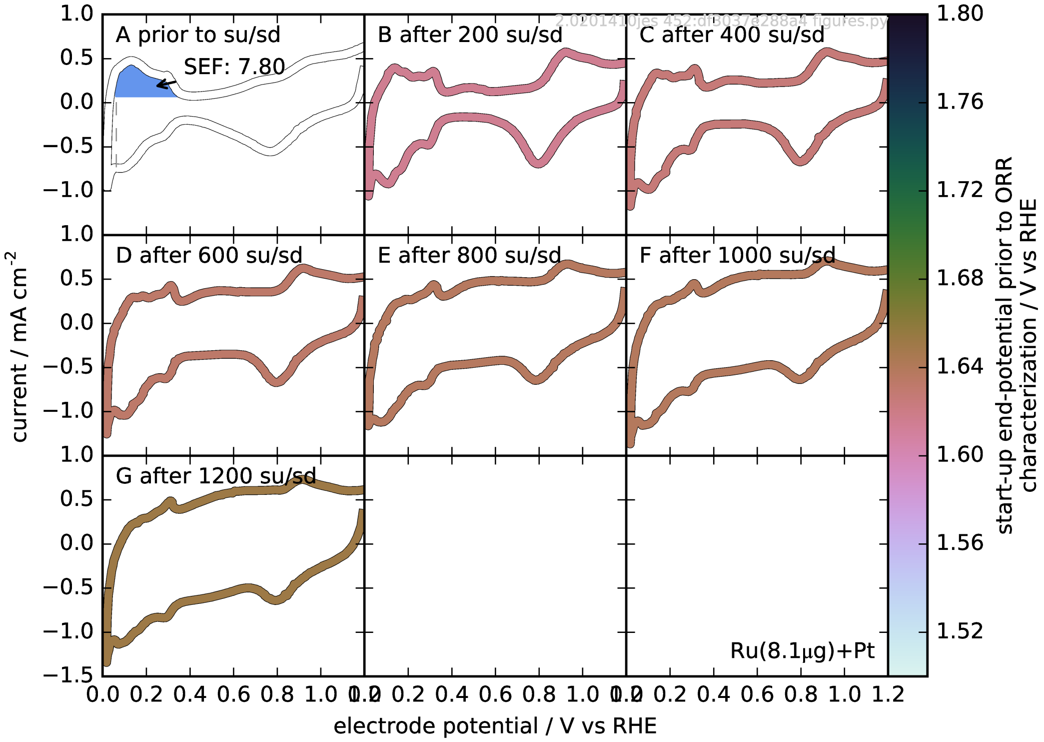


Figure B.9: Ar CVs from the intermix $Pt_{1-x}Ru_{x,x=0.15}$ (8.1 $\mu g_{Ru}\ cm^{-2}$, 85 $\mu g_{Pt}\ cm^{-2}$) sample in Figure 4.10.

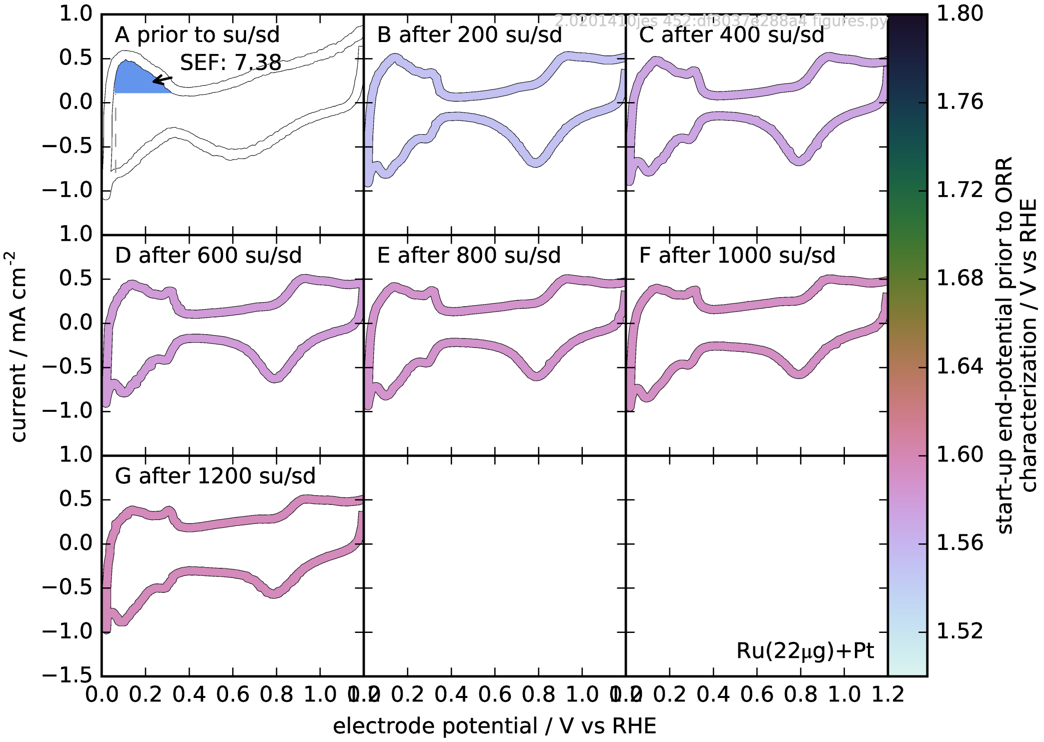


Figure B.10: Ar CVs from the intermix $Pt_{1-x}Ru_{x,x=0.33}$ ($22\ \mu g_{Ru}\ cm^{-2}$, $85\ \mu g_{Pt}\ cm^{-2}$) sample in Figure 4.10.

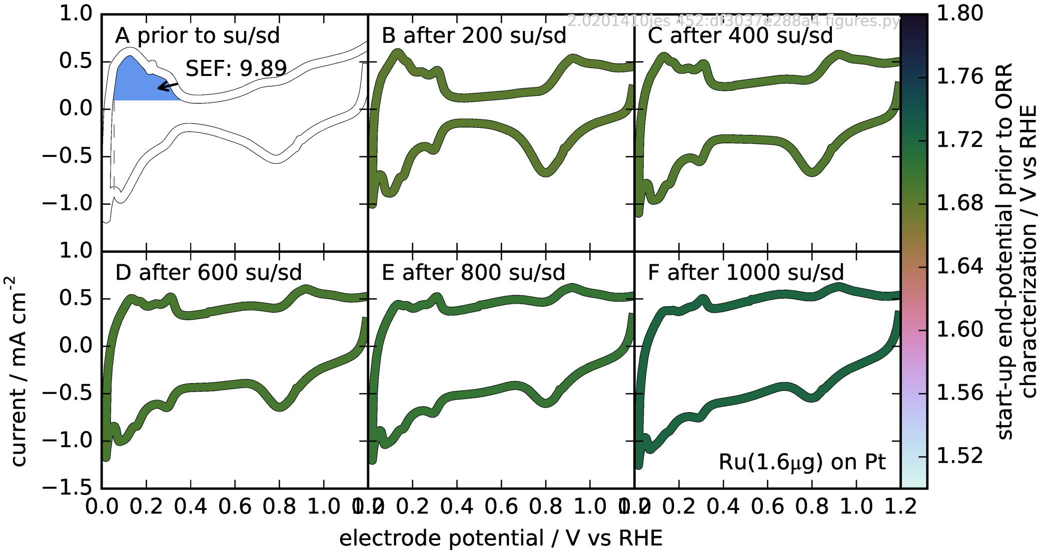


Figure B.11: Ar CVs from the overlayer $Pt_{1-x}Ru_{x,x=0.035}$ ($1.6\ \mu g_{Ru}\ cm^{-2}$, $85\ \mu g_{Pt}\ cm^{-2}$) sample in Figure 4.11.

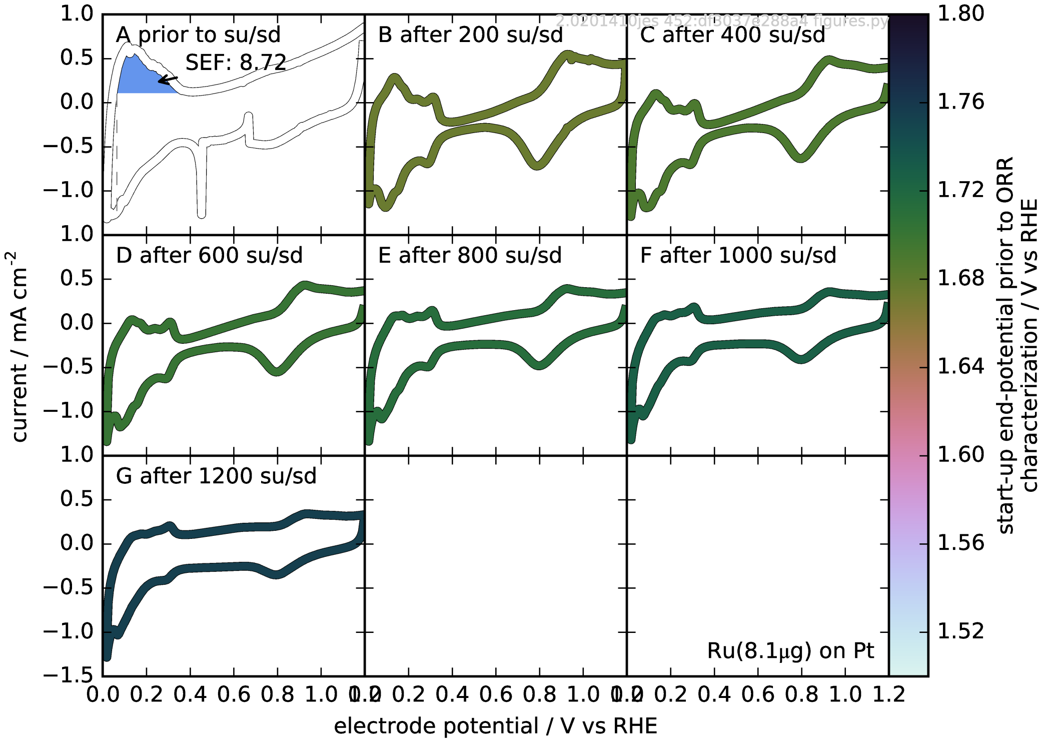


Figure B.12: Ar CVs from the overlayer $Pt_{1-x}Ru_{x,x=0.15}$ (8.1 $\mu g_{Ru}\, cm^{-2}$, 85 $\mu g_{Pt}\, cm^{-2}$) sample in Figure 4.11.

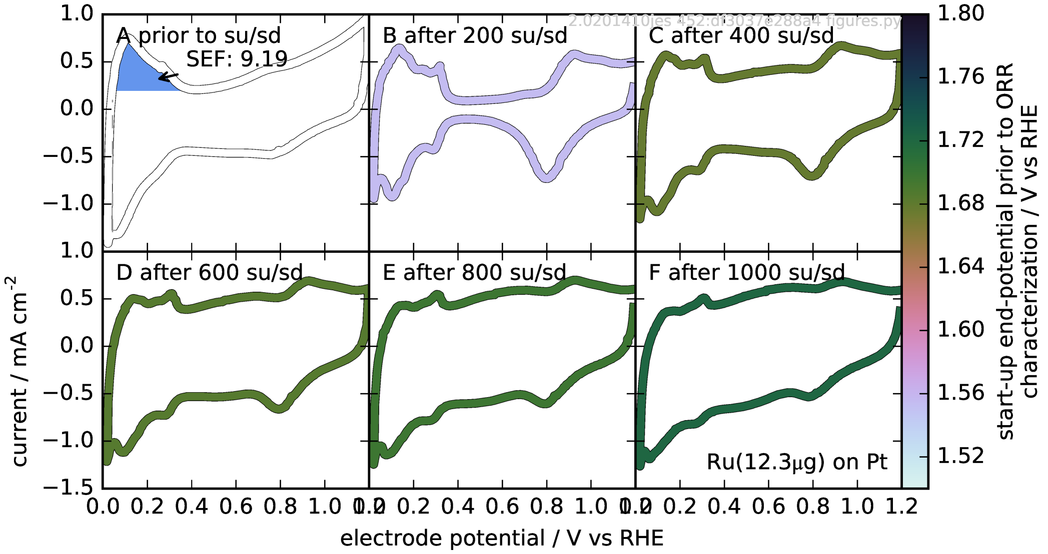


Figure B.13: Ar CVs from the overlayer $Pt_{1-x}Ru_{x,x=0.22}$ (12.3 $\mu g_{Ru}\, cm^{-2}$, 85 $\mu g_{Pt}\, cm^{-2}$) sample in Figure 4.11.

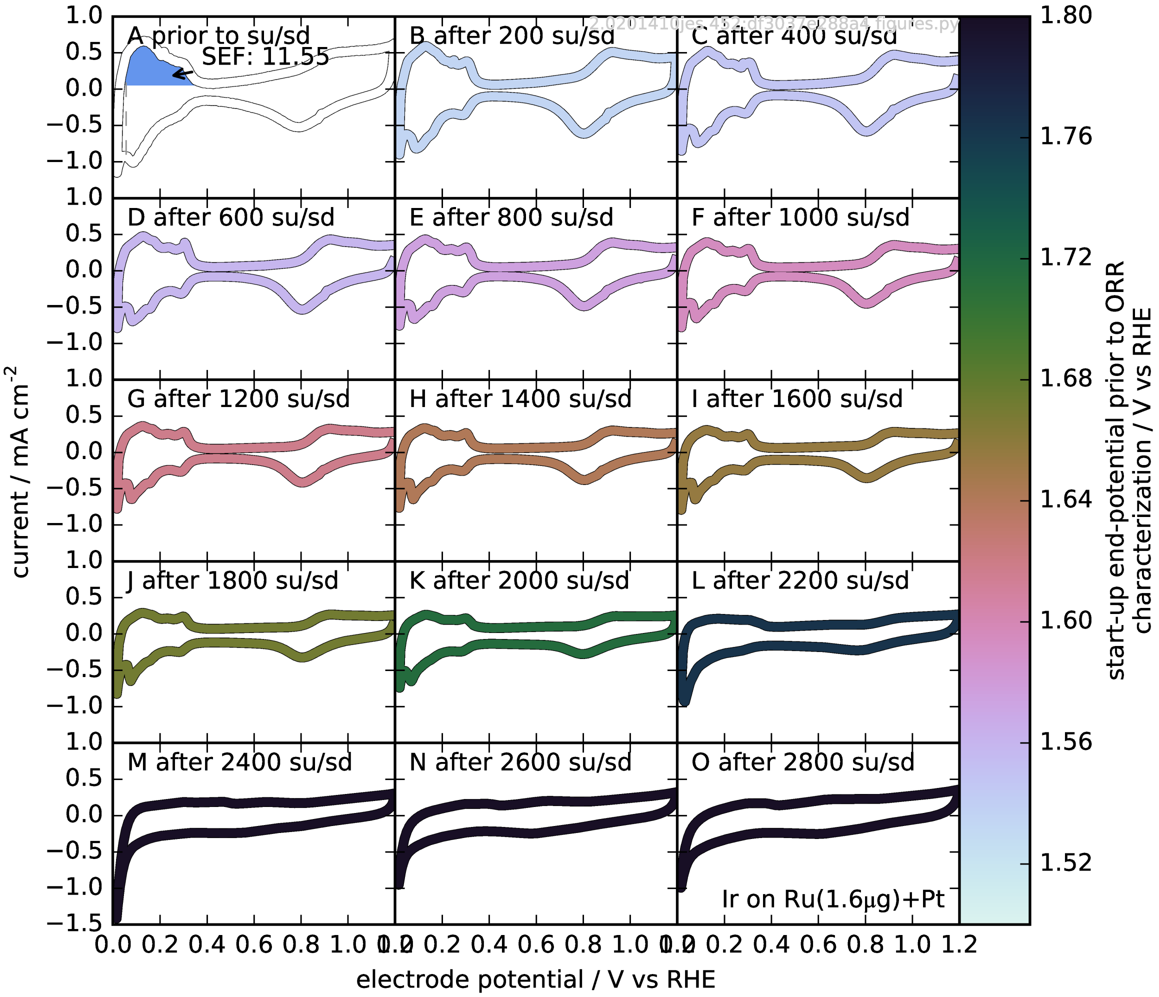


Figure B.14: Ar CVs from the 6 $\mu g_{Ir}\, cm^{-2}$ on 1.6 $\mu g_{Ru}\, cm^{-2}$ intermixed with 85 $\mu g_{Pt}\, cm^{-2}$ sample in Figure 4.16.

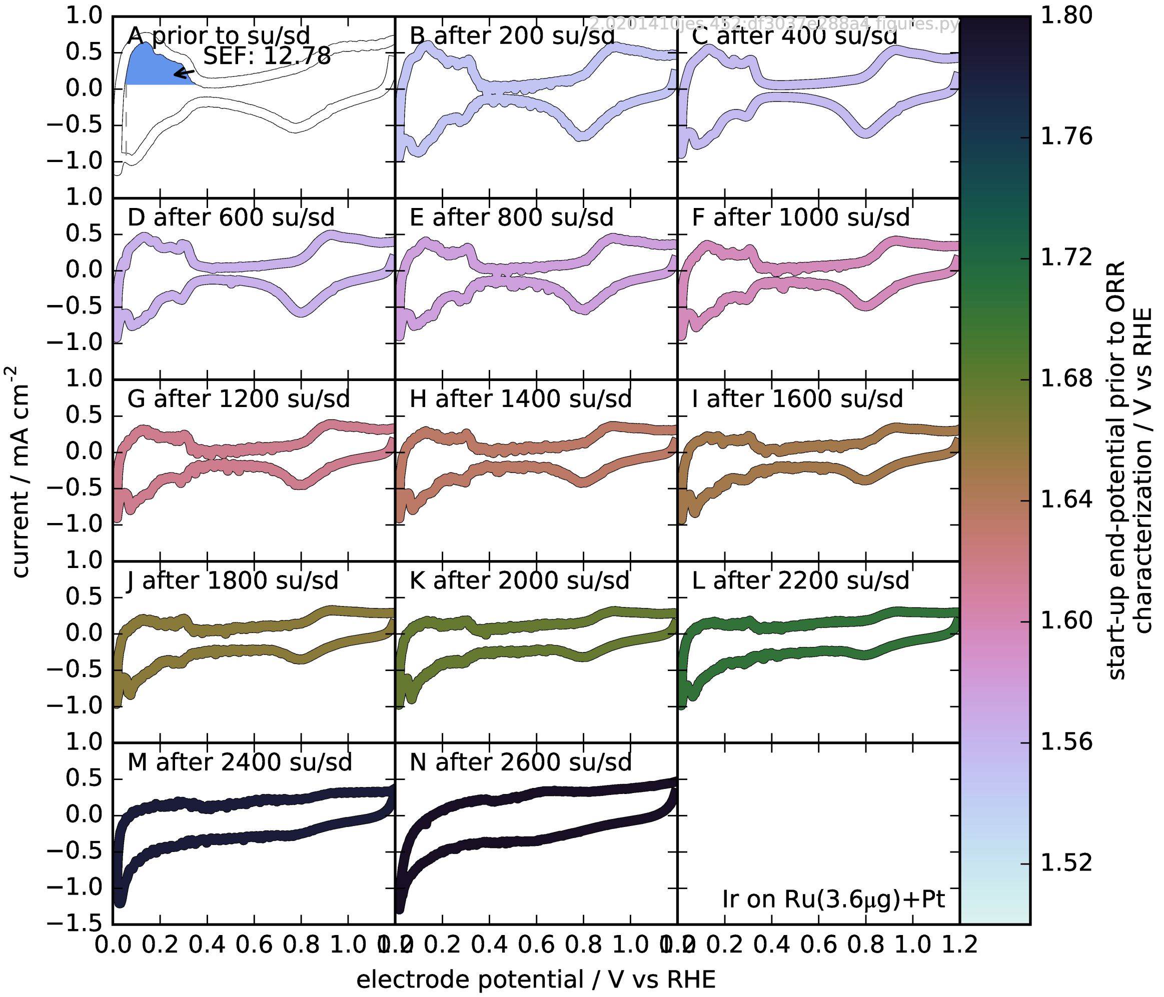


Figure B.15: Ar CVs from the 6 $\mu g_{Ir}\, cm^{-2}$ on 3.6 $\mu g_{Ru}\, cm^{-2}$ intermixed with 85 $\mu g_{Pt}\, cm^{-2}$ sample in Figure 4.16.

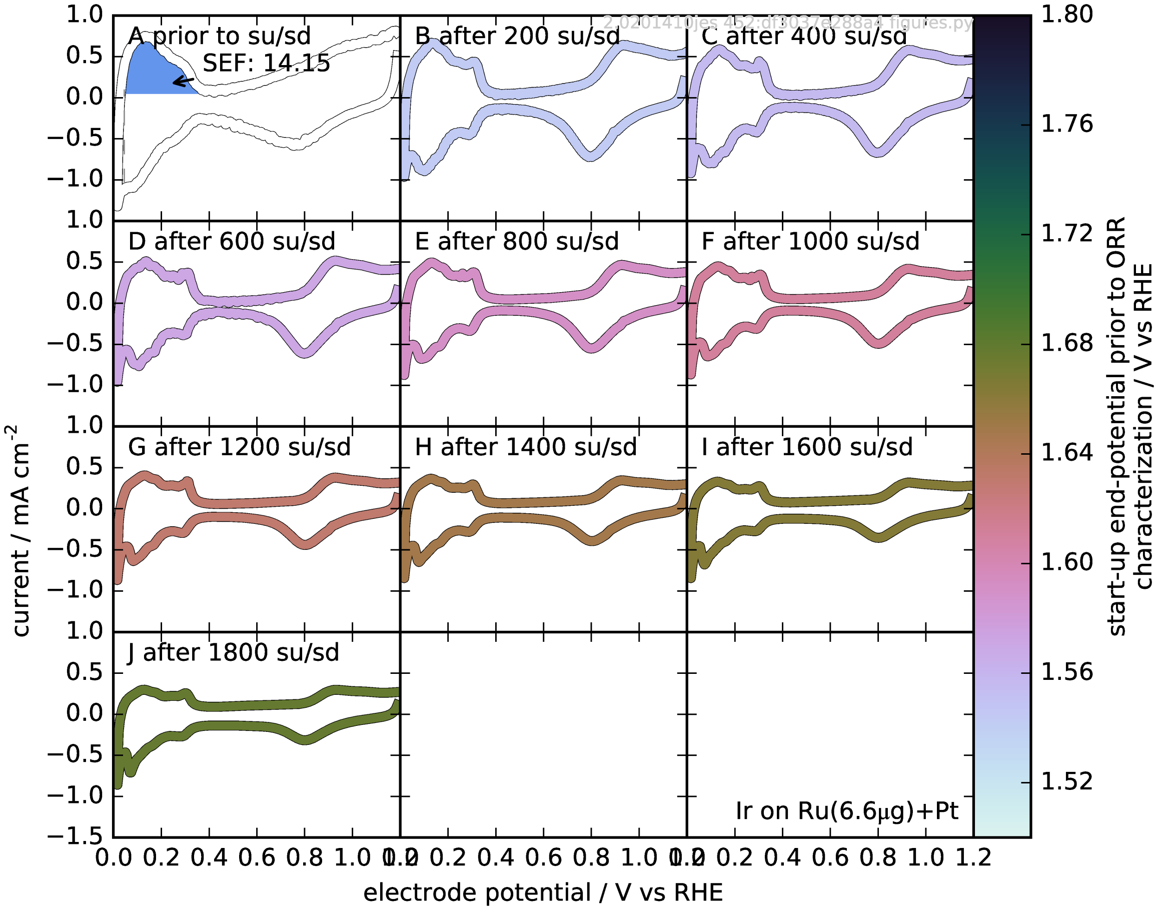


Figure B.16: Ar CVs from the 6 $\mu g_{Ir}\, cm^{-2}$ on 6.6 $\mu g_{Ru}\, cm^{-2}$ intermixed with 85 $\mu g_{Pt}\, cm^{-2}$ sample in Figure 4.16.

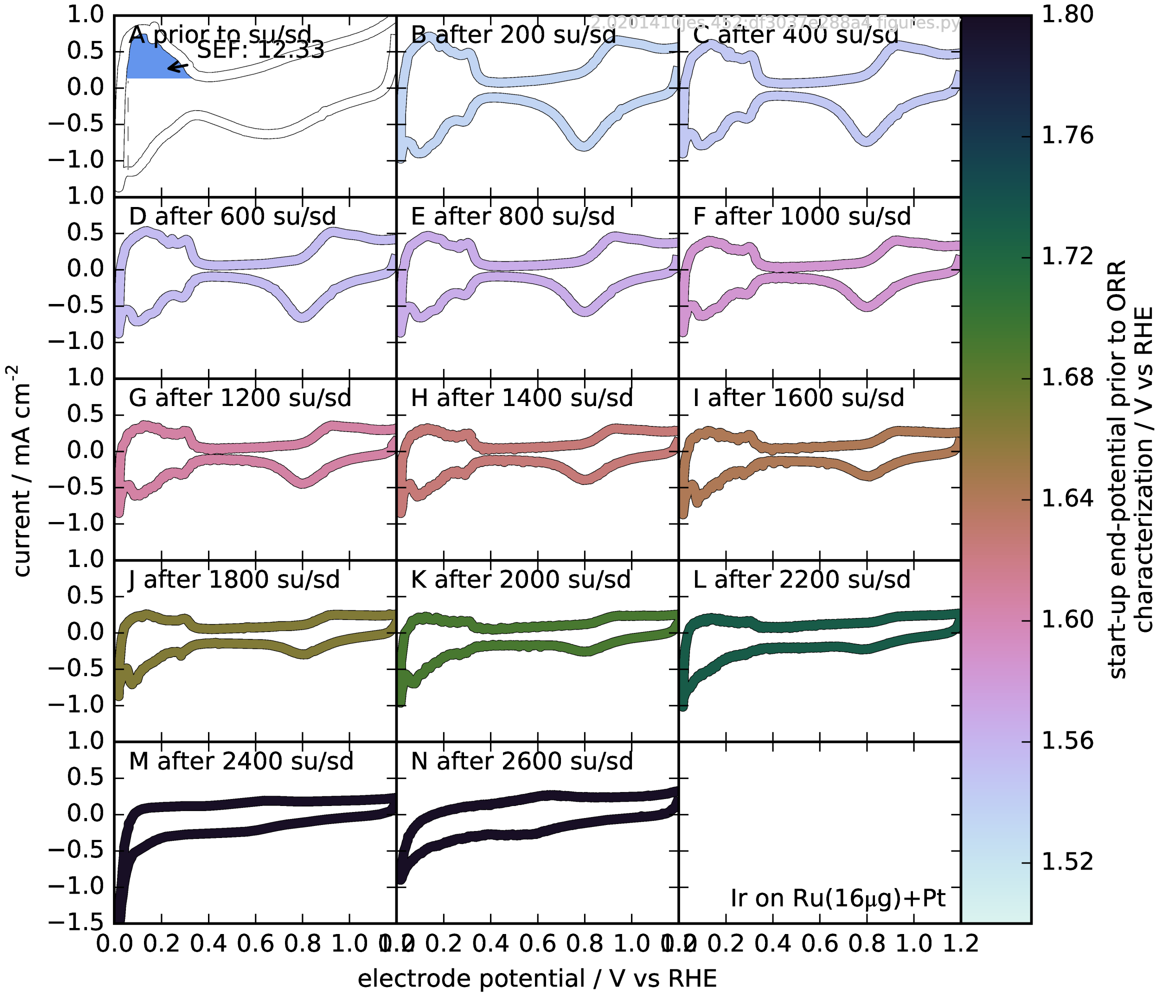


Figure B.17: Ar CVs from the 6 $\mu g_{Ir}\, cm^{-2}$ on 16 $\mu g_{Ru}\, cm^{-2}$ intermixed with 85 $\mu g_{Pt}\, cm^{-2}$ sample in Figure 4.16.

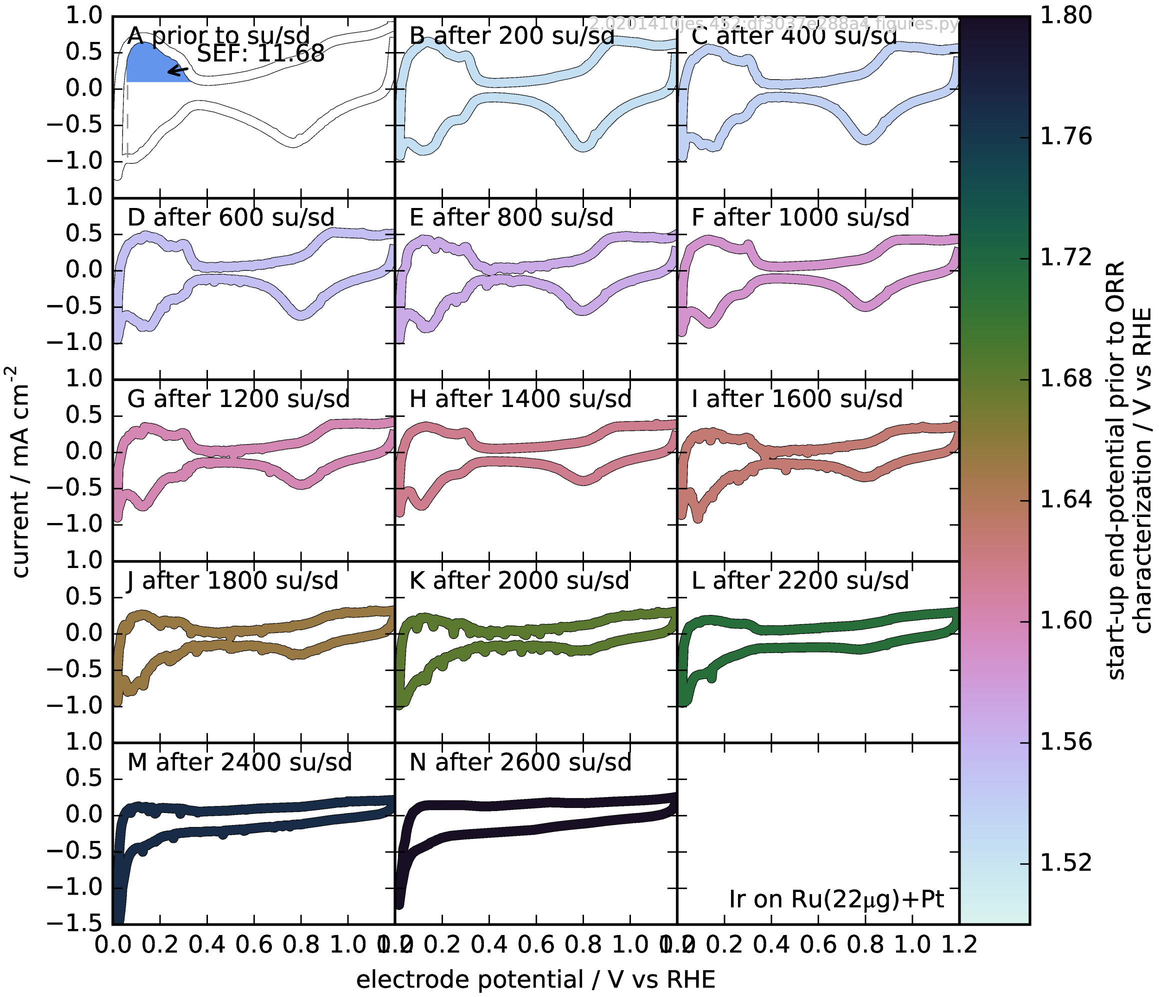


Figure B.18: Ar CVs from the 6 $\mu g_{Ir}\, cm^{-2}$ on 22 $\mu g_{Ru}\, cm^{-2}$ intermixed with 85 $\mu g_{Pt}\, cm^{-2}$ sample in Figure 4.16.

Appendix C

Supporting Information for Chapter 5

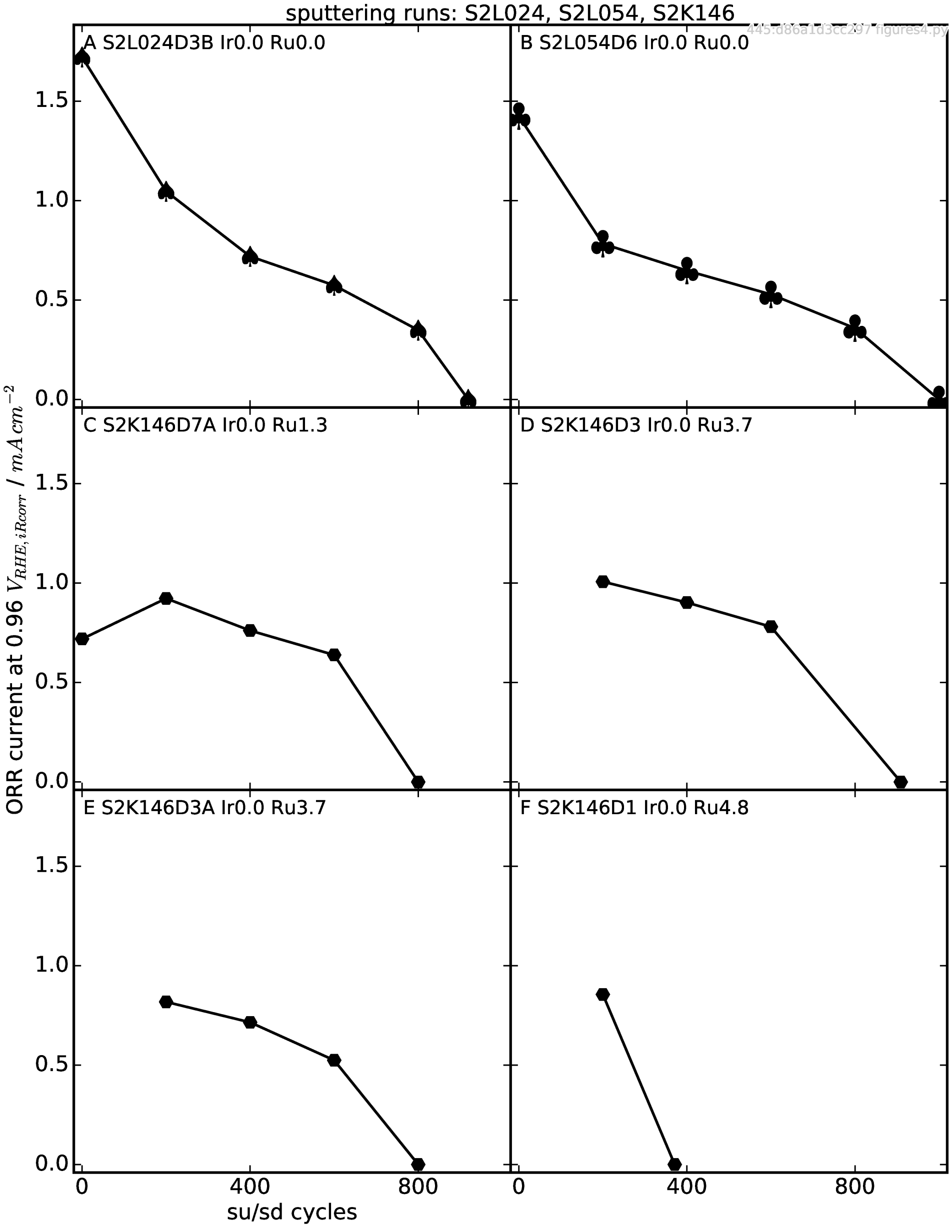


Figure C.1: The ORR activity vs. SU/SD cycles for pure Pt samples (85 $\mu g\, cm^{-2}$, sputtering runs S2L024 and S2L054) and samples from a Ru-ramp ($0 - 5\, \mu g_{Ru}\, cm^{-2}$ on Pt, S2K146) sputtering run.

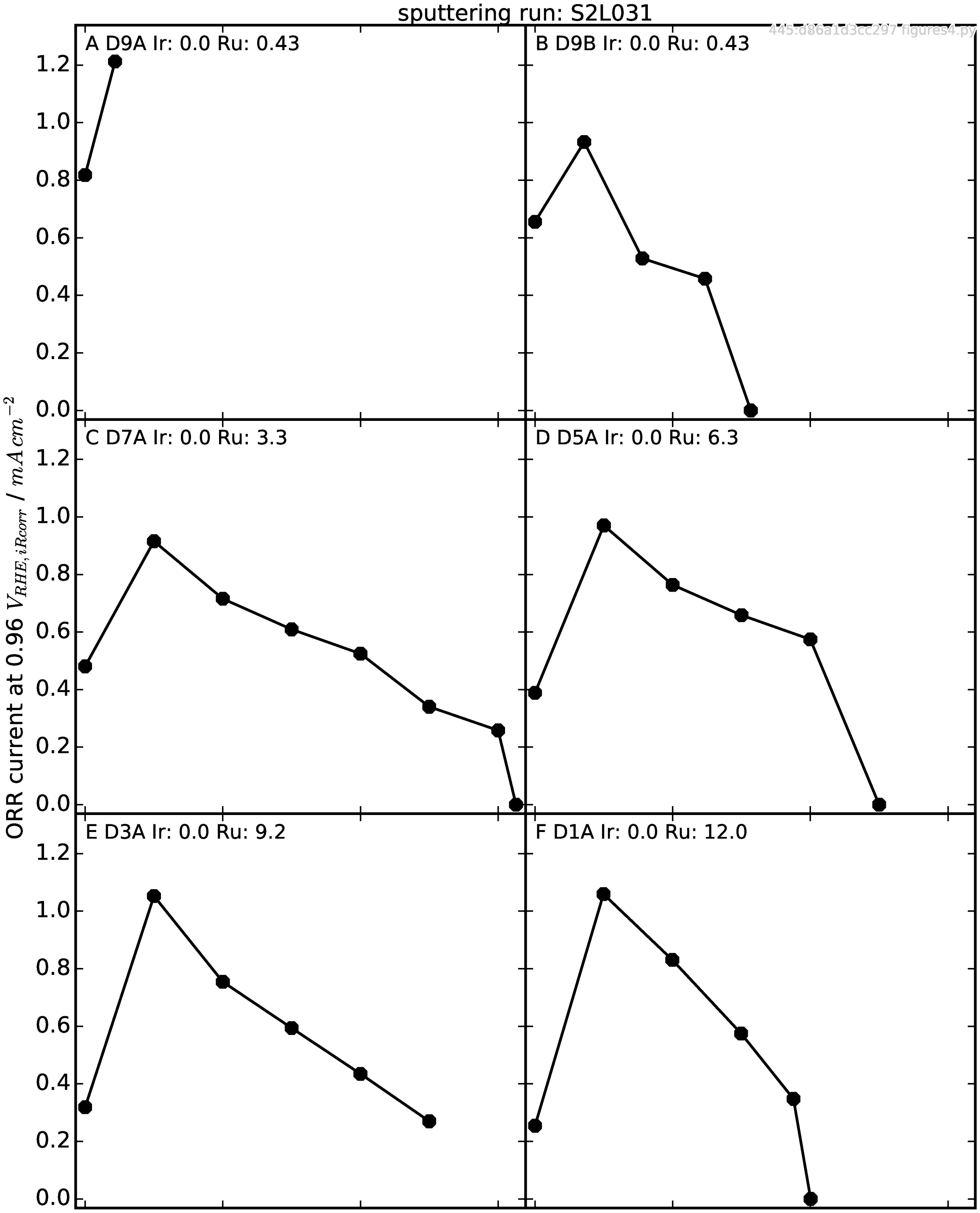


Figure C.2: The ORR activity vs. SU/SD cycles for samples from a Ru-ramp (0 – $12\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2L031) sputtering run.

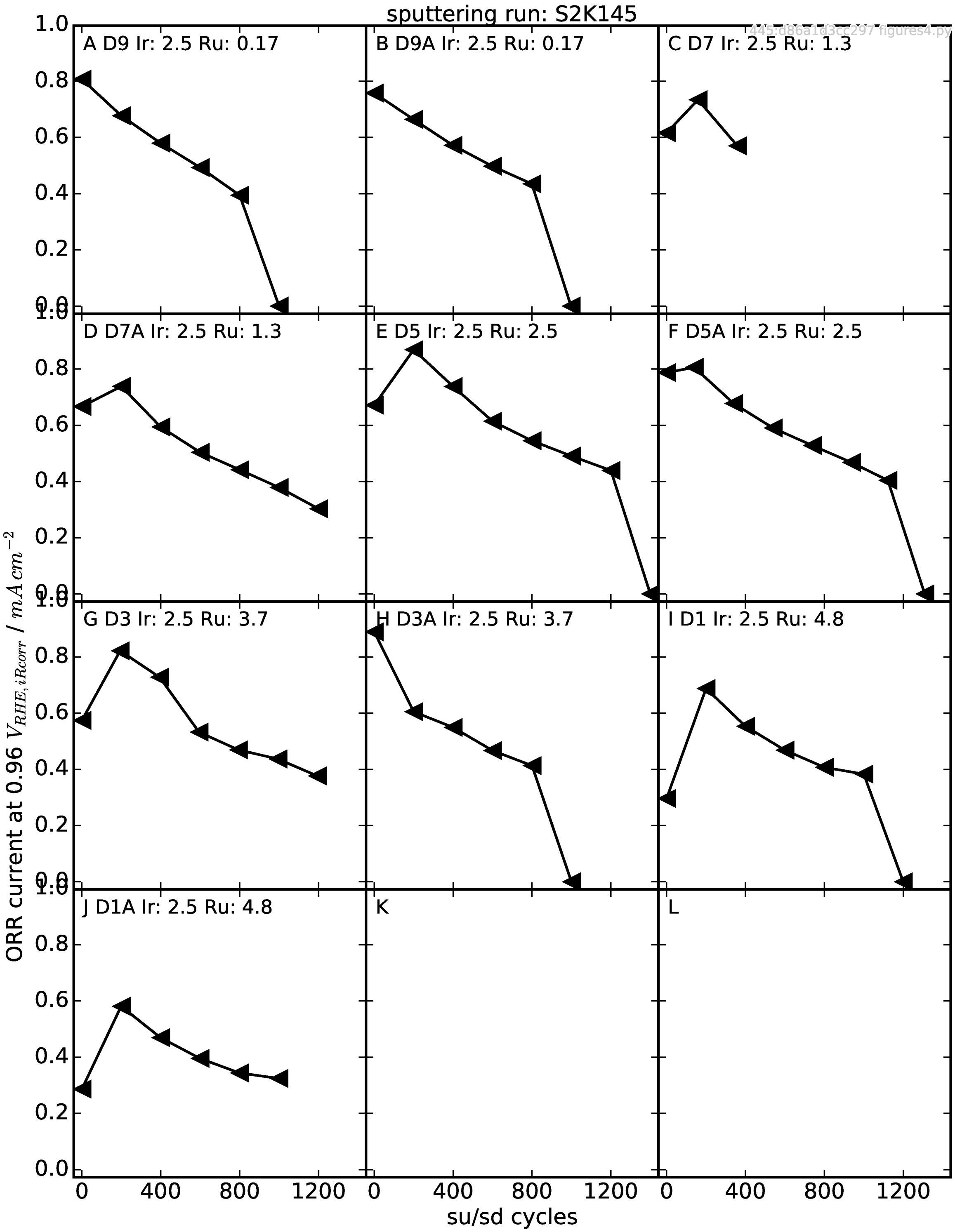


Figure C.3: The ORR activity vs. SU/SD cycles for samples from an Ir on Ru-ramp ($2.5\,\mu g_{Ir}\,cm^{-2}$ on $0-5\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2K145) sputtering run.

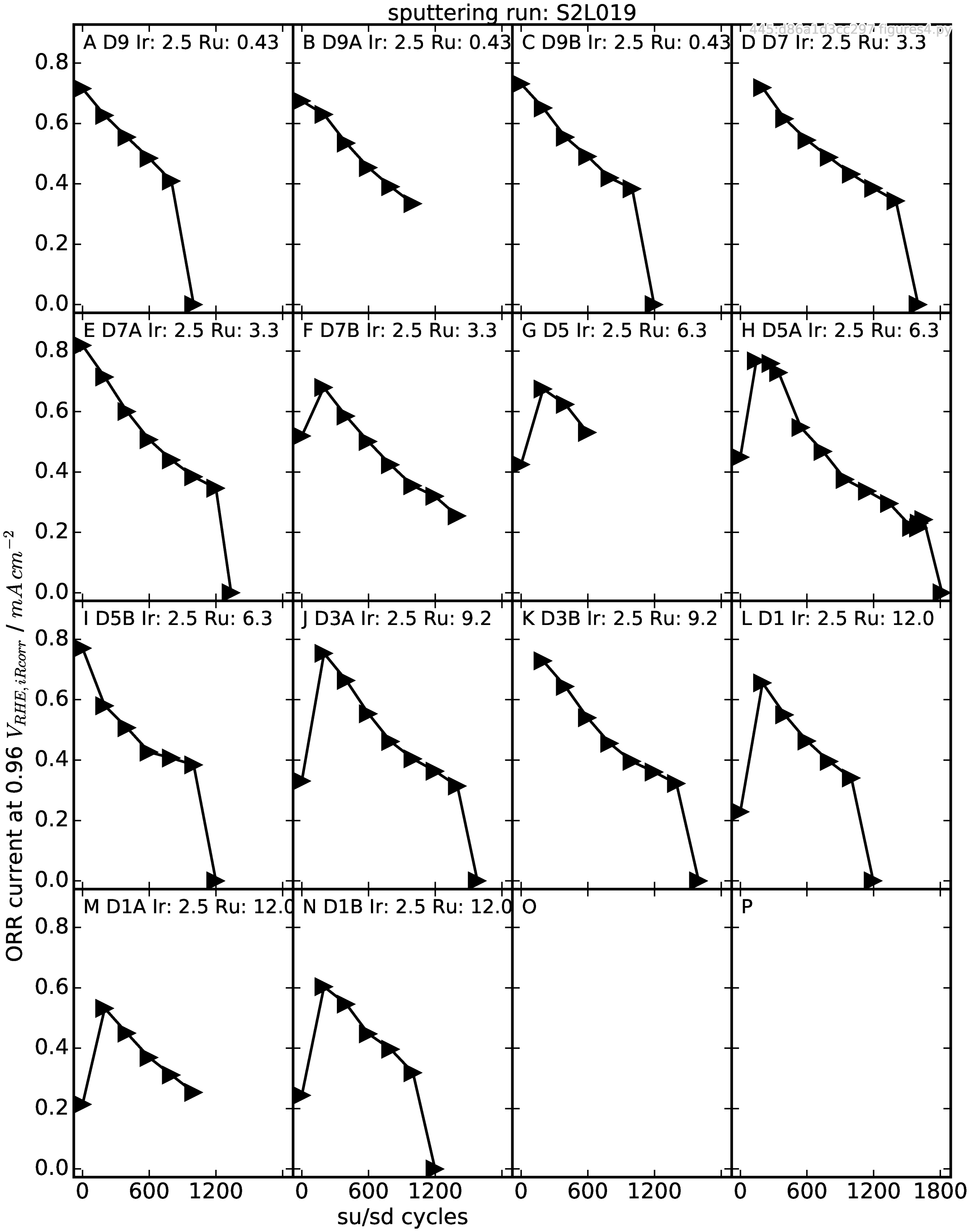


Figure C.4: The ORR activity vs. SU/SD cycles for samples from an Ir on Ru-ramp ($2.5\,\mu g_{Ir}\,cm^{-2}$ on $0-12\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2L019) sputtering run.

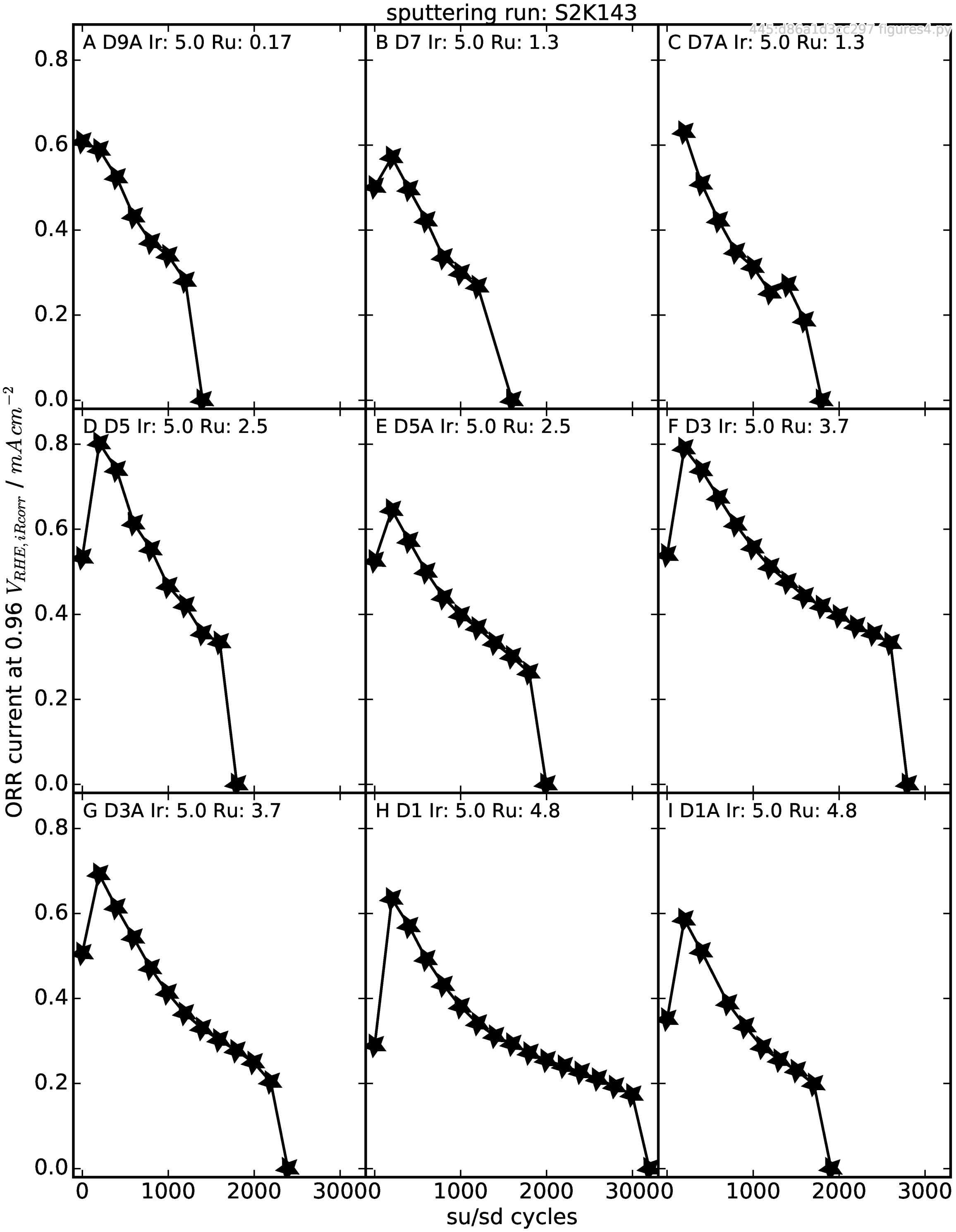


Figure C.5: The ORR activity vs. SU/SD cycles for samples from an Ir on Ru-ramp ($5\,\mu g_{Ir}\,cm^{-2}$ on $0-5\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2K143) sputtering run.

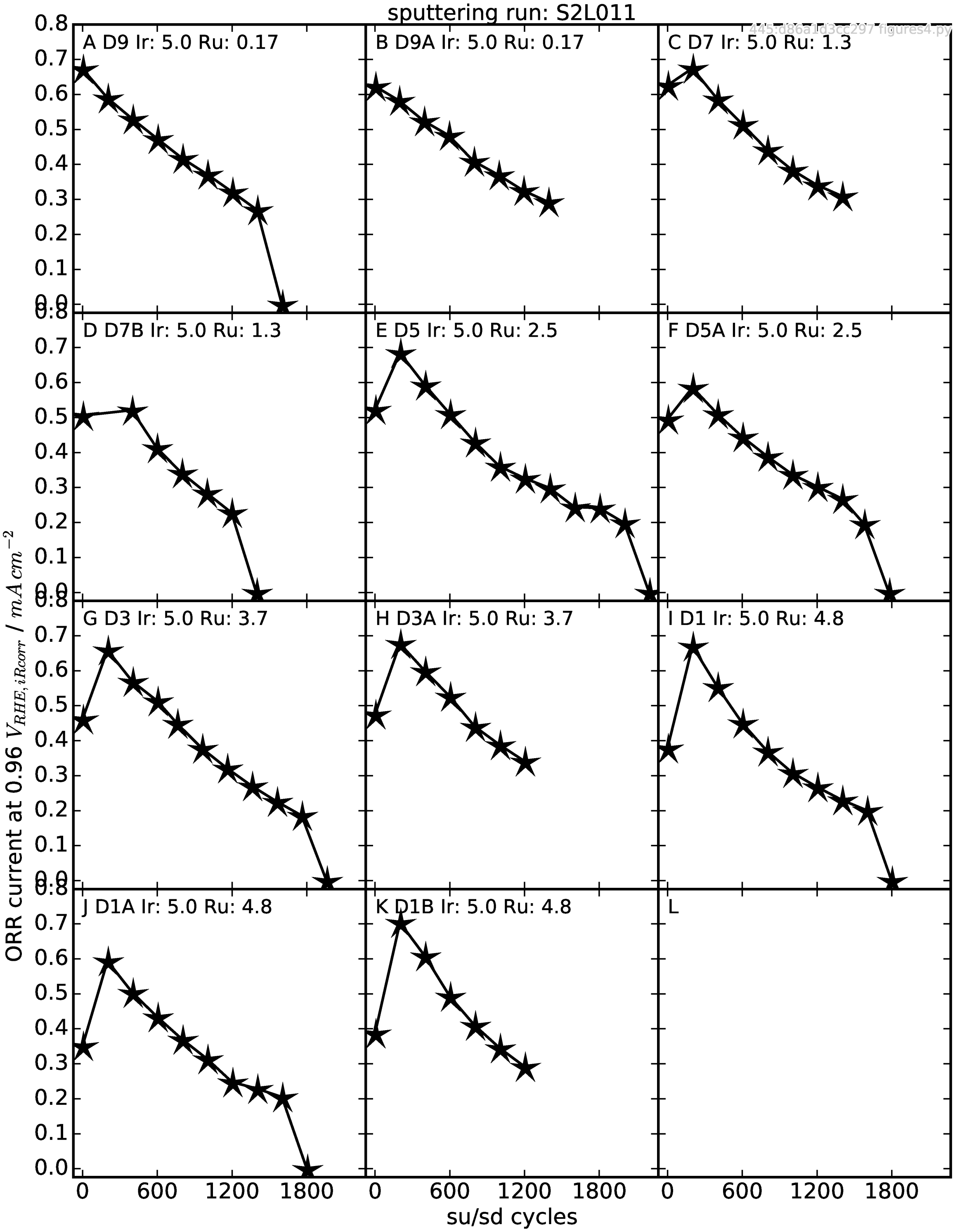


Figure C.6: The ORR activity vs. SU/SD cycles for samples from an Ir on Ru-ramp ($5\,\mu g_{Ir}\,cm^{-2}$ on $0-5\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2L011) sputtering run.

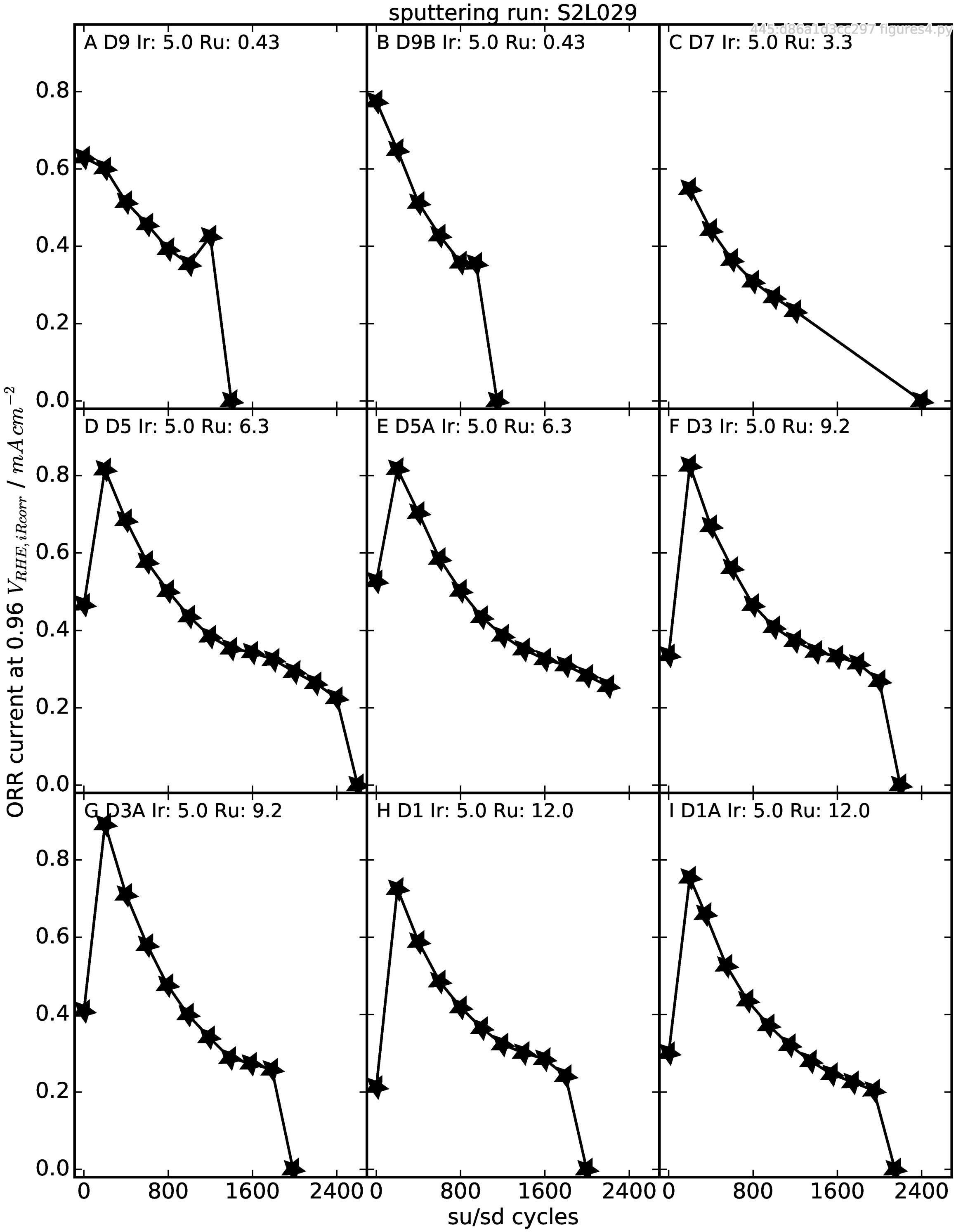


Figure C.7: The ORR activity vs. SU/SD cycles for samples from an Ir on Ru-ramp ($5\,\mu g_{Ir}\,cm^{-2}$ on $0 - 12\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2L029) sputtering run.

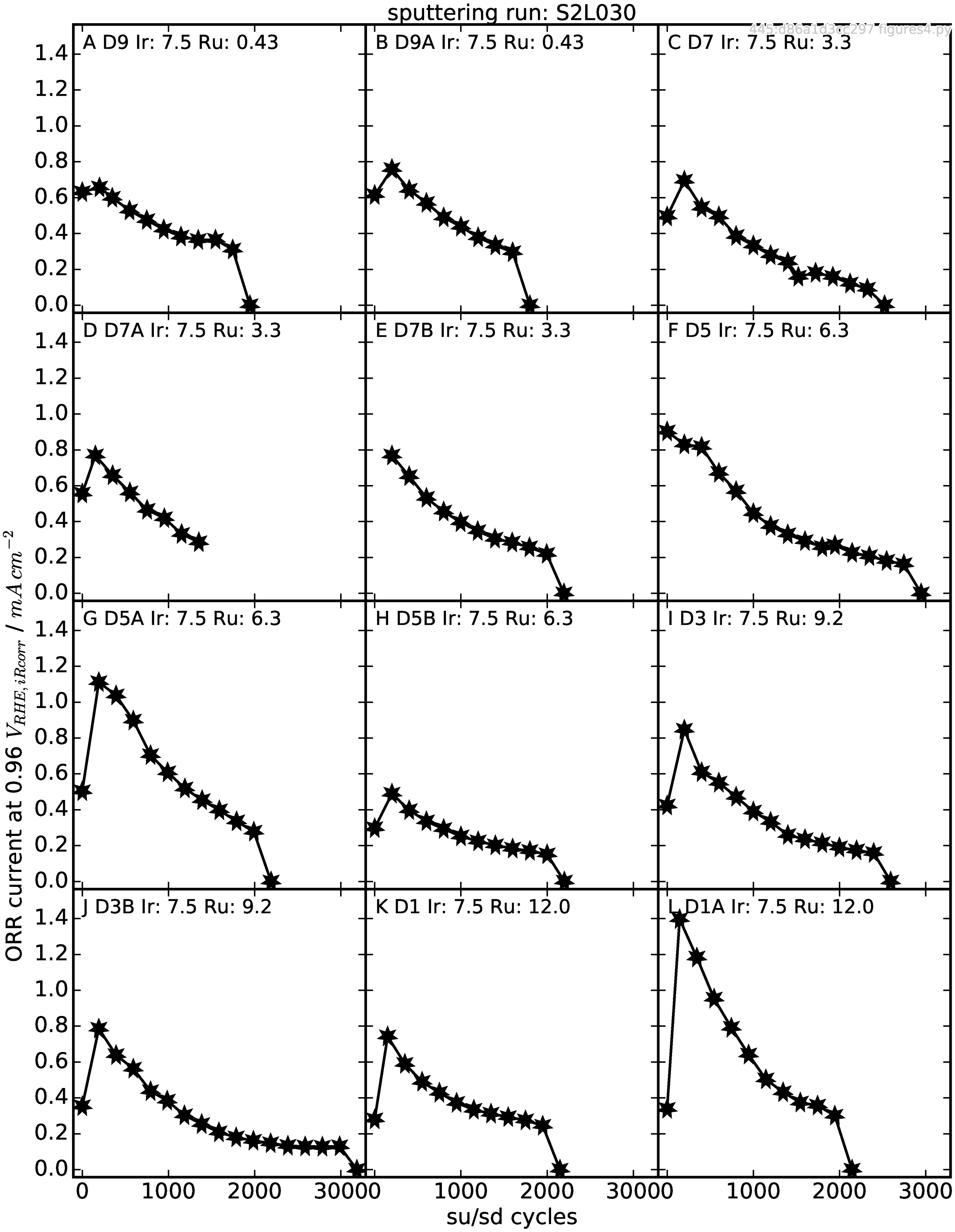


Figure C.8: The ORR activity vs. SU/SD cycles for samples from an Ir on Ru-ramp ($7.5\,\mu g_{Ir}\,cm^{-2}$ on $0-12\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2L029) sputtering run.

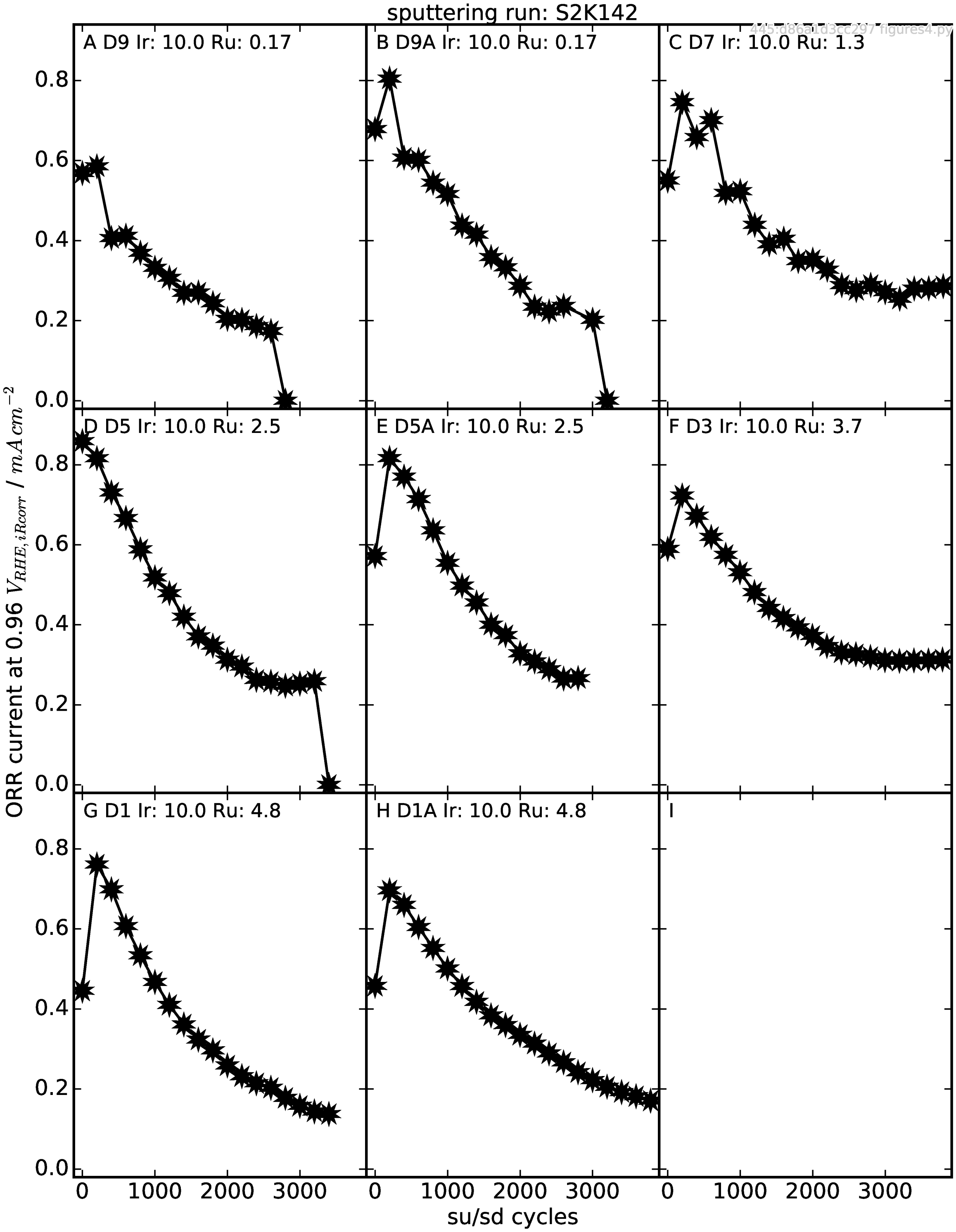


Figure C.9: The ORR activity vs. SU/SD cycles for samples from an Ir on Ru-ramp ($10\,\mu g_{Ir}\,cm^{-2}$ on $0-5\,\mu g_{Ru}\,cm^{-2}$ on Pt, S2K142) sputtering run.

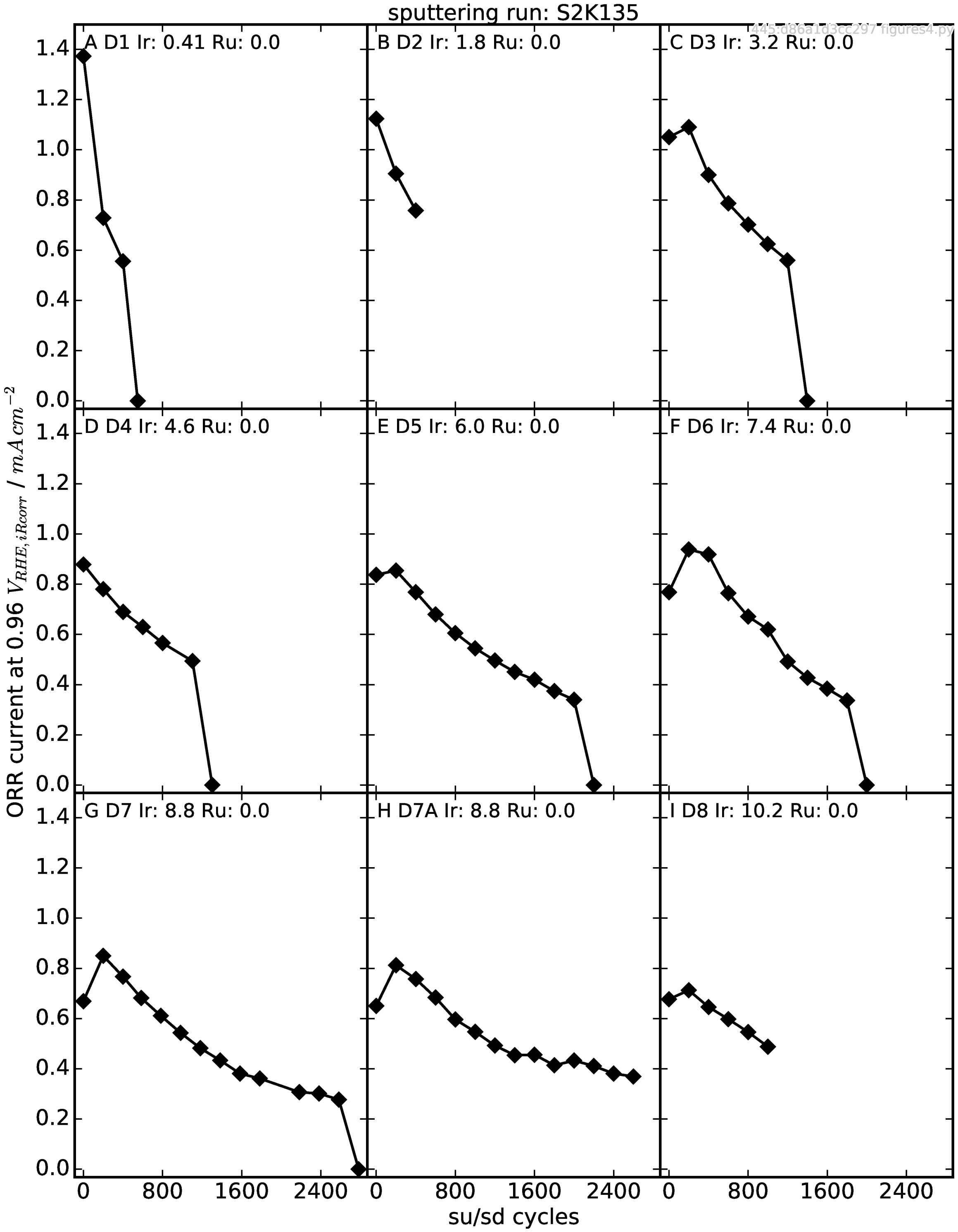


Figure C.10: The ORR activity vs. SU/SD cycles for samples from an Ir-ramp (0 – $12\,\mu g_{Ir}\,cm^{-2}$ on Pt, S2K135) sputtering run.

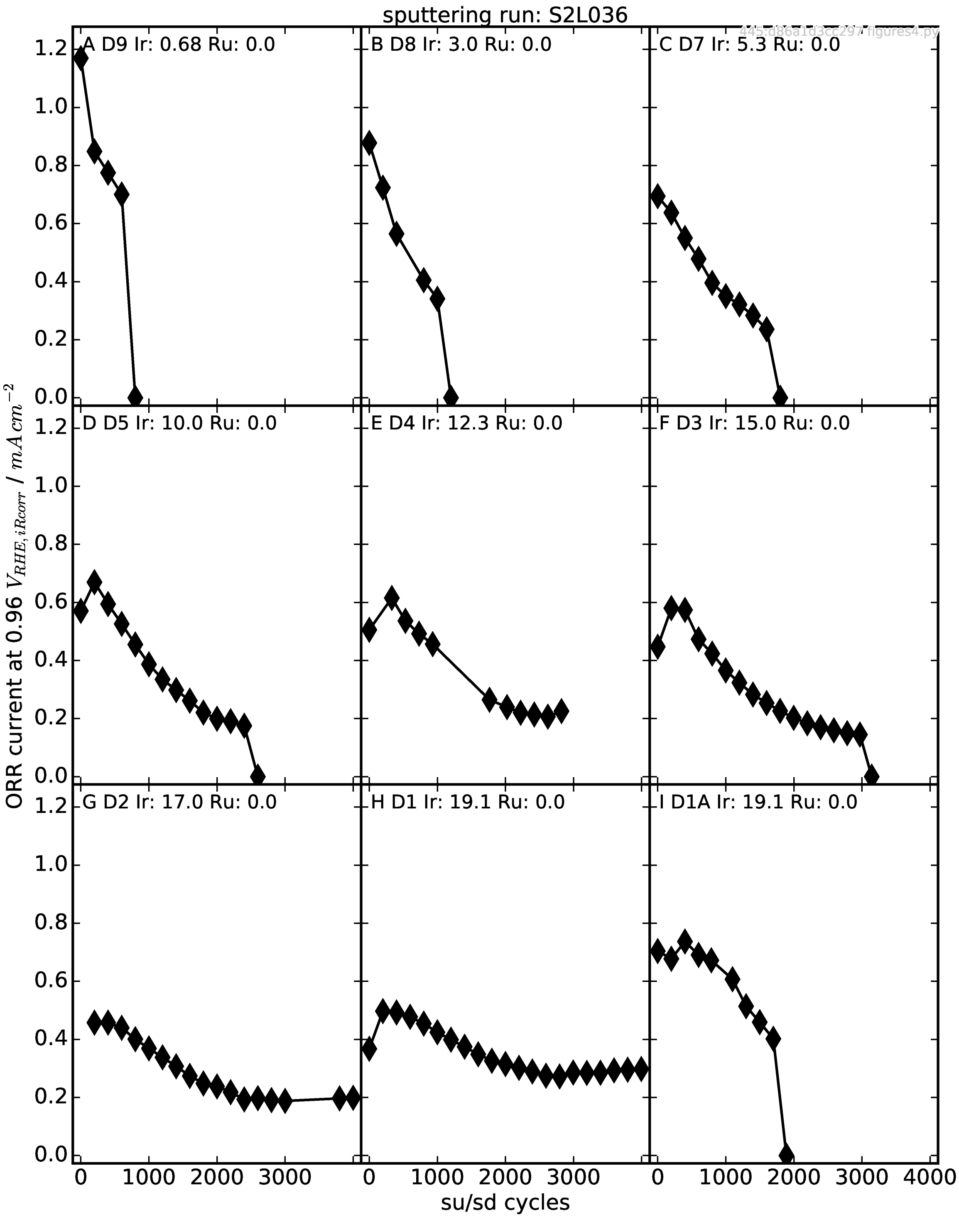
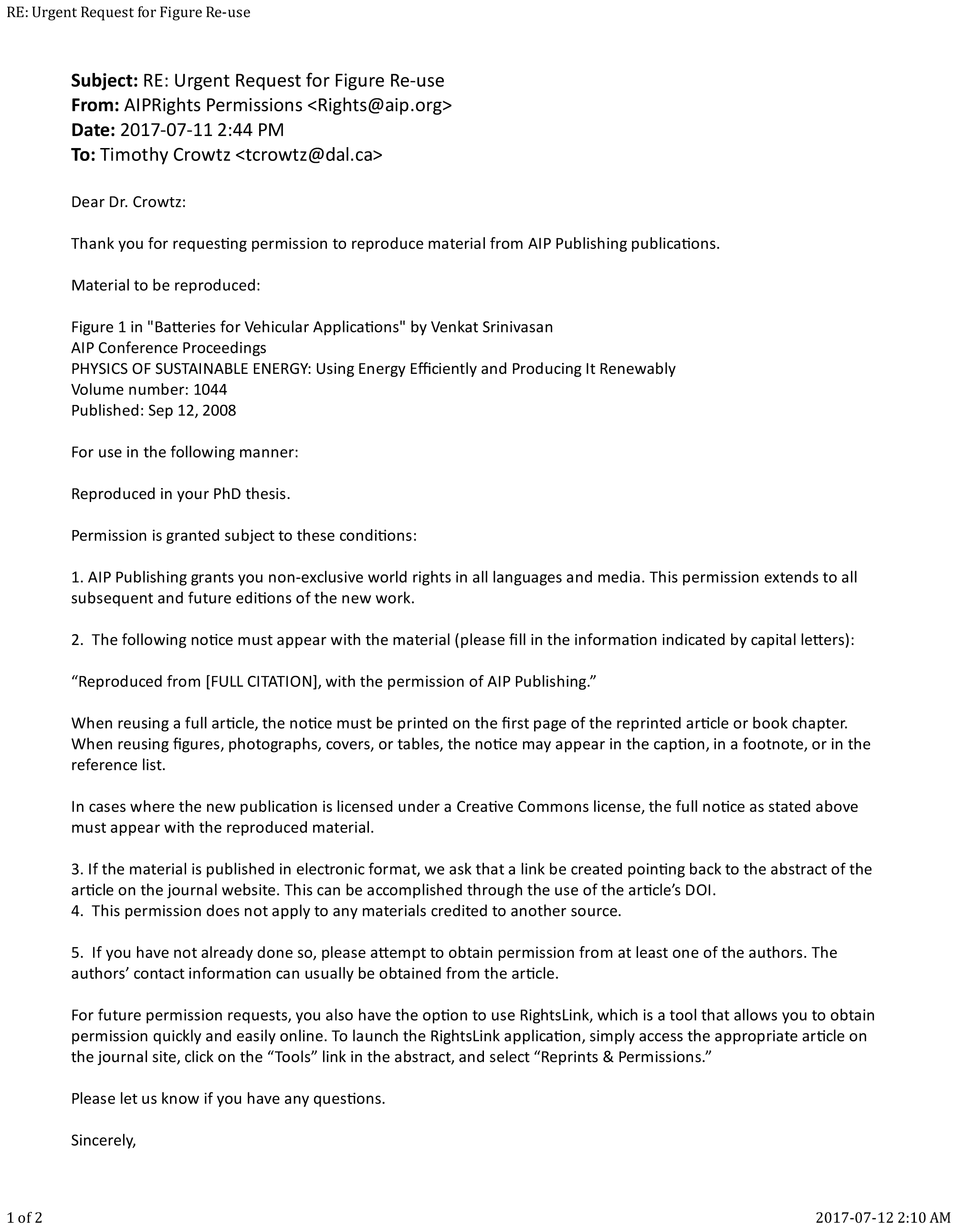


Figure C.11: The ORR activity vs. SU/SD cycles for samples from an Ir-ramp ($0 - 20\,\mu g_{Ir}\,cm^{-2}$ on Pt, S2L036) sputtering run.

Appendix D

Copyright Information

Permission for Figure 1.1



RE: Urgent Request for Figure Re-use

Subject: RE: Urgent Request for Figure Re-use
From: AIPRights Permissions <Rights@aip.org>
Date: 2017-07-11 2:44 PM
To: Timothy Crowtz <tcrowtz@dal.ca>

Dear Dr. Crowtz:

Thank you for requesting permission to reproduce material from AIP Publishing publications.

Material to be reproduced:

Figure 1 in "Batteries for Vehicular Applications" by Venkat Srinivasan
AIP Conference Proceedings
PHYSICS OF SUSTAINABLE ENERGY: Using Energy Efficiently and Producing It Renewably
Volume number: 1044
Published: Sep 12, 2008

For use in the following manner:

Reproduced in your PhD thesis.

Permission is granted subject to these conditions:

1. AIP Publishing grants you non-exclusive world rights in all languages and media. This permission extends to all subsequent and future editions of the new work.

2. The following notice must appear with the material (please fill in the information indicated by capital letters):

“Reproduced from [FULL CITATION], with the permission of AIP Publishing.”

When reusing a full article, the notice must be printed on the first page of the reprinted article or book chapter. When reusing figures, photographs, covers, or tables, the notice may appear in the caption, in a footnote, or in the reference list.

In cases where the new publication is licensed under a Creative Commons license, the full notice as stated above must appear with the reproduced material.

3. If the material is published in electronic format, we ask that a link be created pointing back to the abstract of the article on the journal website. This can be accomplished through the use of the article’s DOI.
4. This permission does not apply to any materials credited to another source.

5. If you have not already done so, please attempt to obtain permission from at least one of the authors. The authors’ contact information can usually be obtained from the article.

For future permission requests, you also have the option to use RightsLink, which is a tool that allows you to obtain permission quickly and easily online. To launch the RightsLink application, simply access the appropriate article on the journal site, click on the “Tools” link in the abstract, and select “Reprints & Permissions.”

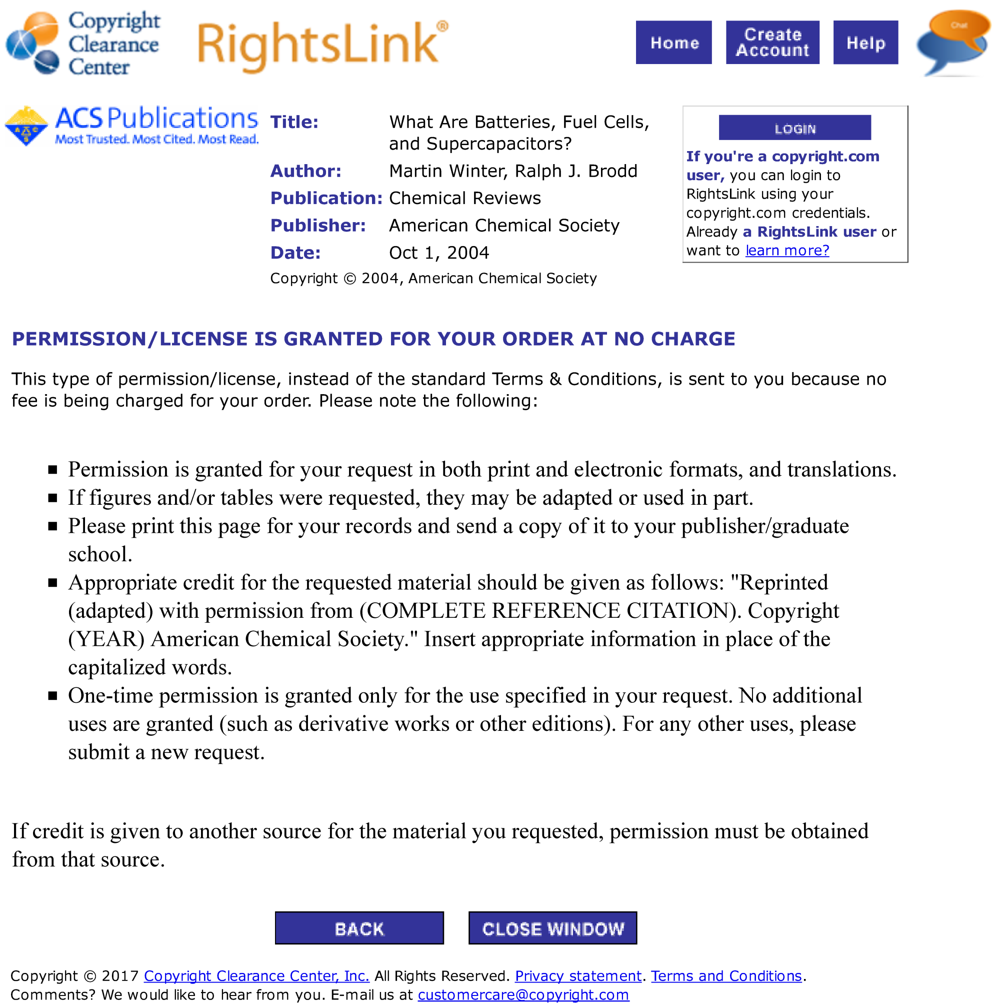
Please let us know if you have any questions.

Sincerely,

1 of 2 2017-07-12 2:10 AM

Permission for Figure 1.2

Rightslink® by Copyright Clearance Center https://s100.copyright.com/AppDispatchServlet



Title: What Are Batteries, Fuel Cells, and Supercapacitors?
Author: Martin Winter, Ralph J. Brodd
Publication: Chemical Reviews
Publisher: American Chemical Society
Date: Oct 1, 2004

Copyright © 2004, American Chemical Society

If you're a copyright.com user, you can login to RightsLink using your copyright.com credentials. Already **a RightsLink user** or want to learn more?

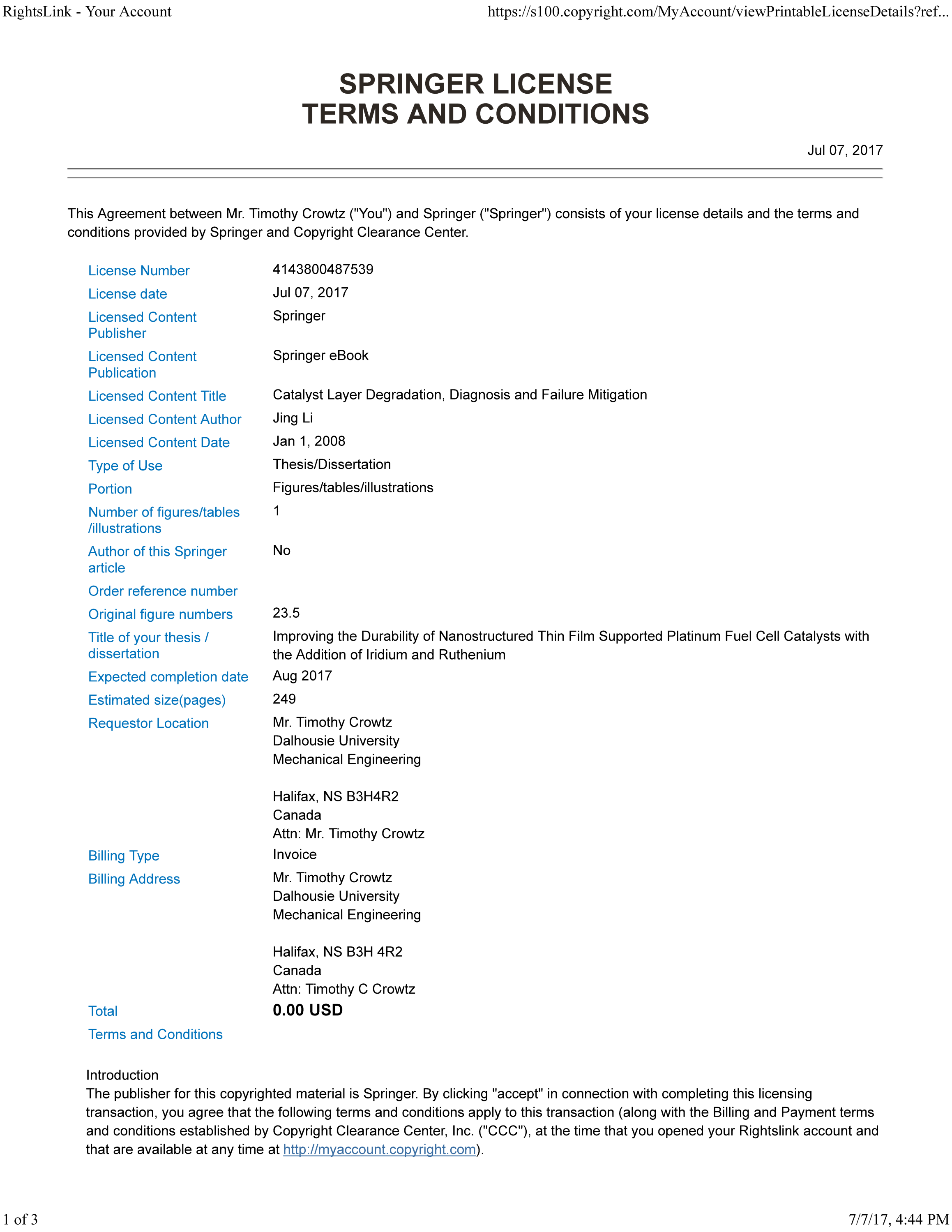
PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

Permission for Figure 1.3



SPRINGER LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This Agreement between Mr. Timothy Crowtz ("You") and Springer ("Springer") consists of your license details and the terms and conditions provided by Springer and Copyright Clearance Center.

License Number	4143800487539
License date	Jul 07, 2017
Licensed Content Publisher	Springer
Licensed Content Publication	Springer eBook
Licensed Content Title	Catalyst Layer Degradation, Diagnosis and Failure Mitigation
Licensed Content Author	Jing Li
Licensed Content Date	Jan 1, 2008
Type of Use	Thesis/Dissertation
Portion	Figures/tables/illustrations
Number of figures/tables /illustrations	1
Author of this Springer article	No
Order reference number	
Original figure numbers	23.5
Title of your thesis / dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size(pages)	249
Requestor Location	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Billing Type	Invoice
Billing Address	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H 4R2 Canada Attn: Timothy C Crowtz
Total	**0.00 USD**
Terms and Conditions	

Introduction
The publisher for this copyrighted material is Springer. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

Limited License
With reference to your request to reuse material on which Springer controls the copyright, permission is granted for the use indicated in your enquiry under the following conditions:
- Licenses are for one-time use only with a maximum distribution equal to the number stated in your request.
- Springer material represents original material which does not carry references to other sources. If the material in question appears with a credit to another source, this permission is not valid and authorization has to be obtained from the original copyright holder.
- This permission
• is non-exclusive
• is only valid if no personal rights, trademarks, or competitive products are infringed.
• explicitly excludes the right for derivatives.
- Springer does not supply original artwork or content.
- According to the format which you have selected, the following conditions apply accordingly:
• Print and Electronic: This License include use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
• Print: This License excludes use in electronic form.
• Electronic: This License only pertains to use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
For any electronic use not mentioned, please contact Springer at permissions.springer@spi-global.com.
- Although Springer controls the copyright to the material and is entitled to negotiate on rights, this license is only valid subject to courtesy information to the author (address is given in the article/chapter).
- If you are an STM Signatory or your work will be published by an STM Signatory and you are requesting to reuse figures/tables /illustrations or single text extracts, permission is granted according to STM Permissions Guidelines: http://www.stm-assoc.org/permissions-guidelines/
For any electronic use not mentioned in the Guidelines, please contact Springer at permissions.springer@spi-global.com. If you request to reuse more content than stipulated in the STM Permissions Guidelines, you will be charged a permission fee for the excess content.
Permission is valid upon payment of the fee as indicated in the licensing process. If permission is granted free of charge on this occasion, that does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.
-If your request is for reuse in a Thesis, permission is granted free of charge under the following conditions:
This license is valid for one-time use only for the purpose of defending your thesis and with a maximum of 100 extra copies in paper. If the thesis is going to be published, permission needs to be reobtained.
- includes use in an electronic form, provided it is an author-created version of the thesis on his/her own website and his/her university's repository, including UMI (according to the definition on the Sherpa website: http://www.sherpa.ac.uk/romeo/);
- is subject to courtesy information to the co-author or corresponding author.
Geographic Rights: Scope
Licenses may be exercised anywhere in the world.
Altering/Modifying Material: Not Permitted
Figures, tables, and illustrations may be altered minimally to serve your work. You may not alter or modify text in any manner. Abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of the author(s).
Reservation of Rights
Springer reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction and (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
License Contingent on Payment
While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by Springer or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received by the date due, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and Springer reserves the right to take any and all action to protect its copyright in the materials.
Copyright Notice: Disclaimer
You must include the following copyright and permission notice in connection with any reproduction of the licensed material: "Springer book/journal title, chapter/article title, volume, year of publication, page, name(s) of author(s), (original copyright notice as given in the publication in which the material was originally published) "With permission of Springer"
In case of use of a graph or illustration, the caption of the graph or illustration must be included, as it is indicated in the original

publication.

Warranties: None

Springer makes no representations or warranties with respect to the licensed material and adopts on its own behalf the limitations and disclaimers established by CCC on its behalf in its Billing and Payment terms and conditions for this licensing transaction.

Indemnity

You hereby indemnify and agree to hold harmless Springer and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

No Transfer of License

This license is personal to you and may not be sublicensed, assigned, or transferred by you without Springer's written permission.

No Amendment Except in Writing

This license may not be amended except in a writing signed by both parties (or, in the case of Springer, by CCC on Springer's behalf).

Objection to Contrary Terms

Springer hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

Jurisdiction

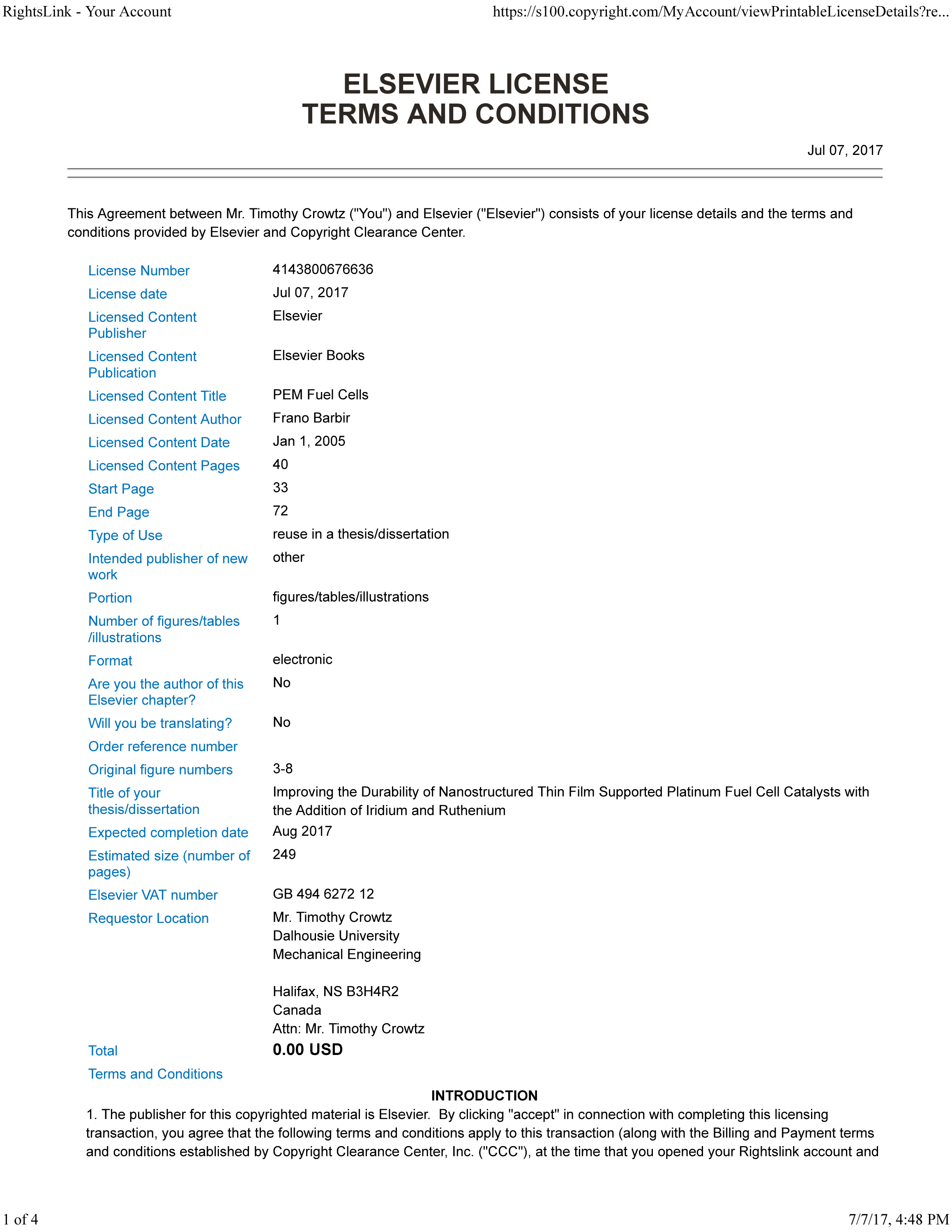
All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in the Federal Republic of Germany, in accordance with German law.

Other conditions:

V 12AUG2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 1.5



ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This Agreement between Mr. Timothy Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4143800676636
License date	Jul 07, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Elsevier Books
Licensed Content Title	PEM Fuel Cells
Licensed Content Author	Frano Barbir
Licensed Content Date	Jan 1, 2005
Licensed Content Pages	40
Start Page	33
End Page	72
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier chapter?	No
Will you be translating?	No
Order reference number	
Original figure numbers	3-8
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and

that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include

permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a

summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

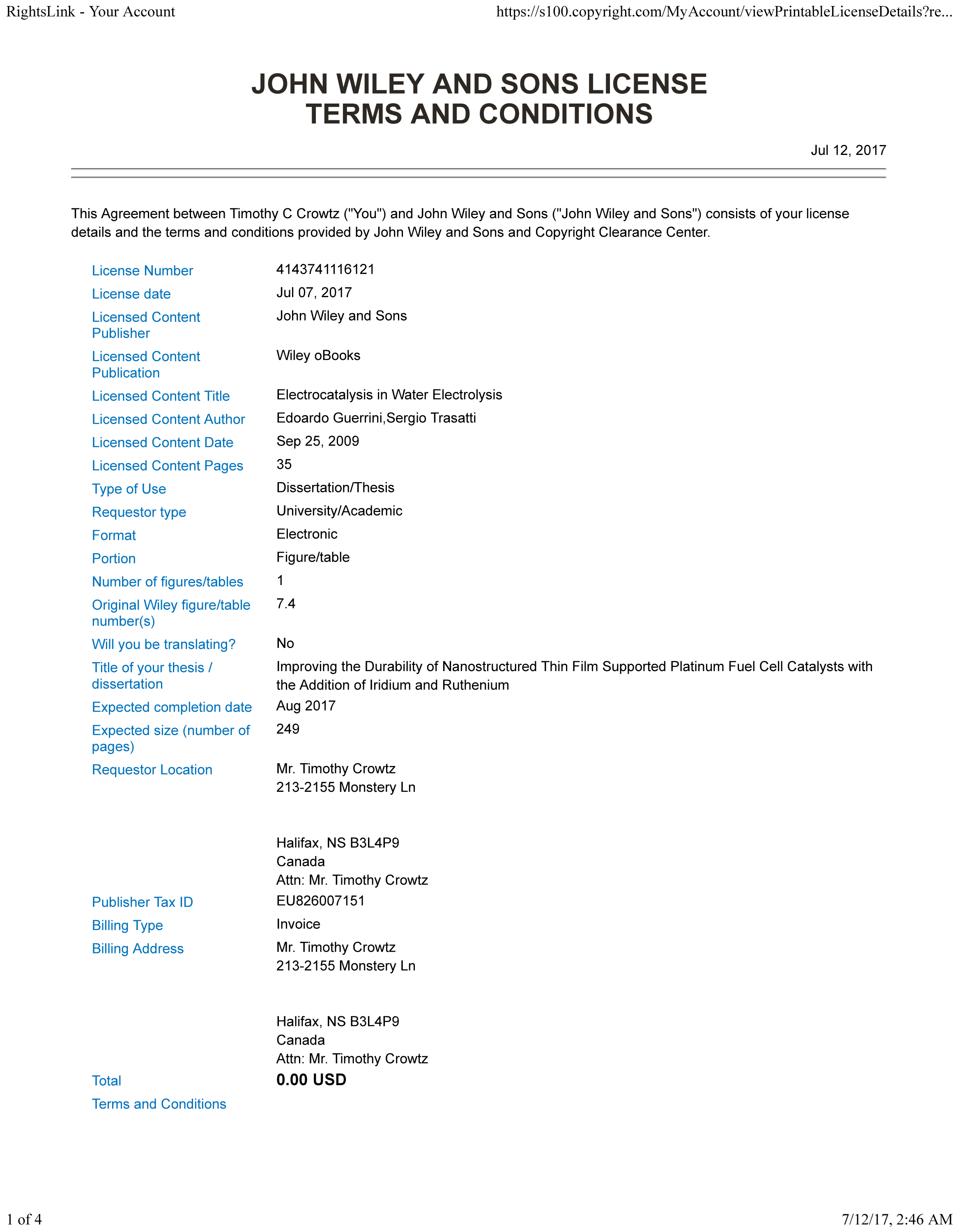
Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 1.6



JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Jul 12, 2017

This Agreement between Timothy C Crowtz ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	4143741116121
License date	Jul 07, 2017
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Wiley oBooks
Licensed Content Title	Electrocatalysis in Water Electrolysis
Licensed Content Author	Edoardo Guerrini,Sergio Trasatti
Licensed Content Date	Sep 25, 2009
Licensed Content Pages	35
Type of Use	Dissertation/Thesis
Requestor type	University/Academic
Format	Electronic
Portion	Figure/table
Number of figures/tables	1
Original Wiley figure/table number(s)	7.4
Will you be translating?	No
Title of your thesis / dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Expected size (number of pages)	249
Requestor Location	Mr. Timothy Crowtz 213-2155 Monstery Ln Halifax, NS B3L4P9 Canada Attn: Mr. Timothy Crowtz
Publisher Tax ID	EU826007151
Billing Type	Invoice
Billing Address	Mr. Timothy Crowtz 213-2155 Monstery Ln Halifax, NS B3L4P9 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a"Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at http://myaccount.copyright.com).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order,** is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner.**For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts,** You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING,

PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS
Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.
The Creative Commons Attribution License
The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-
Creative Commons Attribution Non-Commercial License
The Creative Commons Attribution Non-Commercial (CC-BY-NC)License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License
The Creative Commons Attribution Non-Commercial-NoDerivs License (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)
Use by commercial "for-profit" organizations
Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.
Further details can be found on Wiley Online Library http://olabout.wiley.com/WileyCDA/Section/id-410895.html

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 1.7

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This Agreement between Mr. Timothy Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4143800833288
License date	Jul 07, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Electrochemistry Communications
Licensed Content Title	Avoid the quasi-equilibrium assumption when evaluating the electrocatalytic oxygen evolution reaction mechanism by Tafel slope analysis
Licensed Content Author	Aaron T. Marshall,Laurent Vaisson-Béthune
Licensed Content Date	Dec 1, 2015
Licensed Content Volume	61
Licensed Content Issue	n/a
Licensed Content Pages	4
Start Page	23
End Page	26
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	3
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
    - via their non-commercial person homepage or blog
    - by updating a preprint in arXiv or RePEc with the accepted manuscript
    - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
    - directly by providing copies to their students or to research collaborators for their personal use
    - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
    - via non-commercial hosting platforms such as their institutional repository
    - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.1, 2.20, 2.21, 2.25 and 2.24

Creative Commons Legal Code

Attribution-NonCommercial-NoDerivatives 4.0 International

Official translations of this license are available in other languages.

Creative Commons Corporation (“Creative Commons”) is not a law firm and does not provide legal services or legal advice. Distribution of Creative Commons public licenses does not create a lawyer-client or other relationship. Creative Commons makes its licenses and related information available on an “as-is” basis. Creative Commons gives no warranties regarding its licenses, any material licensed under their terms and conditions, or any related information. Creative Commons disclaims all liability for damages resulting from their use to the fullest extent possible.

Using Creative Commons Public Licenses

Creative Commons public licenses provide a standard set of terms and conditions that creators and other rights holders may use to share original works of authorship and other material subject to copyright and certain other rights specified in the public license below. The following considerations are for informational purposes only, are not exhaustive, and do not form part of our licenses.

> ***Considerations for licensors:*** *Our public licenses are intended for use by those authorized to give the public permission to use material in ways otherwise restricted by copyright and certain other rights. Our licenses are irrevocable. Licensors should read and understand the terms and conditions of the license they choose before applying it. Licensors should also secure all rights necessary before applying our licenses so that the public can reuse the material as expected. Licensors should clearly mark any material not subject to the license. This includes other CC-licensed material, or material used under an exception or limitation to copyright. More considerations for licensors.*
>
> ***Considerations for the public:*** *By using one of our public licenses, a licensor grants the public permission to use the licensed material under specified terms and conditions. If the licensor’s permission is not necessary for any reason–for example, because of any applicable exception or limitation to copyright–then that use is not regulated by the license. Our licenses grant only permissions under copyright and certain other rights that a licensor has authority to grant. Use of the licensed material may still be restricted for other reasons, including because others have copyright or other rights in the material. A licensor may make special requests, such as asking that all changes be marked or described. Although not required by our licenses, you are encouraged to respect those requests where reasonable. More considerations for the public.*

Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International Public License

By exercising the Licensed Rights (defined below), You accept and agree to be bound by the terms and conditions of this Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International Public License ("Public License"). To the extent this Public License may be interpreted as a contract, You are granted the Licensed Rights in consideration of Your acceptance of these terms and conditions, and the Licensor grants You such rights in consideration of benefits the Licensor receives from making the

Licensed Material available under these terms and conditions.

Section 1 – Definitions.

a. **Adapted Material** means material subject to Copyright and Similar Rights that is derived from or based upon the Licensed Material and in which the Licensed Material is translated, altered, arranged, transformed, or otherwise modified in a manner requiring permission under the Copyright and Similar Rights held by the Licensor. For purposes of this Public License, where the Licensed Material is a musical work, performance, or sound recording, Adapted Material is always produced where the Licensed Material is synched in timed relation with a moving image.
b. **Copyright and Similar Rights** means copyright and/or similar rights closely related to copyright including, without limitation, performance, broadcast, sound recording, and Sui Generis Database Rights, without regard to how the rights are labeled or categorized. For purposes of this Public License, the rights specified in Section 2(b)(1)-(2) are not Copyright and Similar Rights.
c. **Effective Technological Measures** means those measures that, in the absence of proper authority, may not be circumvented under laws fulfilling obligations under Article 11 of the WIPO Copyright Treaty adopted on December 20, 1996, and/or similar international agreements.
d. **Exceptions and Limitations** means fair use, fair dealing, and/or any other exception or limitation to Copyright and Similar Rights that applies to Your use of the Licensed Material.
e. **Licensed Material** means the artistic or literary work, database, or other material to which the Licensor applied this Public License.
f. **Licensed Rights** means the rights granted to You subject to the terms and conditions of this Public License, which are limited to all Copyright and Similar Rights that apply to Your use of the Licensed Material and that the Licensor has authority to license.
g. **Licensor** means the individual(s) or entity(ies) granting rights under this Public License.
h. **NonCommercial** means not primarily intended for or directed towards commercial advantage or monetary compensation. For purposes of this Public License, the exchange of the Licensed Material for other material subject to Copyright and Similar Rights by digital file-sharing or similar means is NonCommercial provided there is no payment of monetary compensation in connection with the exchange.
i. **Share** means to provide material to the public by any means or process that requires permission under the Licensed Rights, such as reproduction, public display, public performance, distribution, dissemination, communication, or importation, and to make material available to the public including in ways that members of the public may access the material from a place and at a time individually chosen by them.
j. **Sui Generis Database Rights** means rights other than copyright resulting from Directive 96/9/EC of the European Parliament and of the Council of 11 March 1996 on the legal protection of databases, as amended and/or succeeded, as well as other essentially equivalent rights anywhere in the world.
k. **You** means the individual or entity exercising the Licensed Rights under this Public License. **Your** has a corresponding meaning.

Section 2 – Scope.

a. **License grant**.
    1. Subject to the terms and conditions of this Public License, the Licensor hereby grants You a worldwide, royalty-free, non-sublicensable, non-exclusive, irrevocable license to exercise the Licensed Rights in the Licensed Material to:
        A. reproduce and Share the Licensed Material, in whole or in part, for NonCommercial purposes only; and
        B. produce and reproduce, but not Share, Adapted Material for NonCommercial purposes only.
    2. Exceptions and Limitations. For the avoidance of doubt, where Exceptions and Limitations apply to Your use, this Public License does not apply, and You do not need to comply with its terms and conditions.
    3. Term. The term of this Public License is specified in Section 6(a).
    4. Media and formats; technical modifications allowed. The Licensor authorizes You to exercise the Licensed Rights in all media and formats whether now known or hereafter created, and to make technical modifications necessary to do so. The Licensor waives and/or agrees not to assert any right or authority to forbid You from making technical

modifications necessary to exercise the Licensed Rights, including technical modifications necessary to circumvent Effective Technological Measures. For purposes of this Public License, simply making modifications authorized by this Section 2(a)(4) never produces Adapted Material.

5. Downstream recipients.
    - A. Offer from the Licensor – Licensed Material. Every recipient of the Licensed Material automatically receives an offer from the Licensor to exercise the Licensed Rights under the terms and conditions of this Public License.
    - B. No downstream restrictions. You may not offer or impose any additional or different terms or conditions on, or apply any Effective Technological Measures to, the Licensed Material if doing so restricts exercise of the Licensed Rights by any recipient of the Licensed Material.
6. No endorsement. Nothing in this Public License constitutes or may be construed as permission to assert or imply that You are, or that Your use of the Licensed Material is, connected with, or sponsored, endorsed, or granted official status by, the Licensor or others designated to receive attribution as provided in Section 3(a)(1)(A)(i).

b. **Other rights**.

1. Moral rights, such as the right of integrity, are not licensed under this Public License, nor are publicity, privacy, and/or other similar personality rights; however, to the extent possible, the Licensor waives and/or agrees not to assert any such rights held by the Licensor to the limited extent necessary to allow You to exercise the Licensed Rights, but not otherwise.
2. Patent and trademark rights are not licensed under this Public License.
3. To the extent possible, the Licensor waives any right to collect royalties from You for the exercise of the Licensed Rights, whether directly or through a collecting society under any voluntary or waivable statutory or compulsory licensing scheme. In all other cases the Licensor expressly reserves any right to collect such royalties, including when the Licensed Material is used other than for NonCommercial purposes.

Section 3 – License Conditions.

Your exercise of the Licensed Rights is expressly made subject to the following conditions.

a. **Attribution**.

1. If You Share the Licensed Material, You must:
    - A. retain the following if it is supplied by the Licensor with the Licensed Material:
        - i. identification of the creator(s) of the Licensed Material and any others designated to receive attribution, in any reasonable manner requested by the Licensor (including by pseudonym if designated);
        - ii. a copyright notice;
        - iii. a notice that refers to this Public License;
        - iv. a notice that refers to the disclaimer of warranties;
        - v. a URI or hyperlink to the Licensed Material to the extent reasonably practicable;
    - B. indicate if You modified the Licensed Material and retain an indication of any previous modifications; and
    - C. indicate the Licensed Material is licensed under this Public License, and include the text of, or the URI or hyperlink to, this Public License.

    For the avoidance of doubt, You do not have permission under this Public License to Share Adapted Material.
2. You may satisfy the conditions in Section 3(a)(1) in any reasonable manner based on the medium, means, and context in which You Share the Licensed Material. For example, it may be reasonable to satisfy the conditions by providing a URI or hyperlink to a resource that includes the required information.
3. If requested by the Licensor, You must remove any of the information required by Section 3(a)(1)(A) to the extent reasonably practicable.

Section 4 – Sui Generis Database Rights.

Where the Licensed Rights include Sui Generis Database Rights that apply to Your use of the Licensed Material:

a. for the avoidance of doubt, Section 2(a)(1) grants You the right to extract, reuse, reproduce, and Share all or a substantial portion of the contents of the database for NonCommercial purposes only and provided You do not Share Adapted Material;
b. if You include all or a substantial portion of the database contents in a database in which You have Sui Generis Database Rights, then the database in which You have Sui Generis Database Rights (but not its individual contents) is Adapted Material; and
c. You must comply with the conditions in Section 3(a) if You Share all or a substantial portion of the contents of the database.

For the avoidance of doubt, this Section 4 supplements and does not replace Your obligations under this Public License where the Licensed Rights include other Copyright and Similar Rights.

Section 5 – Disclaimer of Warranties and Limitation of Liability.

a. **Unless otherwise separately undertaken by the Licensor, to the extent possible, the Licensor offers the Licensed Material as-is and as-available, and makes no representations or warranties of any kind concerning the Licensed Material, whether express, implied, statutory, or other. This includes, without limitation, warranties of title, merchantability, fitness for a particular purpose, non-infringement, absence of latent or other defects, accuracy, or the presence or absence of errors, whether or not known or discoverable. Where disclaimers of warranties are not allowed in full or in part, this disclaimer may not apply to You.**
b. **To the extent possible, in no event will the Licensor be liable to You on any legal theory (including, without limitation, negligence) or otherwise for any direct, special, indirect, incidental, consequential, punitive, exemplary, or other losses, costs, expenses, or damages arising out of this Public License or use of the Licensed Material, even if the Licensor has been advised of the possibility of such losses, costs, expenses, or damages. Where a limitation of liability is not allowed in full or in part, this limitation may not apply to You.**

c. The disclaimer of warranties and limitation of liability provided above shall be interpreted in a manner that, to the extent possible, most closely approximates an absolute disclaimer and waiver of all liability.

Section 6 – Term and Termination.

a. This Public License applies for the term of the Copyright and Similar Rights licensed here. However, if You fail to comply with this Public License, then Your rights under this Public License terminate automatically.

b. Where Your right to use the Licensed Material has terminated under Section 6(a), it reinstates:

   1. automatically as of the date the violation is cured, provided it is cured within 30 days of Your discovery of the violation; or
   2. upon express reinstatement by the Licensor.

   For the avoidance of doubt, this Section 6(b) does not affect any right the Licensor may have to seek remedies for Your violations of this Public License.
c. For the avoidance of doubt, the Licensor may also offer the Licensed Material under separate terms or conditions or stop distributing the Licensed Material at any time; however, doing so will not terminate this Public License.
d. Sections 1, 5, 6, 7, and 8 survive termination of this Public License.

Section 7 – Other Terms and Conditions.

a. The Licensor shall not be bound by any additional or different terms or conditions communicated by You unless expressly agreed.
b. Any arrangements, understandings, or agreements regarding the Licensed Material not stated

herein are separate from and independent of the terms and conditions of this Public License.

Section 8 – Interpretation.

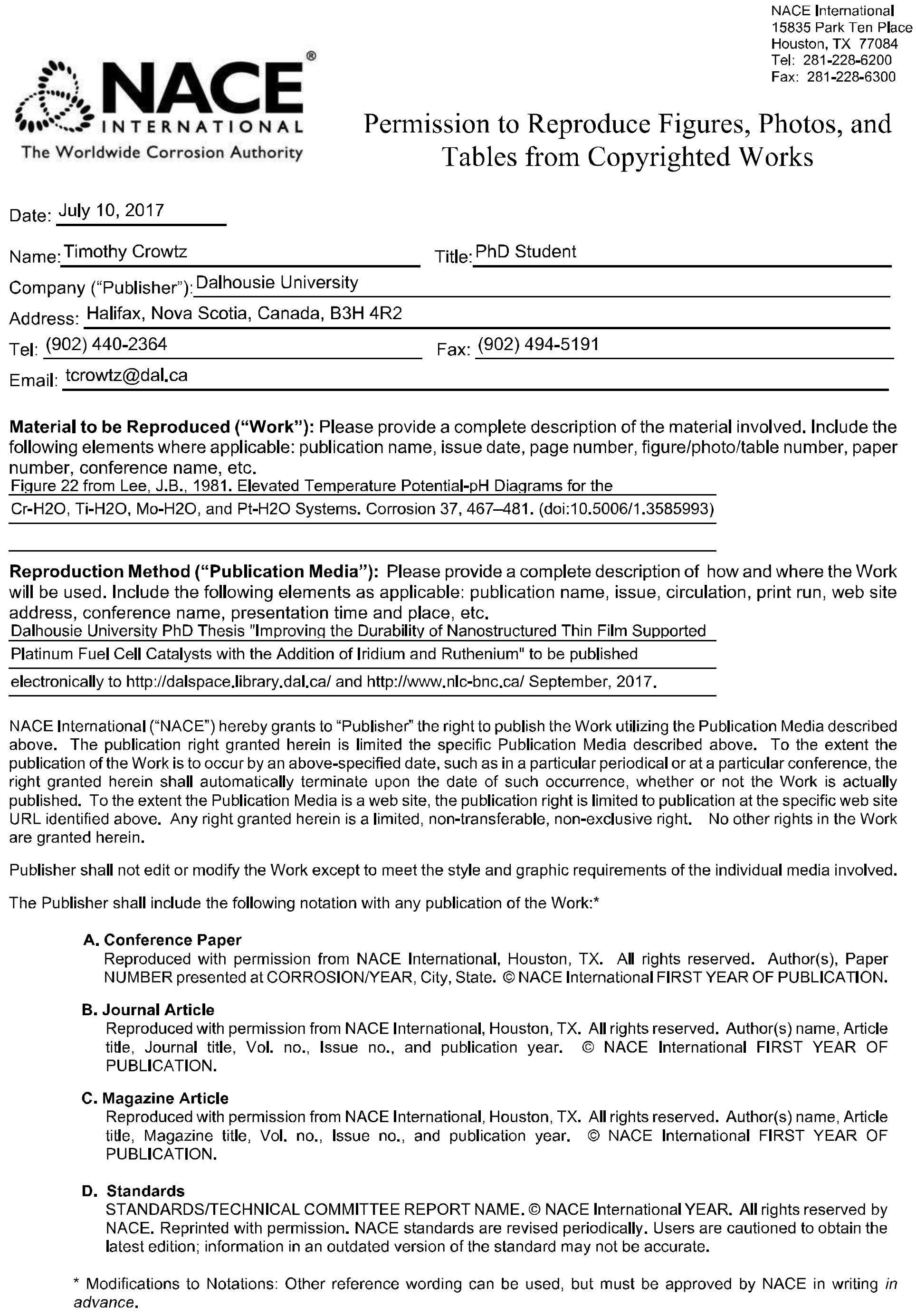
a. For the avoidance of doubt, this Public License does not, and shall not be interpreted to, reduce, limit, restrict, or impose conditions on any use of the Licensed Material that could lawfully be made without permission under this Public License.
b. To the extent possible, if any provision of this Public License is deemed unenforceable, it shall be automatically reformed to the minimum extent necessary to make it enforceable. If the provision cannot be reformed, it shall be severed from this Public License without affecting the enforceability of the remaining terms and conditions.
c. No term or condition of this Public License will be waived and no failure to comply consented to unless expressly agreed to by the Licensor.
d. Nothing in this Public License constitutes or may be interpreted as a limitation upon, or waiver of, any privileges and immunities that apply to the Licensor or You, including from the legal processes of any jurisdiction or authority.

Creative Commons is not a party to its public licenses. Notwithstanding, Creative Commons may elect to apply one of its public licenses to material it publishes and in those instances will be considered the “Licensor.” The text of the Creative Commons public licenses is dedicated to the public domain under the CC0 Public Domain Dedication. Except for the limited purpose of indicating that material is shared under a Creative Commons public license or as otherwise permitted by the Creative Commons policies published at creativecommons.org/policies, Creative Commons does not authorize the use of the trademark “Creative Commons” or any other trademark or logo of Creative Commons without its prior written consent including, without limitation, in connection with any unauthorized modifications to any of its public licenses or any other arrangements, understandings, or agreements concerning use of licensed material. For the avoidance of doubt, this paragraph does not form part of the public licenses.

Creative Commons may be contacted at creativecommons.org.

Additional languages available: Bahasa Indonesia, Deutsch, français, hrvatski, Nederlands, norsk, polski, suomeksi, svenska, te reo Māori, Türkçe, українська, العربية, 日本語. Please read the FAQ for more information about official translations.

Permission for Figure 2.2



NACE International
15835 Park Ten Place
Houston, TX 77084
Tel: 281-228-6200
Fax: 281-228-6300

NACE®
INTERNATIONAL
The Worldwide Corrosion Authority

Permission to Reproduce Figures, Photos, and Tables from Copyrighted Works

Date: July 10, 2017

Name: Timothy Crowtz Title: PhD Student

Company ("Publisher"): Dalhousie University

Address: Halifax, Nova Scotia, Canada, B3H 4R2

Tel: (902) 440-2364 Fax: (902) 494-5191

Email: tcrowtz@dal.ca

Material to be Reproduced ("Work"): Please provide a complete description of the material involved. Include the following elements where applicable: publication name, issue date, page number, figure/photo/table number, paper number, conference name, etc.

Figure 22 from Lee, J.B., 1981. Elevated Temperature Potential-pH Diagrams for the Cr-H2O, Ti-H2O, Mo-H2O, and Pt-H2O Systems. Corrosion 37, 467–481. (doi:10.5006/1.3585993)

Reproduction Method ("Publication Media"): Please provide a complete description of how and where the Work will be used. Include the following elements as applicable: publication name, issue, circulation, print run, web site address, conference name, presentation time and place, etc.

Dalhousie University PhD Thesis "Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium" to be published electronically to http://dalspace.library.dal.ca/ and http://www.nlc-bnc.ca/ September, 2017.

NACE International ("NACE") hereby grants to "Publisher" the right to publish the Work utilizing the Publication Media described above. The publication right granted herein is limited the specific Publication Media described above. To the extent the publication of the Work is to occur by an above-specified date, such as in a particular periodical or at a particular conference, the right granted herein shall automatically terminate upon the date of such occurrence, whether or not the Work is actually published. To the extent the Publication Media is a web site, the publication right is limited to publication at the specific web site URL identified above. Any right granted herein is a limited, non-transferable, non-exclusive right. No other rights in the Work are granted herein.

Publisher shall not edit or modify the Work except to meet the style and graphic requirements of the individual media involved.

The Publisher shall include the following notation with any publication of the Work:*

A. **Conference Paper**
Reproduced with permission from NACE International, Houston, TX. All rights reserved. Author(s), Paper NUMBER presented at CORROSION/YEAR, City, State. © NACE International FIRST YEAR OF PUBLICATION.

B. **Journal Article**
Reproduced with permission from NACE International, Houston, TX. All rights reserved. Author(s) name, Article title, Journal title, Vol. no., Issue no., and publication year. © NACE International FIRST YEAR OF PUBLICATION.

C. **Magazine Article**
Reproduced with permission from NACE International, Houston, TX. All rights reserved. Author(s) name, Article title, Magazine title, Vol. no., Issue no., and publication year. © NACE International FIRST YEAR OF PUBLICATION.

D. **Standards**
STANDARDS/TECHNICAL COMMITTEE REPORT NAME. © NACE International YEAR. All rights reserved by NACE. Reprinted with permission. NACE standards are revised periodically. Users are cautioned to obtain the latest edition; information in an outdated version of the standard may not be accurate.

* Modifications to Notations: Other reference wording can be used, but must be approved by NACE in writing *in advance*.

The Publisher shall include full bibliographic citations of or references to the original NACE source, where applicable.

Publisher shall obtain a copy of the original Work directly from NACE International and shall not utilize copies of the Work from other sources, including the author(s).

To the extent the Work is published on a web site as authorized herein, the Work shall be posted in a file format that does not allow the content of the Work to be easily copied from the Web Site or changed.

As between NACE and Publisher, Publisher acknowledges that NACE owns all rights in the Works.

Publisher shall not be entitled to any compensation for its efforts in promoting the Work.

THE WORK IS PROVIDED "AS IS." ALL EXPRESS OR IMPLIED COVENANTS, CONDITIONS, REPRESENTATIONS OR WARRANTIES, INCLUDING ANY IMPLIED WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE OR CONDITIONS OF ACCURACY, COMPLETENESS OR QUALITY AND THOSE ARISING BY STATUTE OR OTHERWISE IN LAW, ARE HEREBY DISCLAIMED.

IN NO EVENT WILL NACE BE LIABLE FOR ANY DIRECT, INDIRECT, PUNITIVE, SPECIAL, INCIDENTAL OR CONSEQUENTIAL DAMAGES IN CONNECTION WITH OR RELATED TO THIS AGREEMENT (INCLUDING LOSS OF PROFITS, USE, DATA, OR OTHER ECONOMIC ADVANTAGE), HOWSOEVER ARISING.

This Agreement and the rights granted herein may be terminated immediately by NACE upon breach of this Agreement by Publisher. Unless earlier terminated, this Agreement and the rights granted herein will automatically terminate 6 months from the Date set forth above. If the Work has not been published within that time period, a new Agreement must be obtained.

Publisher may not, directly or indirectly, sell, assign, sublicense, lease, rent, distribute, or otherwise transfer this Agreement or any rights granted herein, without the prior written consent of NACE.

If any provision of this Agreement is found to be unenforceable, then this Agreement shall be deemed to be amended by modifying such provision to the extent necessary to make it legal and enforceable while preserving its intent. The remainder of this Agreement shall not be affected by such modification.

This Agreement does not create, and shall not be construed to create, any employer-employee, joint venture or partnership relationship between the parties. No officer, employee, agent, servant or independent contractor of either party shall at any time be deemed to be an employee, servant, agent or contractor of any other party for any purpose whatsoever.

This Agreement shall be governed by, and construed and enforced in accordance with, the laws of the State of Texas, without regard to the choice of law provisions of that State.

This Agreement shall only be effective if signed by authorized representatives of both parties. This Agreement constitutes the entire Agreement between the parties with respect to the subject matter of this Agreement. Any change, modification or waiver hereto must be in writing and signed by authorized representatives of both parties.

Other Terms & Conditions: ______________________________

Publisher hereby requests permission to publish the Work described above and agrees to comply with all Terms and Conditions listed above.

Request submitted by:
Timothy Crowtz
Printed Name
Timothy Crowtz
Title
PhD Student
Signature
signature redacted in archival copy fo
compliance with privacy law
Date
July 10, 2017

Request agreed to by:
N/A
Lead Author Printed Name
Timothy Crowtz
Lead Author Title
PhD Student
Lead Author Signature
signature redacted in archival copy for
compliance with privacy law
Date
July, 10, 2017

Request approved by NACE:
Daniela Freeman
Printed Name
Audience Development Manager
signature redacted in archival copy for
compliance with privacy law
Signature
7/11/2017
Date

Permission for Figure 2.4

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Jul 07, 2017

This Agreement between Mr. Timothy Crowtz ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	4143820205618
License date	Jul 07, 2017
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Angewandte Chemie International Edition
Licensed Content Title	Dissolution of Platinum: Limits for the Deployment of Electrochemical Energy Conversion?
Licensed Content Author	Angel A. Topalov,Ioannis Katsounaros,Michael Auinger,Serhiy Cherevko,Josef C. Meier,Sebastian O. Klemm,Karl J. J. Mayrhofer
Licensed Content Date	Nov 4, 2012
Licensed Content Pages	3
Type of Use	Dissertation/Thesis
Requestor type	University/Academic
Format	Electronic
Portion	Figure/table
Number of figures/tables	1
Original Wiley figure/table number(s)	1a, 1b, 1c
Will you be translating?	No
Title of your thesis / dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Expected size (number of pages)	249
Requestor Location	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Publisher Tax ID	EU826007151
Billing Type	Invoice
Billing Address	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H 4R2 Canada Attn: Timothy C Crowtz
Total	**0.00 USD**
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a"Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at http://myaccount.copyright.com).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order,** is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner.**For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts,** You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING,

PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS
Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.
The Creative Commons Attribution License
The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-
Creative Commons Attribution Non-Commercial License
The Creative Commons Attribution Non-Commercial (CC-BY-NC)License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Permission for Figures 2.5, 2.6 and 2.7

Creative Commons Legal Code

Attribution 3.0 Unported

CREATIVE COMMONS CORPORATION IS NOT A LAW FIRM AND DOES NOT PROVIDE LEGAL SERVICES. DISTRIBUTION OF THIS LICENSE DOES NOT CREATE AN ATTORNEY-CLIENT RELATIONSHIP. CREATIVE COMMONS PROVIDES THIS INFORMATION ON AN "AS-IS" BASIS. CREATIVE COMMONS MAKES NO WARRANTIES REGARDING THE INFORMATION PROVIDED, AND DISCLAIMS LIABILITY FOR DAMAGES RESULTING FROM ITS USE.

License

THE WORK (AS DEFINED BELOW) IS PROVIDED UNDER THE TERMS OF THIS CREATIVE COMMONS PUBLIC LICENSE ("CCPL" OR "LICENSE"). THE WORK IS PROTECTED BY COPYRIGHT AND/OR OTHER APPLICABLE LAW. ANY USE OF THE WORK OTHER THAN AS AUTHORIZED UNDER THIS LICENSE OR COPYRIGHT LAW IS PROHIBITED.

BY EXERCISING ANY RIGHTS TO THE WORK PROVIDED HERE, YOU ACCEPT AND AGREE TO BE BOUND BY THE TERMS OF THIS LICENSE. TO THE EXTENT THIS LICENSE MAY BE CONSIDERED TO BE A CONTRACT, THE LICENSOR GRANTS YOU THE RIGHTS CONTAINED HERE IN CONSIDERATION OF YOUR ACCEPTANCE OF SUCH TERMS AND CONDITIONS.

1. Definitions

a. **"Adaptation"** means a work based upon the Work, or upon the Work and other pre-existing works, such as a translation, adaptation, derivative work, arrangement of music or other alterations of a literary or artistic work, or phonogram or performance and includes cinematographic adaptations or any other form in which the Work may be recast, transformed, or adapted including in any form recognizably derived from the original, except that a work that constitutes a Collection will not be considered an Adaptation for the purpose of this License. For the avoidance of doubt, where the Work is a musical work, performance or phonogram, the synchronization of the Work in timed-relation with a moving image ("synching") will be considered an Adaptation for the purpose of this License.
b. **"Collection"** means a collection of literary or artistic works, such as encyclopedias and anthologies, or performances, phonograms or broadcasts, or other works or subject matter other than works listed in Section 1(f) below, which, by reason of the selection and arrangement of their contents, constitute intellectual creations, in which the Work is included in its entirety in unmodified form along with one or more other contributions, each constituting separate and independent works in themselves, which together are assembled into a collective whole. A work that constitutes a Collection will not be considered an Adaptation (as defined above) for the purposes of this License.
c. **"Distribute"** means to make available to the public the original and copies of the Work or Adaptation, as appropriate, through sale or other transfer of ownership.
d. **"Licensor"** means the individual, individuals, entity or entities that offer(s) the Work under the terms of this License.
e. **"Original Author"** means, in the case of a literary or artistic work, the individual, individuals, entity or entities who created the Work or if no individual or entity can be identified, the publisher; and in addition (i) in the case of a performance the actors, singers, musicians, dancers, and other persons who act, sing, deliver, declaim, play in, interpret or otherwise perform literary or artistic works or expressions of folklore; (ii) in the case of a phonogram the producer being the person or legal entity who first fixes the sounds of a performance or other sounds; and, (iii) in the case of broadcasts, the organization that transmits the broadcast.
f. **"Work"** means the literary and/or artistic work offered under the terms of this License including

without limitation any production in the literary, scientific and artistic domain, whatever may be the mode or form of its expression including digital form, such as a book, pamphlet and other writing; a lecture, address, sermon or other work of the same nature; a dramatic or dramatico-musical work; a choreographic work or entertainment in dumb show; a musical composition with or without words; a cinematographic work to which are assimilated works expressed by a process analogous to cinematography; a work of drawing, painting, architecture, sculpture, engraving or lithography; a photographic work to which are assimilated works expressed by a process analogous to photography; a work of applied art; an illustration, map, plan, sketch or three-dimensional work relative to geography, topography, architecture or science; a performance; a broadcast; a phonogram; a compilation of data to the extent it is protected as a copyrightable work; or a work performed by a variety or circus performer to the extent it is not otherwise considered a literary or artistic work.

g. **"You"** means an individual or entity exercising rights under this License who has not previously violated the terms of this License with respect to the Work, or who has received express permission from the Licensor to exercise rights under this License despite a previous violation.
h. **"Publicly Perform"** means to perform public recitations of the Work and to communicate to the public those public recitations, by any means or process, including by wire or wireless means or public digital performances; to make available to the public Works in such a way that members of the public may access these Works from a place and at a place individually chosen by them; to perform the Work to the public by any means or process and the communication to the public of the performances of the Work, including by public digital performance; to broadcast and rebroadcast the Work by any means including signs, sounds or images.
i. **"Reproduce"** means to make copies of the Work by any means including without limitation by sound or visual recordings and the right of fixation and reproducing fixations of the Work, including storage of a protected performance or phonogram in digital form or other electronic medium.

2. Fair Dealing Rights. Nothing in this License is intended to reduce, limit, or restrict any uses free from copyright or rights arising from limitations or exceptions that are provided for in connection with the copyright protection under copyright law or other applicable laws.

3. License Grant. Subject to the terms and conditions of this License, Licensor hereby grants You a worldwide, royalty-free, non-exclusive, perpetual (for the duration of the applicable copyright) license to exercise the rights in the Work as stated below:

a. to Reproduce the Work, to incorporate the Work into one or more Collections, and to Reproduce the Work as incorporated in the Collections;
b. to create and Reproduce Adaptations provided that any such Adaptation, including any translation in any medium, takes reasonable steps to clearly label, demarcate or otherwise identify that changes were made to the original Work. For example, a translation could be marked "The original work was translated from English to Spanish," or a modification could indicate "The original work has been modified.";
c. to Distribute and Publicly Perform the Work including as incorporated in Collections; and,
d. to Distribute and Publicly Perform Adaptations.

e. For the avoidance of doubt:

    i. **Non-waivable Compulsory License Schemes**. In those jurisdictions in which the right to collect royalties through any statutory or compulsory licensing scheme cannot be waived, the Licensor reserves the exclusive right to collect such royalties for any exercise by You of the rights granted under this License;
    ii. **Waivable Compulsory License Schemes**. In those jurisdictions in which the right to collect royalties through any statutory or compulsory licensing scheme can be waived, the Licensor waives the exclusive right to collect such royalties for any exercise by You of the rights granted under this License; and,
    iii. **Voluntary License Schemes**. The Licensor waives the right to collect royalties, whether individually or, in the event that the Licensor is a member of a collecting society that administers voluntary licensing schemes, via that society, from any exercise by You of the rights granted under this License.

The above rights may be exercised in all media and formats whether now known or hereafter devised. The above rights include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. Subject to Section 8(f), all rights not expressly granted by Licensor are hereby reserved.

4. Restrictions. The license granted in Section 3 above is expressly made subject to and limited by the following restrictions:

a. You may Distribute or Publicly Perform the Work only under the terms of this License. You must include a copy of, or the Uniform Resource Identifier (URI) for, this License with every copy of the Work You Distribute or Publicly Perform. You may not offer or impose any terms on the Work that restrict the terms of this License or the ability of the recipient of the Work to exercise the rights granted to that recipient under the terms of the License. You may not sublicense the Work. You must keep intact all notices that refer to this License and to the disclaimer of warranties with every copy of the Work You Distribute or Publicly Perform. When You Distribute or Publicly Perform the Work, You may not impose any effective technological measures on the Work that restrict the ability of a recipient of the Work from You to exercise the rights granted to that recipient under the terms of the License. This Section 4(a) applies to the Work as incorporated in a Collection, but this does not require the Collection apart from the Work itself to be made subject to the terms of this License. If You create a Collection, upon notice from any Licensor You must, to the extent practicable, remove from the Collection any credit as required by Section 4(b), as requested. If You create an Adaptation, upon notice from any Licensor You must, to the extent practicable, remove from the Adaptation any credit as required by Section 4(b), as requested.
b. If You Distribute, or Publicly Perform the Work or any Adaptations or Collections, You must, unless a request has been made pursuant to Section 4(a), keep intact all copyright notices for the Work and provide, reasonable to the medium or means You are utilizing: (i) the name of the Original Author (or pseudonym, if applicable) if supplied, and/or if the Original Author and/or Licensor designate another party or parties (e.g., a sponsor institute, publishing entity, journal) for attribution ("Attribution Parties") in Licensor's copyright notice, terms of service or by other reasonable means, the name of such party or parties; (ii) the title of the Work if supplied; (iii) to the extent reasonably practicable, the URI, if any, that Licensor specifies to be associated with the Work, unless such URI does not refer to the copyright notice or licensing information for the Work; and (iv) , consistent with Section 3(b), in the case of an Adaptation, a credit identifying the use of the Work in the Adaptation (e.g., "French translation of the Work by Original Author," or "Screenplay based on original Work by Original Author"). The credit required by this Section 4 (b) may be implemented in any reasonable manner; provided, however, that in the case of a Adaptation or Collection, at a minimum such credit will appear, if a credit for all contributing authors of the Adaptation or Collection appears, then as part of these credits and in a manner at least as prominent as the credits for the other contributing authors. For the avoidance of doubt, You may only use the credit required by this Section for the purpose of attribution in the manner set out above and, by exercising Your rights under this License, You may not implicitly or explicitly assert or imply any connection with, sponsorship or endorsement by the Original Author, Licensor and/or Attribution Parties, as appropriate, of You or Your use of the Work, without the separate, express prior written permission of the Original Author, Licensor and/or Attribution Parties.
c. Except as otherwise agreed in writing by the Licensor or as may be otherwise permitted by applicable law, if You Reproduce, Distribute or Publicly Perform the Work either by itself or as part of any Adaptations or Collections, You must not distort, mutilate, modify or take other derogatory action in relation to the Work which would be prejudicial to the Original Author's honor or reputation. Licensor agrees that in those jurisdictions (e.g. Japan), in which any exercise of the right granted in Section 3(b) of this License (the right to make Adaptations) would be deemed to be a distortion, mutilation, modification or other derogatory action prejudicial to the Original Author's honor and reputation, the Licensor will waive or not assert, as appropriate, this Section, to the fullest extent permitted by the applicable national law, to enable You to reasonably exercise Your right under Section 3(b) of this License (right to make Adaptations) but not otherwise.

5. Representations, Warranties and Disclaimer

UNLESS OTHERWISE MUTUALLY AGREED TO BY THE PARTIES IN WRITING, LICENSOR OFFERS THE WORK AS-IS AND MAKES NO REPRESENTATIONS OR WARRANTIES OF ANY KIND CONCERNING THE WORK, EXPRESS, IMPLIED, STATUTORY OR OTHERWISE, INCLUDING, WITHOUT LIMITATION, WARRANTIES OF TITLE, MERCHANTIBILITY, FITNESS FOR A PARTICULAR PURPOSE, NONINFRINGEMENT, OR THE ABSENCE OF LATENT OR OTHER DEFECTS,

ACCURACY, OR THE PRESENCE OF ABSENCE OF ERRORS, WHETHER OR NOT DISCOVERABLE. SOME JURISDICTIONS DO NOT ALLOW THE EXCLUSION OF IMPLIED WARRANTIES, SO SUCH EXCLUSION MAY NOT APPLY TO YOU.

6. Limitation on Liability. EXCEPT TO THE EXTENT REQUIRED BY APPLICABLE LAW, IN NO EVENT WILL LICENSOR BE LIABLE TO YOU ON ANY LEGAL THEORY FOR ANY SPECIAL, INCIDENTAL, CONSEQUENTIAL, PUNITIVE OR EXEMPLARY DAMAGES ARISING OUT OF THIS LICENSE OR THE USE OF THE WORK, EVEN IF LICENSOR HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES.

7. Termination

a. This License and the rights granted hereunder will terminate automatically upon any breach by You of the terms of this License. Individuals or entities who have received Adaptations or Collections from You under this License, however, will not have their licenses terminated provided such individuals or entities remain in full compliance with those licenses. Sections 1, 2, 5, 6, 7, and 8 will survive any termination of this License.
b. Subject to the above terms and conditions, the license granted here is perpetual (for the duration of the applicable copyright in the Work). Notwithstanding the above, Licensor reserves the right to release the Work under different license terms or to stop distributing the Work at any time; provided, however that any such election will not serve to withdraw this License (or any other license that has been, or is required to be, granted under the terms of this License), and this License will continue in full force and effect unless terminated as stated above.

8. Miscellaneous

a. Each time You Distribute or Publicly Perform the Work or a Collection, the Licensor offers to the recipient a license to the Work on the same terms and conditions as the license granted to You under this License.
b. Each time You Distribute or Publicly Perform an Adaptation, Licensor offers to the recipient a license to the original Work on the same terms and conditions as the license granted to You under this License.
c. If any provision of this License is invalid or unenforceable under applicable law, it shall not affect the validity or enforceability of the remainder of the terms of this License, and without further action by the parties to this agreement, such provision shall be reformed to the minimum extent necessary to make such provision valid and enforceable.
d. No term or provision of this License shall be deemed waived and no breach consented to unless such waiver or consent shall be in writing and signed by the party to be charged with such waiver or consent.
e. This License constitutes the entire agreement between the parties with respect to the Work licensed here. There are no understandings, agreements or representations with respect to the Work not specified here. Licensor shall not be bound by any additional provisions that may appear in any communication from You. This License may not be modified without the mutual written agreement of the Licensor and You.
f. The rights granted under, and the subject matter referenced, in this License were drafted utilizing the terminology of the Berne Convention for the Protection of Literary and Artistic Works (as amended on September 28, 1979), the Rome Convention of 1961, the WIPO Copyright Treaty of 1996, the WIPO Performances and Phonograms Treaty of 1996 and the Universal Copyright Convention (as revised on July 24, 1971). These rights and subject matter take effect in the relevant jurisdiction in which the License terms are sought to be enforced according to the corresponding provisions of the implementation of those treaty provisions in the applicable national law. If the standard suite of rights granted under applicable copyright law includes additional rights not granted under this License, such additional rights are deemed to be included in the License; this License is not intended to restrict the license of any rights under applicable law.

Creative Commons Notice

Creative Commons is not a party to this License, and makes no warranty whatsoever in connection with the Work. Creative Commons will not be liable to You or any party on any legal theory for any damages whatsoever, including without limitation any general, special, incidental or consequential

Permission for Figure 2.8

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This Agreement between Mr. Timothy Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4143821163004
License date	Jul 07, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Electroanalytical Chemistry
Licensed Content Title	Selective oxide growth at a rhodium-platinum alloy under potential cycling conditions in base
Licensed Content Author	Laurence D. Burke,Eugene J.M. O'Sullivan
Licensed Content Date	Sep 25, 1980
Licensed Content Volume	112
Licensed Content Issue	2
Licensed Content Pages	6
Start Page	247
End Page	252
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	3
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.9 and 2.36

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This Agreement between Mr. Timothy Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4143800266779
License date	Jul 07, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Nano Energy
Licensed Content Title	Durability of platinum-based fuel cell electrocatalysts: Dissolution of bulk and nanoscale platinum
Licensed Content Author	Serhiy Cherevko,Nadiia Kulyk,Karl J.J. Mayrhofer
Licensed Content Date	Nov 1, 2016
Licensed Content Volume	29
Licensed Content Issue	n/a
Licensed Content Pages	24
Start Page	275
End Page	298
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	13
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms

and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science

/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
    - via their non-commercial person homepage or blog
    - by updating a preprint in arXiv or RePEc with the accepted manuscript
    - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
    - directly by providing copies to their students or to research collaborators for their personal use
    - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
    - via non-commercial hosting platforms such as their institutional repository
    - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor

may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.11

Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This is a License Agreement between Mr. Timothy Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4143840023938
License date	Jul 07, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	Electrochemical Society. Meeting Abstracts
Licensed content date	Jan 1, 1960
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	image/photo
Number of images/photos requested	2
Title or numeric reference of the portion(s)	Figure 1a and 1c
Title of the article or chapter the portion is from	Abstract #1313, Honolulu PRiME 2012
Editor of portion(s)	N/A
Author of portion(s)	K.L. More
Volume of serial or monograph.	N/A
Page range of the portion	105
Publication date of portion	October, 2012
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication
With incidental promotional use	no

The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order

Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.

3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on "net 30" terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.

3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is "one-time" (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).

3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.

3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Republished with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. " Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

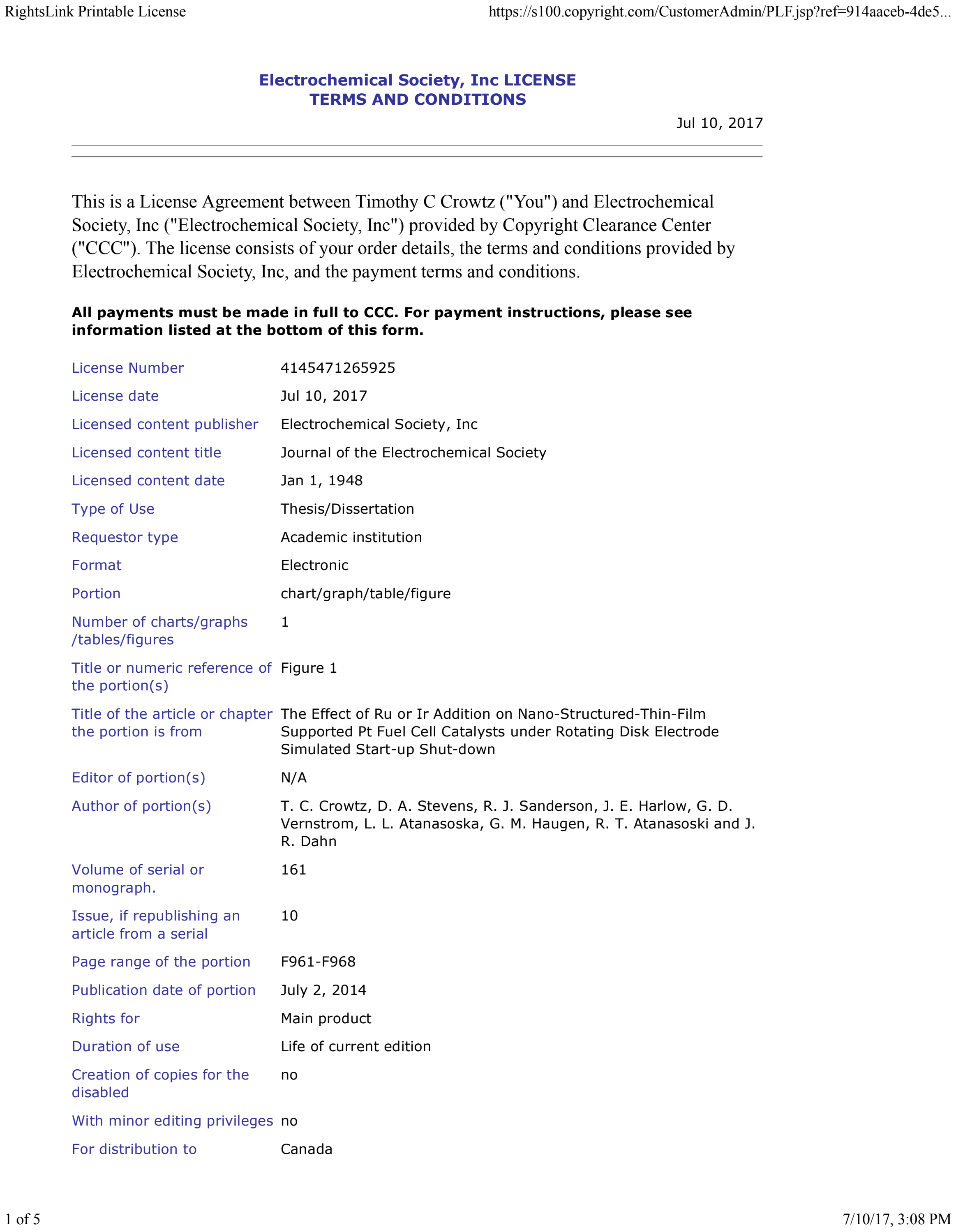
7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.
8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.
8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.
8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.
8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.
v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.12



RightsLink Printable License https://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=914aaceb-4de5...

Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145471265925
License date	Jul 10, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	Journal of the Electrochemical Society
Licensed content date	Jan 1, 1948
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	1
Title or numeric reference of the portion(s)	Figure 1
Title of the article or chapter the portion is from	The Effect of Ru or Ir Addition on Nano-Structured-Thin-Film Supported Pt Fuel Cell Catalysts under Rotating Disk Electrode Simulated Start-up Shut-down
Editor of portion(s)	N/A
Author of portion(s)	T. C. Crowtz, D. A. Stevens, R. J. Sanderson, J. E. Harlow, G. D. Vernstrom, L. L. Atanasoska, G. M. Haugen, R. T. Atanasoski and J. R. Dahn
Volume of serial or monograph.	161
Issue, if republishing an article from a serial	10
Page range of the portion	F961-F968
Publication date of portion	July 2, 2014
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada

1 of 5 7/10/17, 3:08 PM

In the following language(s)	Original language of publication
With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University PhD Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.
3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.
3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on “net 30” terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.
3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is “one-time” (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).
3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.
3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation,

in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most

closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC’s privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User’s rights in the new material which includes the Work(s) licensed under this Service.

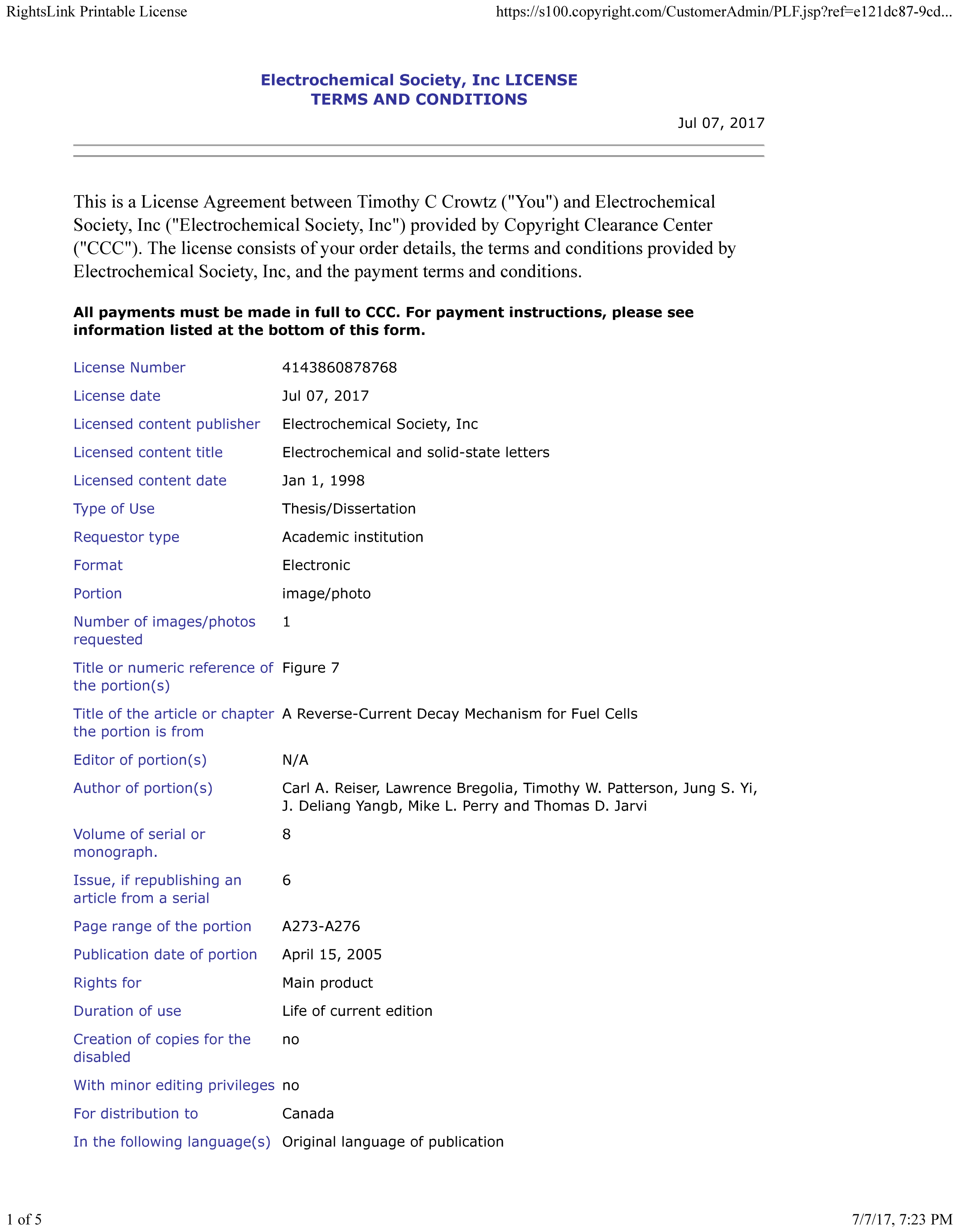
8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.13



Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4143860878768
License date	Jul 07, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	Electrochemical and solid-state letters
Licensed content date	Jan 1, 1998
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	image/photo
Number of images/photos requested	1
Title or numeric reference of the portion(s)	Figure 7
Title of the article or chapter the portion is from	A Reverse-Current Decay Mechanism for Fuel Cells
Editor of portion(s)	N/A
Author of portion(s)	Carl A. Reiser, Lawrence Bregolia, Timothy W. Patterson, Jung S. Yi, J. Deliang Yangb, Mike L. Perry and Thomas D. Jarvi
Volume of serial or monograph.	8
Issue, if republishing an article from a serial	6
Page range of the portion	A273-A276
Publication date of portion	April 15, 2005
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication

With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University Thesis
The proposed price	0
Title of New Work	The Effect of Ru or Ir Addition on Nano-Structured-Thin-Film Supported Pt Fuel Cell Catalysts under Rotating Disk Electrode Simulated Start-up Shut-down
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.
3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on "net 30" terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.
3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is "one-time" (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).
3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.
3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Republished with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. " Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses

incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.

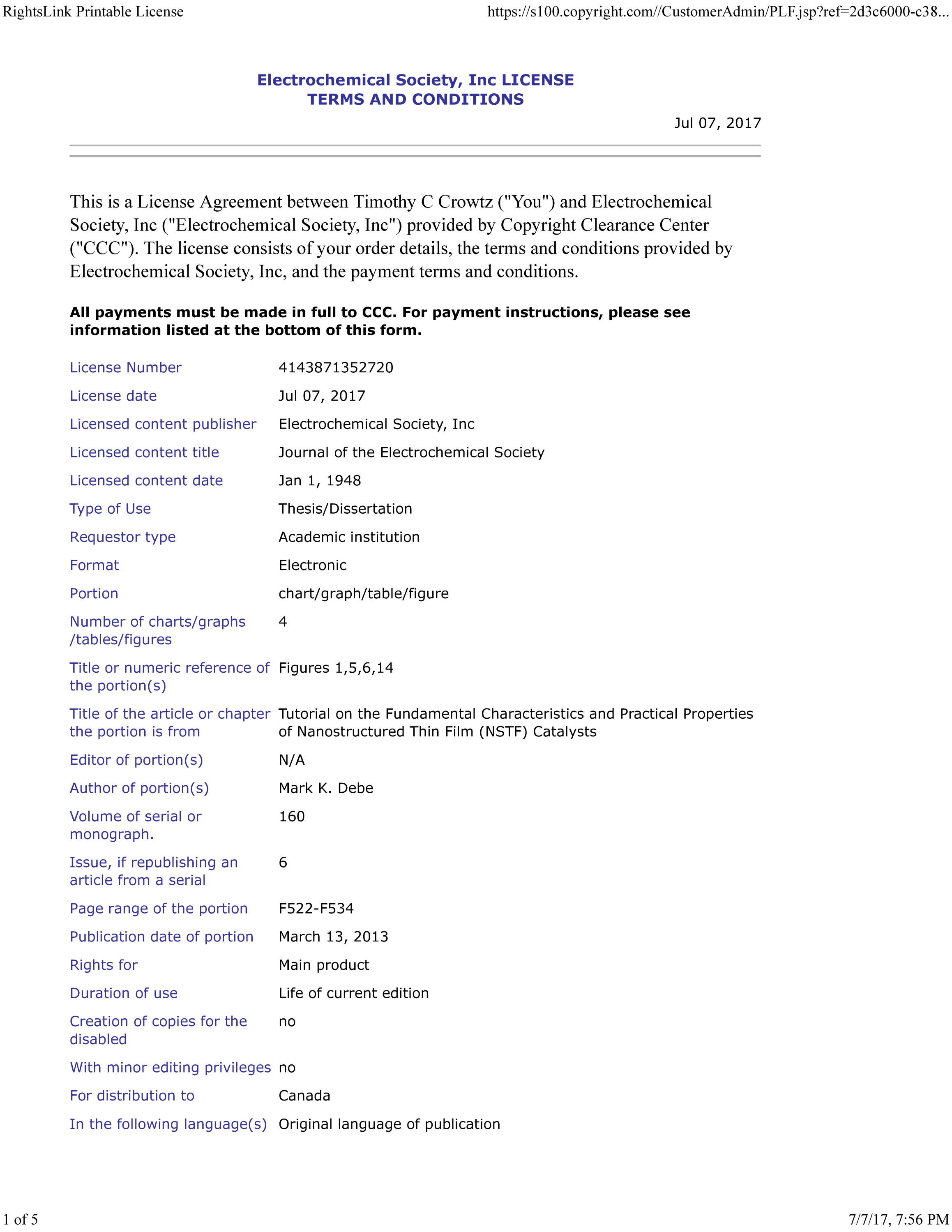
8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figures 2.15, 2.17, 2.18 and 2.19



Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4143871352720
License date	Jul 07, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	Journal of the Electrochemical Society
Licensed content date	Jan 1, 1948
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	4
Title or numeric reference of the portion(s)	Figures 1,5,6,14
Title of the article or chapter the portion is from	Tutorial on the Fundamental Characteristics and Practical Properties of Nanostructured Thin Film (NSTF) Catalysts
Editor of portion(s)	N/A
Author of portion(s)	Mark K. Debe
Volume of serial or monograph.	160
Issue, if republishing an article from a serial	6
Page range of the portion	F522-F534
Publication date of portion	March 13, 2013
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication

With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University Thesis
The proposed price	0
Title of New Work	The Effect of Ru or Ir Addition on Nano-Structured-Thin-Film Supported Pt Fuel Cell Catalysts under Rotating Disk Electrode Simulated Start-up Shut-down
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the "Work(s)"). Copyright Clearance Center, Inc. ("CCC") grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the "Rightsholder"). "Republication", as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. "User", as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a "freelancer" or other third party independent of User and CCC, such party shall be deemed jointly a "User" for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.
3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on “net 30” terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.
3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is “one-time” (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).
3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.
3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses

incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.16

John Wiley and Sons Inc LICENSE
TERMS AND CONDITIONS

Jul 12, 2017

This is a License Agreement between Timothy C Crowtz ("You") and John Wiley and Sons Inc ("John Wiley and Sons Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by John Wiley and Sons Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145510327807
License date	Jul 09, 2017
Licensed content publisher	John Wiley and Sons Inc
Licensed content title	Handbook of fuel cells : fundamentals, technology, and applications
Licensed content date	Jan 1, 2003
Type of Use	Other Published Product
Requestor type	Academic institution
Format	Electronic
Portion	image/photo
Number of images/photos requested	2
Title or numeric reference of the portion(s)	Figure 7b, Figure 8
Title of the article or chapter the portion is from	Novel catalysts, catalysts support and catalysts coated membrane methods (Volume 3, Part 3, pp 576-589)
Editor of portion(s)	Wolf Vielstich, Arnold Lamm, and Hubert A. Gasteiger
Author of portion(s)	M. K. Debe
Volume of serial or monograph.	3
Page range of the portion	582
Publication date of portion	2003
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication
With incidental promotional use	no

The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University PhD Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley material.

This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

In no instance may the total amount of Wiley Materials used in any Main Product, Compilation or Collective work comprise more than 5% (if figures/tables) or 15% (if full articles/chapters) of the (entirety of the) Main Product, Compilation or Collective Work.

Some titles may be available under an Open Access license. It is the Licensors' responsibility to identify the type of Open Access license on which the requested material was published, and comply fully with the terms of that license for the type of use specified Further details can be found on Wiley Online Library http://olabout.wiley.com/WileyCDA/Section/id-410895.html.

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such

republication.
2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a "freelancer" or other third party independent of User and CCC, such party shall be deemed jointly a "User" for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.

3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on "net 30" terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.

3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is "one-time" (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).

3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.

3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.
3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.
4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.
5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.
6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

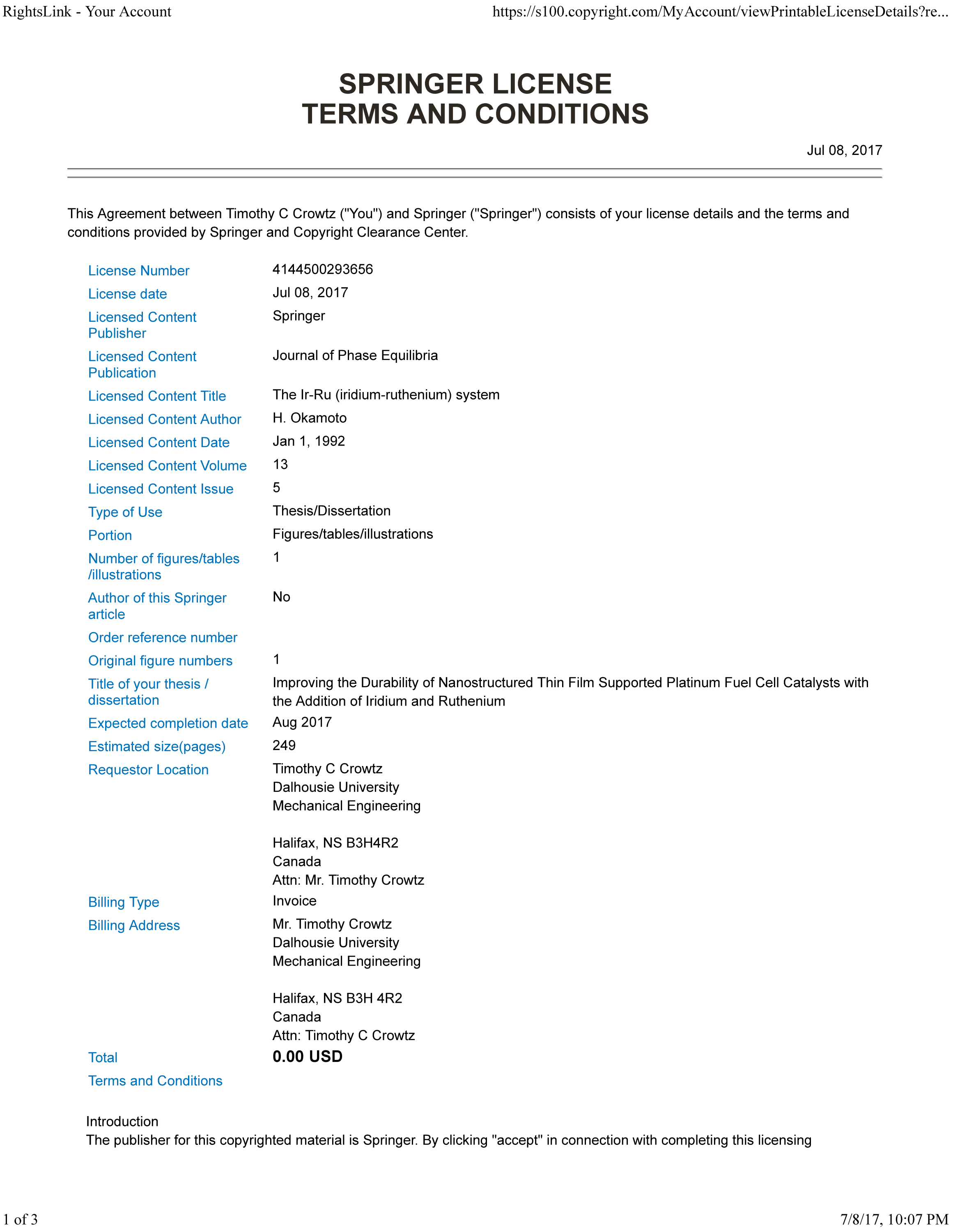
8.2 Use of User-related information collected through the Service is governed by CCC’s privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User’s rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact

Permission for Figure 2.22



SPRINGER LICENSE TERMS AND CONDITIONS

Jul 08, 2017

This Agreement between Timothy C Crowtz ("You") and Springer ("Springer") consists of your license details and the terms and conditions provided by Springer and Copyright Clearance Center.

License Number	4144500293656
License date	Jul 08, 2017
Licensed Content Publisher	Springer
Licensed Content Publication	Journal of Phase Equilibria
Licensed Content Title	The Ir-Ru (iridium-ruthenium) system
Licensed Content Author	H. Okamoto
Licensed Content Date	Jan 1, 1992
Licensed Content Volume	13
Licensed Content Issue	5
Type of Use	Thesis/Dissertation
Portion	Figures/tables/illustrations
Number of figures/tables /illustrations	1
Author of this Springer article	No
Order reference number	
Original figure numbers	1
Title of your thesis / dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size(pages)	249
Requestor Location	Timothy C Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Billing Type	Invoice
Billing Address	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H 4R2 Canada Attn: Timothy C Crowtz
Total	**0.00 USD**
Terms and Conditions	

Introduction

The publisher for this copyrighted material is Springer. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

Limited License

With reference to your request to reuse material on which Springer controls the copyright, permission is granted for the use indicated in your enquiry under the following conditions:

- Licenses are for one-time use only with a maximum distribution equal to the number stated in your request.
- Springer material represents original material which does not carry references to other sources. If the material in question appears with a credit to another source, this permission is not valid and authorization has to be obtained from the original copyright holder.
- This permission

• is non-exclusive

• is only valid if no personal rights, trademarks, or competitive products are infringed.

• explicitly excludes the right for derivatives.

- Springer does not supply original artwork or content.
- According to the format which you have selected, the following conditions apply accordingly:

• Print and Electronic: This License include use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.

• Print: This License excludes use in electronic form.

• Electronic: This License only pertains to use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.

For any electronic use not mentioned, please contact Springer at permissions.springer@spi-global.com.

- Although Springer controls the copyright to the material and is entitled to negotiate on rights, this license is only valid subject to courtesy information to the author (address is given in the article/chapter).
- If you are an STM Signatory or your work will be published by an STM Signatory and you are requesting to reuse figures/tables /illustrations or single text extracts, permission is granted according to STM Permissions Guidelines: http://www.stm-assoc.org/permissions-guidelines/

For any electronic use not mentioned in the Guidelines, please contact Springer at permissions.springer@spi-global.com. If you request to reuse more content than stipulated in the STM Permissions Guidelines, you will be charged a permission fee for the excess content.

Permission is valid upon payment of the fee as indicated in the licensing process. If permission is granted free of charge on this occasion, that does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.

-If your request is for reuse in a Thesis, permission is granted free of charge under the following conditions:

This license is valid for one-time use only for the purpose of defending your thesis and with a maximum of 100 extra copies in paper. If the thesis is going to be published, permission needs to be reobtained.

- includes use in an electronic form, provided it is an author-created version of the thesis on his/her own website and his/her university's repository, including UMI (according to the definition on the Sherpa website: http://www.sherpa.ac.uk/romeo/);
- is subject to courtesy information to the co-author or corresponding author.

Geographic Rights: Scope

Licenses may be exercised anywhere in the world.

Altering/Modifying Material: Not Permitted

Figures, tables, and illustrations may be altered minimally to serve your work. You may not alter or modify text in any manner. Abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of the author(s).

Reservation of Rights

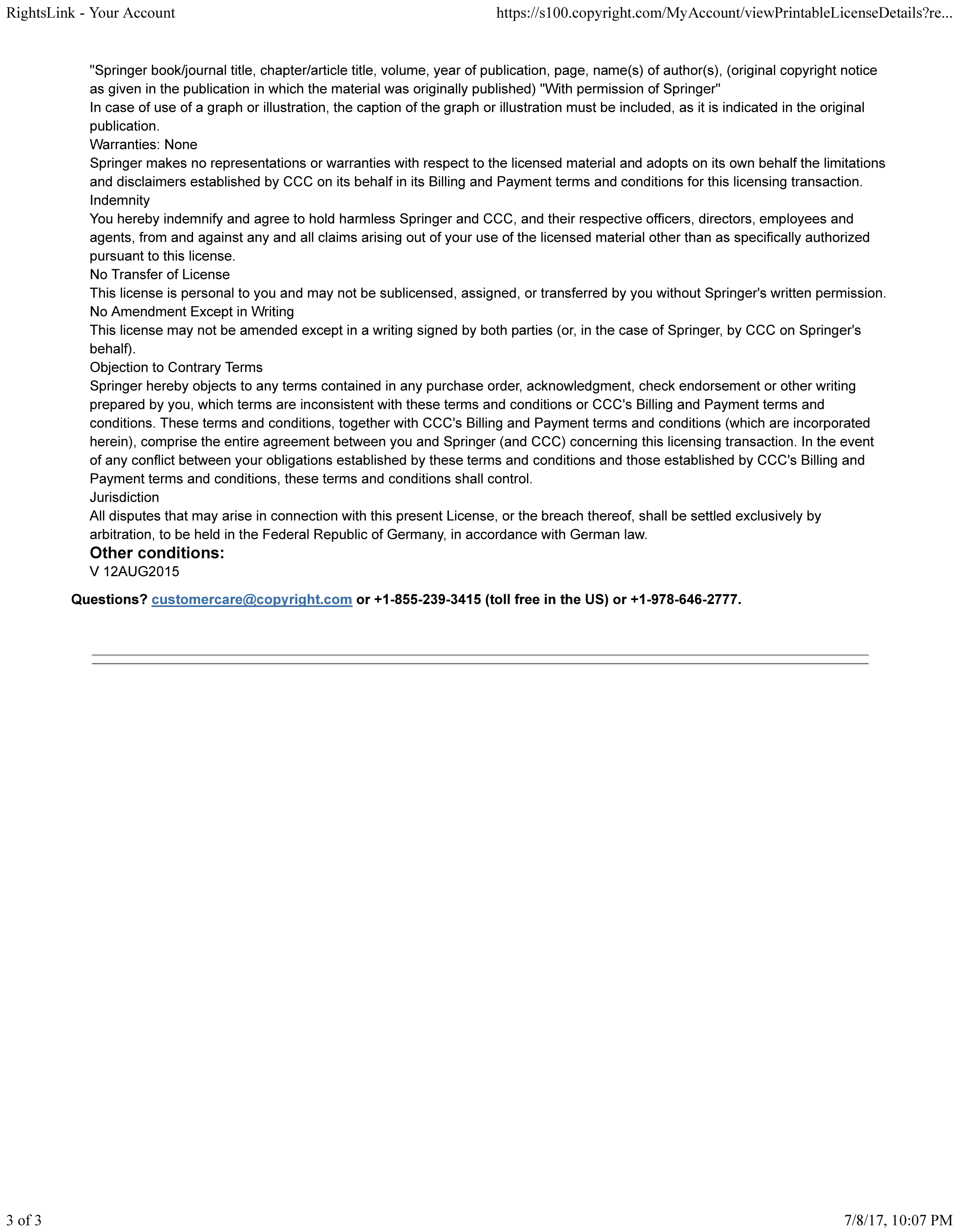
Springer reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction and (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

License Contingent on Payment

While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by Springer or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received by the date due, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and Springer reserves the right to take any and all action to protect its copyright in the materials.

Copyright Notice: Disclaimer

You must include the following copyright and permission notice in connection with any reproduction of the licensed material:



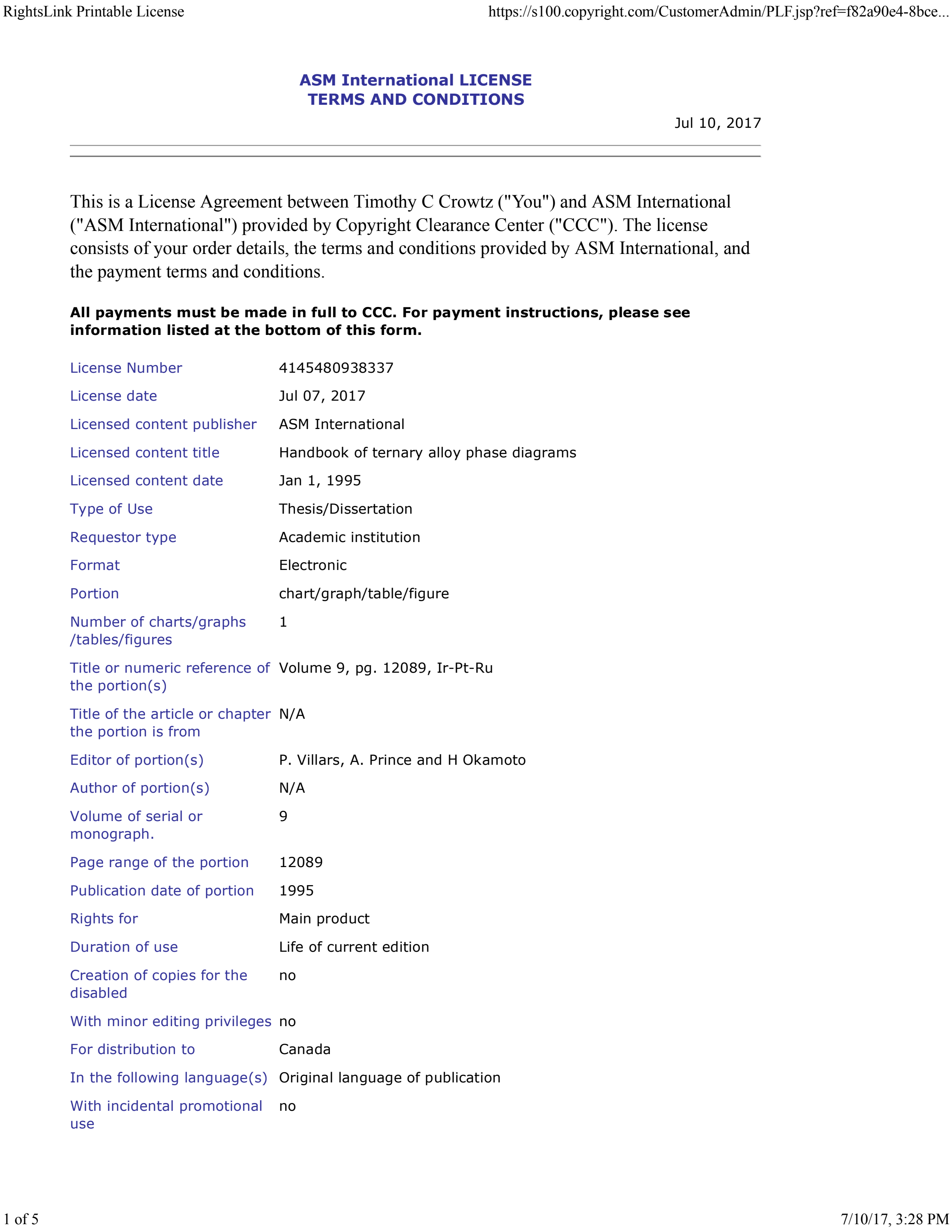
"Springer book/journal title, chapter/article title, volume, year of publication, page, name(s) of author(s), (original copyright notice as given in the publication in which the material was originally published) "With permission of Springer"
In case of use of a graph or illustration, the caption of the graph or illustration must be included, as it is indicated in the original publication.
Warranties: None
Springer makes no representations or warranties with respect to the licensed material and adopts on its own behalf the limitations and disclaimers established by CCC on its behalf in its Billing and Payment terms and conditions for this licensing transaction.
Indemnity
You hereby indemnify and agree to hold harmless Springer and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
No Transfer of License
This license is personal to you and may not be sublicensed, assigned, or transferred by you without Springer's written permission.
No Amendment Except in Writing
This license may not be amended except in a writing signed by both parties (or, in the case of Springer, by CCC on Springer's behalf).
Objection to Contrary Terms
Springer hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
Jurisdiction
All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in the Federal Republic of Germany, in accordance with German law.

Other conditions:

V 12AUG2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.25



ASM International LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This is a License Agreement between Timothy C Crowtz ("You") and ASM International ("ASM International") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by ASM International, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145480938337
License date	Jul 07, 2017
Licensed content publisher	ASM International
Licensed content title	Handbook of ternary alloy phase diagrams
Licensed content date	Jan 1, 1995
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	1
Title or numeric reference of the portion(s)	Volume 9, pg. 12089, Ir-Pt-Ru
Title of the article or chapter the portion is from	N/A
Editor of portion(s)	P. Villars, A. Prince and H Okamoto
Author of portion(s)	N/A
Volume of serial or monograph.	9
Page range of the portion	12089
Publication date of portion	1995
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication
With incidental promotional use	no

The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University Thesis
The proposed price	0
Title of New Work	The Effect of Ru or Ir Addition on Nano-Structured-Thin-Film Supported Pt Fuel Cell Catalysts under Rotating Disk Electrode Simulated Start-up Shut-down
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order

Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.

3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on “net 30” terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.

3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is “one-time” (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).

3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.

3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

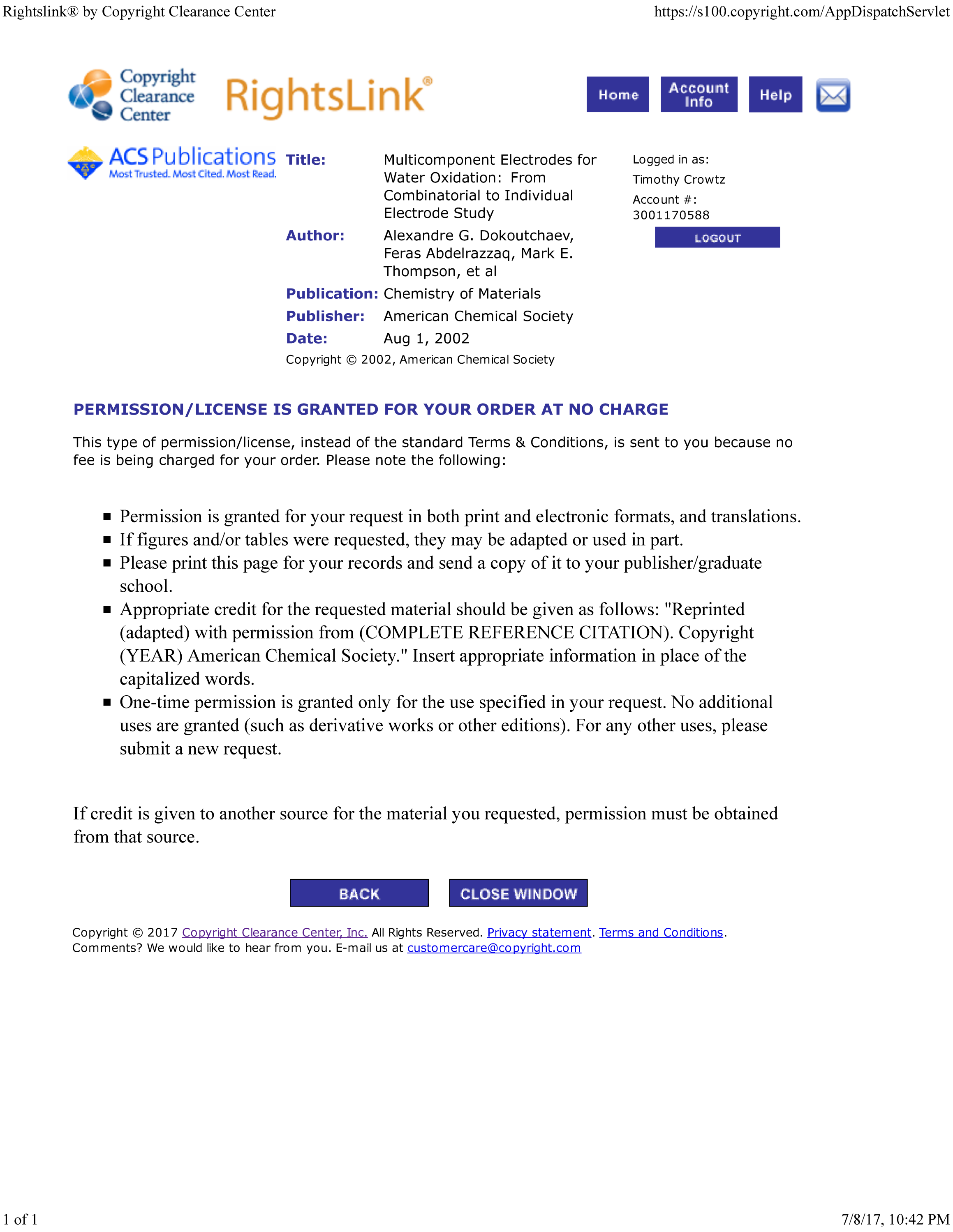
7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.
8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.
8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.
8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.
8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.
v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.26



Rightslink® by Copyright Clearance Center https://s100.copyright.com/AppDispatchServlet

Title:	Multicomponent Electrodes for Water Oxidation: From Combinatorial to Individual Electrode Study
Author:	Alexandre G. Dokoutchaev, Feras Abdelrazzaq, Mark E. Thompson, et al
Publication:	Chemistry of Materials
Publisher:	American Chemical Society
Date:	Aug 1, 2002

Copyright © 2002, American Chemical Society

Logged in as:
Timothy Crowtz
Account #:
3001170588

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

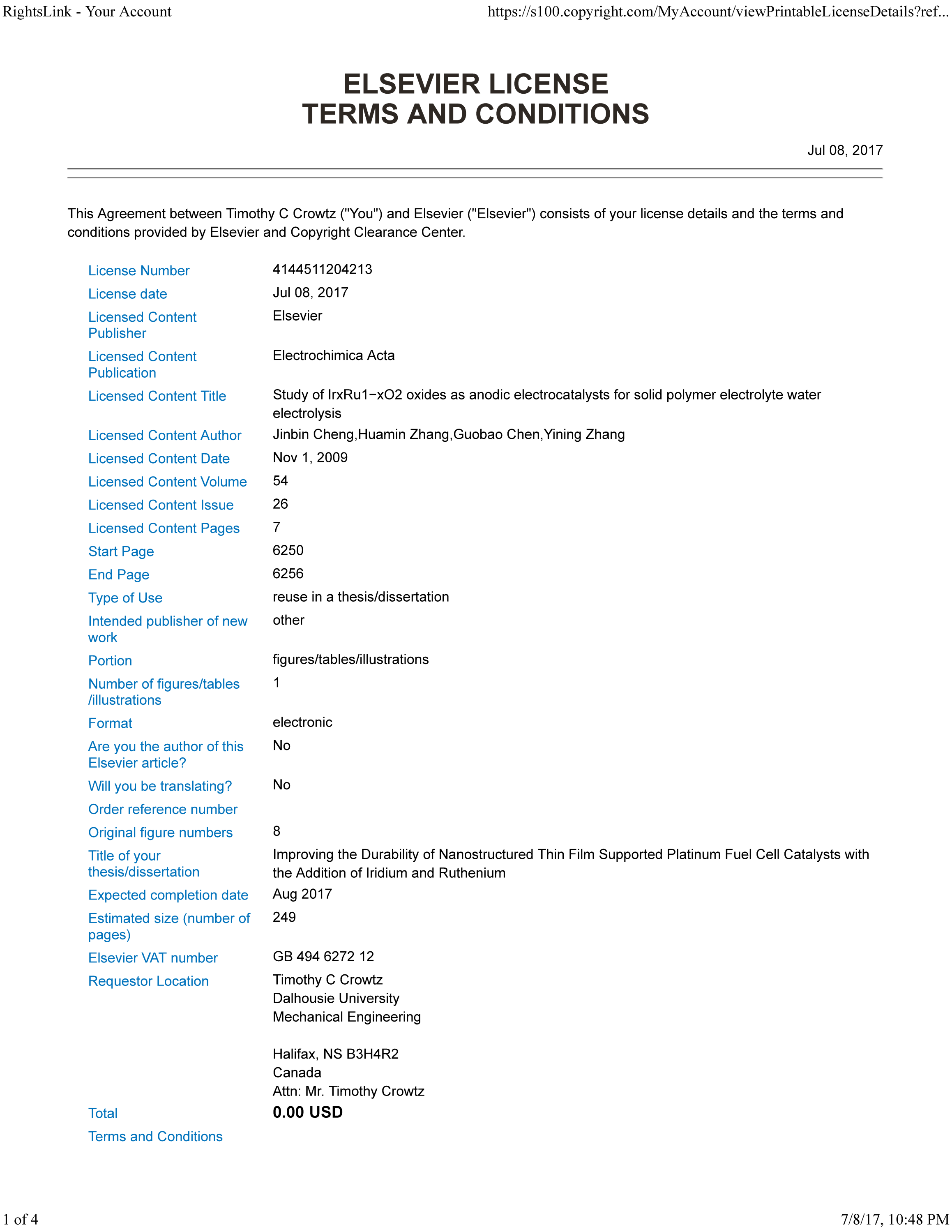
This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

1 of 1 7/8/17, 10:42 PM

Permission for Figure 2.27



RightsLink - Your Account https://s100.copyright.com/MyAccount/viewPrintableLicenseDetails?ref...

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 08, 2017

This Agreement between Timothy C Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4144511204213
License date	Jul 08, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Electrochimica Acta
Licensed Content Title	Study of IrxRu1−xO2 oxides as anodic electrocatalysts for solid polymer electrolyte water electrolysis
Licensed Content Author	Jinbin Cheng,Huamin Zhang,Guobao Chen,Yining Zhang
Licensed Content Date	Nov 1, 2009
Licensed Content Volume	54
Licensed Content Issue	26
Licensed Content Pages	7
Start Page	6250
End Page	6256
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	8
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Timothy C Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

1 of 4 7/8/17, 10:48 PM

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
    - via their non-commercial person homepage or blog
    - by updating a preprint in arXiv or RePEc with the accepted manuscript
    - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
    - directly by providing copies to their students or to research collaborators for their personal use
    - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
    - via non-commercial hosting platforms such as their institutional repository
    - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.34A

Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 08, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4144520889496
License date	Jul 08, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	Journal of the Electrochemical Society
Licensed content date	Jan 1, 1948
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	1
Title or numeric reference of the portion(s)	Figure 7
Title of the article or chapter the portion is from	XPS Studies of Oxygen Evolution on Ru and RuO2 Anodes
Editor of portion(s)	N/A
Author of portion(s)	R. Kötz, H. J. Lewerenz and S. Stucki
Volume of serial or monograph.	130
Issue, if republishing an article from a serial	4
Page range of the portion	825-829
Publication date of portion	1983
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication

With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.
3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on "net 30" terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.
3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is "one-time" (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).
3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.
3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Republished with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. " Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses

incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.34B

Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145400621839
License date	Jul 10, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	Journal of the Electrochemical Society
Licensed content date	Jan 1, 1948
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	1
Title or numeric reference of the portion(s)	Figure 6
Title of the article or chapter the portion is from	Anodic Iridium Oxide Films XPS-Studies of Oxidation State Changes and Formula
Editor of portion(s)	N/A
Author of portion(s)	R. Kötz, H. Neff and S. Stucki
Volume of serial or monograph.	131
Issue, if republishing an article from a serial	1
Page range of the portion	72-77
Publication date of portion	January 1, 1984
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication

With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University PhD Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.
3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on “net 30” terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.
3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is “one-time” (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).
3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.
3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses

incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figures 2.35 and 2.3

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 07, 2017

This Agreement between Mr. Timothy Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4143800266779
License date	Jul 07, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Nano Energy
Licensed Content Title	Durability of platinum-based fuel cell electrocatalysts: Dissolution of bulk and nanoscale platinum
Licensed Content Author	Serhiy Cherevko,Nadiia Kulyk,Karl J.J. Mayrhofer
Licensed Content Date	Nov 1, 2016
Licensed Content Volume	29
Licensed Content Issue	n/a
Licensed Content Pages	24
Start Page	275
End Page	298
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	13
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Mr. Timothy Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms

and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science

/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
    - via their non-commercial person homepage or blog
    - by updating a preprint in arXiv or RePEc with the accepted manuscript
    - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
    - directly by providing copies to their students or to research collaborators for their personal use
    - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
    - via non-commercial hosting platforms such as their institutional repository
    - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor

may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figures 2.37

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This Agreement between Timothy C Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4145410536608
License date	Jul 10, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Electroanalytical Chemistry
Licensed Content Title	Oxygen evolution activity and stability of iridium in acidic media. Part 1. – Metallic iridium
Licensed Content Author	Serhiy Cherevko,Simon Geiger,Olga Kasian,Andrea Mingers,Karl J.J. Mayrhofer
Licensed Content Date	Jul 15, 2016
Licensed Content Volume	773
Licensed Content Issue	n/a
Licensed Content Pages	10
Start Page	69
End Page	78
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	Figure 5c
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Timothy C Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
    - via their non-commercial person homepage or blog
    - by updating a preprint in arXiv or RePEc with the accepted manuscript
    - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
    - directly by providing copies to their students or to research collaborators for their personal use
    - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
    - via non-commercial hosting platforms such as their institutional repository
    - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

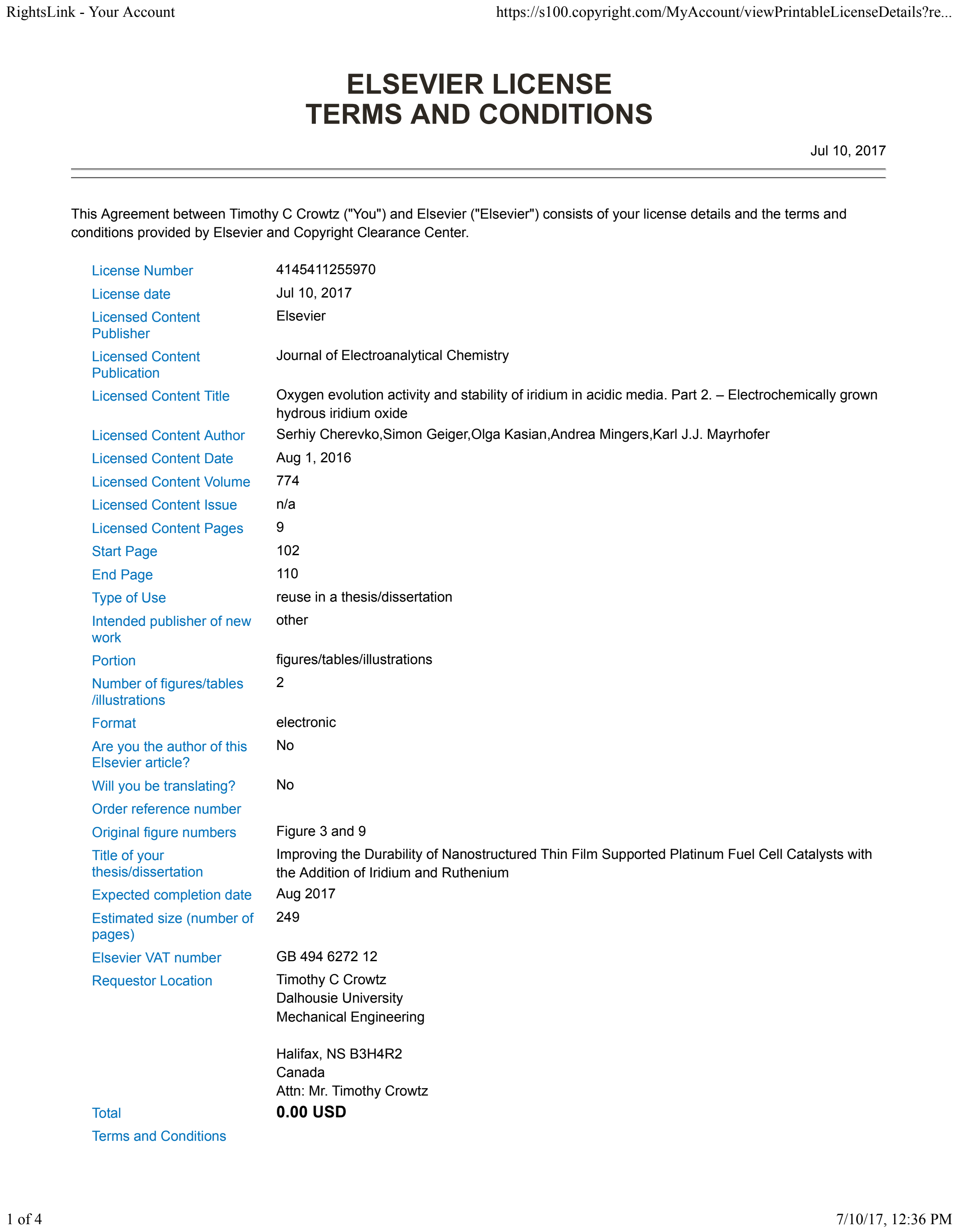
Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figures 2.38 and 2.39



ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This Agreement between Timothy C Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4145411255970
License date	Jul 10, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Electroanalytical Chemistry
Licensed Content Title	Oxygen evolution activity and stability of iridium in acidic media. Part 2. – Electrochemically grown hydrous iridium oxide
Licensed Content Author	Serhiy Cherevko,Simon Geiger,Olga Kasian,Andrea Mingers,Karl J.J. Mayrhofer
Licensed Content Date	Aug 1, 2016
Licensed Content Volume	774
Licensed Content Issue	n/a
Licensed Content Pages	9
Start Page	102
End Page	110
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	2
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	Figure 3 and 9
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Timothy C Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 2.40

Copyright Clearance Center RightsLink®

Home Account Info Help

ACS Publications Most Trusted. Most Cited. Most Read.

Title:	New Insights into Corrosion of Ruthenium and Ruthenium Oxide Nanoparticles in Acidic Media
Author:	Nejc Hodnik, Primož Jovanovič, Andraž Pavlišič, et al
Publication:	The Journal of Physical Chemistry C
Publisher:	American Chemical Society
Date:	May 1, 2015

Copyright © 2015, American Chemical Society

Logged in as:
Timothy Crowtz
Account #:
3001170588
LOGOUT

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

BACK CLOSE WINDOW

Permission for Figure 2.41

ELSEVIER LICENSE TERMS AND CONDITIONS

Jul 10, 2017

This Agreement between Timothy C Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4145420224192
License date	Jul 10, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Electroanalytical Chemistry
Licensed Content Title	A model for anodic hydrous oxide growth at iridium
Licensed Content Author	Peter G. Pickup,V.I. Birss
Licensed Content Date	Mar 25, 1987
Licensed Content Volume	220
Licensed Content Issue	1
Licensed Content Pages	18
Start Page	83
End Page	100
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	Figure 5
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Timothy C Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

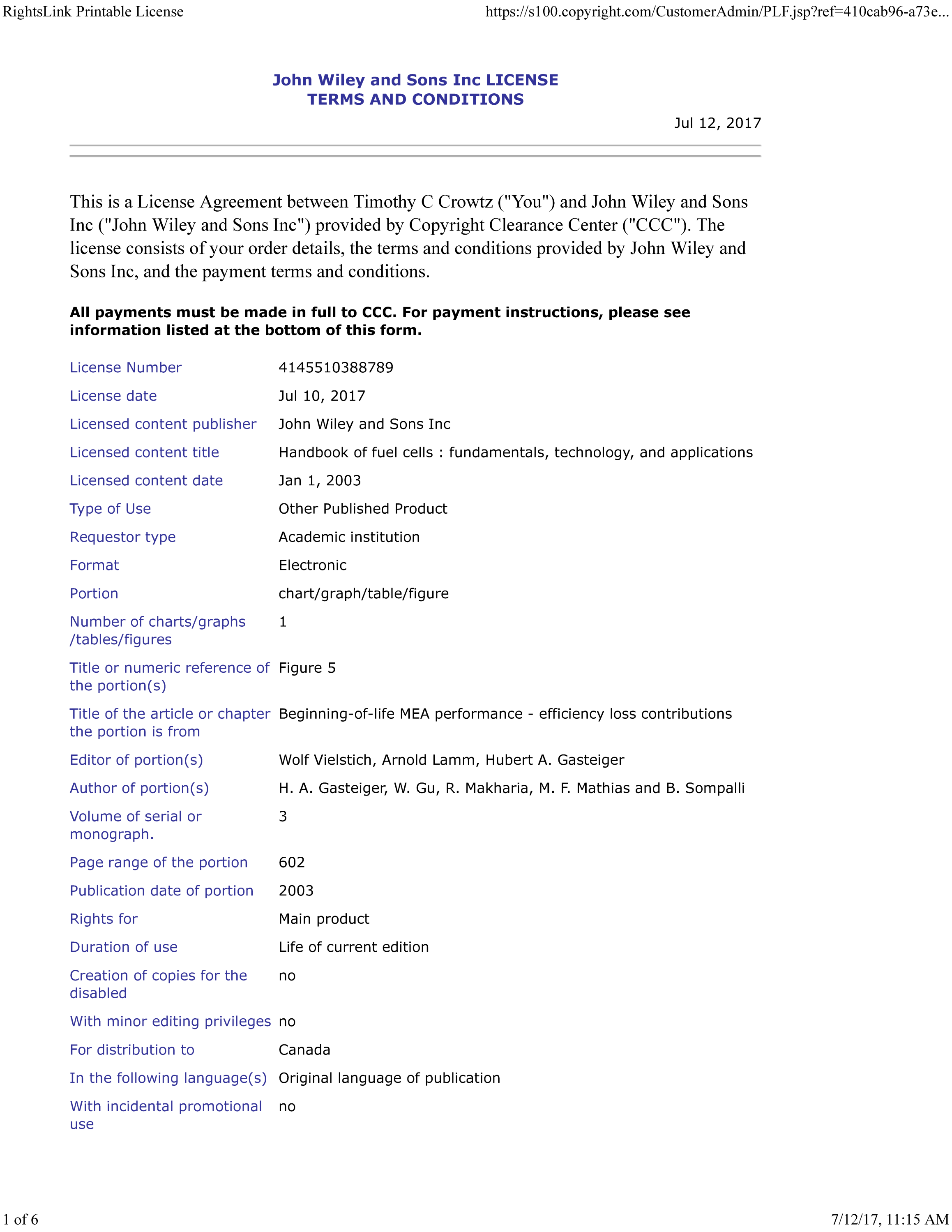
Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 3.2



RightsLink Printable License https://s100.copyright.com/CustomerAdmin/PLF.jsp?ref=410cab96-a73e...

John Wiley and Sons Inc LICENSE
TERMS AND CONDITIONS

Jul 12, 2017

This is a License Agreement between Timothy C Crowtz ("You") and John Wiley and Sons Inc ("John Wiley and Sons Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by John Wiley and Sons Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145510388789
License date	Jul 10, 2017
Licensed content publisher	John Wiley and Sons Inc
Licensed content title	Handbook of fuel cells : fundamentals, technology, and applications
Licensed content date	Jan 1, 2003
Type of Use	Other Published Product
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	1
Title or numeric reference of the portion(s)	Figure 5
Title of the article or chapter the portion is from	Beginning-of-life MEA performance - efficiency loss contributions
Editor of portion(s)	Wolf Vielstich, Arnold Lamm, Hubert A. Gasteiger
Author of portion(s)	H. A. Gasteiger, W. Gu, R. Makharia, M. F. Mathias and B. Sompalli
Volume of serial or monograph.	3
Page range of the portion	602
Publication date of portion	2003
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication
With incidental promotional use	no

1 of 6 7/12/17, 11:15 AM

The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University PhD Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley material.

This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

In no instance may the total amount of Wiley Materials used in any Main Product, Compilation or Collective work comprise more than 5% (if figures/tables) or 15% (if full articles/chapters) of the (entirety of the) Main Product, Compilation or Collective Work.

Some titles may be available under an Open Access license. It is the Licensors' responsibility to identify the type of Open Access license on which the requested material was published, and comply fully with the terms of that license for the type of use specified Further details can be found on Wiley Online Library http://olabout.wiley.com/WileyCDA/Section/id-410895.html.

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such

republication.
2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a "freelancer" or other third party independent of User and CCC, such party shall be deemed jointly a "User" for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.

3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on "net 30" terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.

3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is "one-time" (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).

3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.

3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC’s privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User’s rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact

us at 978-750-8400 or send an e-mail to info@copyright.com.
v 1.1

Permission for Figure 3.5

Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145460546520
License date	Jul 10, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	Journal of the Electrochemical Society
Licensed content date	Jan 1, 1948
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	1
Title or numeric reference of the portion(s)	Figure 2
Title of the article or chapter the portion is from	RDE Measurements of ORR Activity of Pt1 xIrx (0 < x < 0.3) on High Surface Area NSTF-Coated Glassy Carbon Disks
Editor of portion(s)	N/A
Author of portion(s)	Gary Chih-Kang Liu, R. J. Sanderson, George Vernstrom, D. A. Stevens, R. T. Atanasoski, M. K. Debe and J. R. Dahn
Volume of serial or monograph.	157
Issue, if republishing an article from a serial	2
Page range of the portion	B207-B214
Publication date of portion	2010
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication

With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University PhD Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the "Work(s)"). Copyright Clearance Center, Inc. ("CCC") grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the "Rightsholder"). "Republication", as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. "User", as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a "freelancer" or other third party independent of User and CCC, such party shall be deemed jointly a "User" for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.
3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on “net 30” terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.
3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is “one-time” (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).
3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.
3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses

incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 3.10

Re: Copyright Permission Request

Subject: Re: Copyright Permission Request
From: Vincent Chevrier <vincentchevrier@gmail.com>
Date: 2017-07-12 11:56 AM
To: Timothy Crowtz <tcrowtz@dal.ca>

Yes! Glad it can be of use

On Jul 12, 2017 9:52 AM, "Timothy Crowtz" <tcrowtz@dal.ca> wrote:

> Vincent,
> My I have please have permission to reuse your side-on drawing of a magnetron sputtering tunnel (Figure 3.2 from your Masters Thesis "Production, Characterization and Visualization of Quaternary Combinatorial Thin Films"; it's attached if you don't recall what figure I'm talking about) in my PhD thesis, titled "Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium"?
> If so, you could just reply with a "yes" ASAP and I will then include the email in the permissions appendix of my thesis.
> Many thanks,
> Tim

Permission for Figure 3.14

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This Agreement between Timothy C Crowtz ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4145451315671
License date	Jul 10, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Power Sources
Licensed Content Title	Relationship between carbon corrosion and positive electrode potential in a proton-exchange membrane fuel cell during start/stop operation
Licensed Content Author	Jutae Kim,Junhee Lee,Yongsug Tak
Licensed Content Date	Jul 15, 2009
Licensed Content Volume	192
Licensed Content Issue	2
Licensed Content Pages	5
Start Page	674
End Page	678
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	Figure 2
Title of your thesis/dissertation	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Expected completion date	Aug 2017
Estimated size (number of pages)	249
Elsevier VAT number	GB 494 6272 12
Requestor Location	Timothy C Crowtz Dalhousie University Mechanical Engineering Halifax, NS B3H4R2 Canada Attn: Mr. Timothy Crowtz
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu. Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figures 3.17 and 3.18

Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145480090297
License date	Jul 10, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	ECS transactions
Licensed content date	Jan 1, 2005
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	2
Title or numeric reference of the portion(s)	Figure 5 and 6
Title of the article or chapter the portion is from	In-Situ Reference Electrode Testing for Cathode Carbon Corrosion
Editor of portion(s)	N/A
Author of portion(s)	Robert Dross and Bruce Maynard
Volume of serial or monograph.	11
Issue, if republishing an article from a serial	1
Page range of the portion	1059-1068
Publication date of portion	2007
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication

With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University PhD Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.

3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on “net 30” terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.

3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is “one-time” (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).

3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.

3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses

incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Permission for Figure 3.19

Electrochemical Society, Inc LICENSE
TERMS AND CONDITIONS

Jul 10, 2017

This is a License Agreement between Timothy C Crowtz ("You") and Electrochemical Society, Inc ("Electrochemical Society, Inc") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Electrochemical Society, Inc, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	4145480400802
License date	Jul 10, 2017
Licensed content publisher	Electrochemical Society, Inc
Licensed content title	ECS transactions
Licensed content date	Jan 1, 2005
Type of Use	Thesis/Dissertation
Requestor type	Academic institution
Format	Electronic
Portion	chart/graph/table/figure
Number of charts/graphs /tables/figures	1
Title or numeric reference of the portion(s)	Figure 2
Title of the article or chapter the portion is from	Membrane and Catalyst Performance Targets for Automotive Fuel Cells by FCCJ Membrane, Catalyst, MEA WG
Editor of portion(s)	N/A
Author of portion(s)	Atsushi Ohma, Kazuhiko Shinohara, Akihiro Iiyama, Toshihiko Yoshida and Akimasa Daimaru
Volume of serial or monograph.	41
Issue, if republishing an article from a serial	1
Page range of the portion	775-784
Publication date of portion	2011
Rights for	Main product
Duration of use	Life of current edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Canada
In the following language(s)	Original language of publication

With incidental promotional use	no
The lifetime unit quantity of new product	Up to 499
Made available in the following markets	Canada
The requesting person/organization is:	Timothy Crowtz (Dalhousie University)
Order reference number	
Author/Editor	Timothy Crowtz
The standard identifier of New Work	Dalhousie University PhD Thesis
The proposed price	0
Title of New Work	Improving the Durability of Nanostructured Thin Film Supported Platinum Fuel Cell Catalysts with the Addition of Iridium and Ruthenium
Publisher of New Work	Dalhousie University
Expected publication date	Aug 2017
Estimated size (pages)	250
Total (may include CCC user fee)	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

The following terms are individual to this publisher:

None

Other Terms and Conditions:

STANDARD TERMS AND CONDITIONS

1. Description of Service; Defined Terms. This Republication License enables the User to obtain licenses for republication of one or more copyrighted works as described in detail on the relevant Order Confirmation (the “Work(s)”). Copyright Clearance Center, Inc. (“CCC”) grants licenses through the Service on behalf of the rightsholder identified on the Order Confirmation (the “Rightsholder”). “Republication”, as used herein, generally means the inclusion of a Work, in whole or in part, in a new work or works, also as described on the Order Confirmation. “User”, as used herein, means the person or entity making such republication.

2. The terms set forth in the relevant Order Confirmation, and any terms set by the Rightsholder with respect to a particular Work, govern the terms of use of Works in connection with the Service. By using the Service, the person transacting for a republication license on behalf of the User represents and warrants that he/she/it (a) has been duly authorized by the User to accept, and hereby does accept, all such terms and conditions on behalf of User, and (b) shall inform User of all such terms and conditions. In the event such person is a “freelancer” or other third party independent of User and CCC, such party shall be deemed jointly a “User” for purposes of these terms and conditions. In any event, User shall be deemed to have accepted and agreed to all such terms and conditions if User republishes the Work in any fashion.

3. Scope of License; Limitations and Obligations.

3.1 All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The license created by the exchange of an Order Confirmation (and/or any invoice) and payment by User of the full amount set forth on that document includes only those rights expressly set forth in the Order Confirmation and in these terms and conditions, and conveys no other rights in the Work(s) to User. All rights not expressly granted are hereby reserved.
3.2 General Payment Terms: You may pay by credit card or through an account with us payable at the end of the month. If you and we agree that you may establish a standing account with CCC, then the following terms apply: Remit Payment to: Copyright Clearance Center, 29118 Network Place, Chicago, IL 60673-1291. Payments Due: Invoices are payable upon their delivery to you (or upon our notice to you that they are available to you for downloading). After 30 days, outstanding amounts will be subject to a service charge of 1-1/2% per month or, if less, the maximum rate allowed by applicable law. Unless otherwise specifically set forth in the Order Confirmation or in a separate written agreement signed by CCC, invoices are due and payable on “net 30” terms. While User may exercise the rights licensed immediately upon issuance of the Order Confirmation, the license is automatically revoked and is null and void, as if it had never been issued, if complete payment for the license is not received on a timely basis either from User directly or through a payment agent, such as a credit card company.
3.3 Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) is “one-time” (including the editions and product family specified in the license), (ii) is non-exclusive and non-transferable and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Order Confirmation or invoice and/or in these terms and conditions. Upon completion of the licensed use, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work (except for copies printed on paper in accordance with this license and still in User's stock at the end of such period).
3.4 In the event that the material for which a republication license is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) which are identified in such material as having been used by permission, User is responsible for identifying, and seeking separate licenses (under this Service or otherwise) for, any of such third party materials; without a separate license, such third party materials may not be used.
3.5 Use of proper copyright notice for a Work is required as a condition of any license granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: “Republished with permission of [Rightsholder’s name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc. ” Such notice must be provided in a reasonably legible font size and must be placed either immediately adjacent to the Work as used (for example, as part of a by-line or footnote but not as a separate electronic link) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

3.6 User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

4. Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy or other tangible or intangible property.

5. Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for this license. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors and assigns.

6. Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED “AS IS”. CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

7. Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the license set forth in the Order Confirmation and/or these terms and conditions, shall be a material breach of the license created by the Order Confirmation and these terms and conditions. Any breach not cured within 30 days of written notice thereof shall result in immediate termination of such license without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses

incurred in collecting such payment.

8. **Miscellaneous.**

8.1 User acknowledges that CCC may, from time to time, make changes or additions to the Service or to these terms and conditions, and CCC reserves the right to send notice to the User by electronic mail or otherwise for the purposes of notifying User of such changes or additions; provided that any such changes or additions shall not apply to permissions already secured and paid for.

8.2 Use of User-related information collected through the Service is governed by CCC's privacy policy, available online here: http://www.copyright.com/content/cc3/en/tools/footer/privacypolicy.html.

8.3 The licensing transaction described in the Order Confirmation is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the license created by the Order Confirmation and these terms and conditions or any rights granted hereunder; provided, however, that User may assign such license in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in the new material which includes the Work(s) licensed under this Service.

8.4 No amendment or waiver of any terms is binding unless set forth in writing and signed by the parties. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the licensing transaction described in the Order Confirmation, which terms are in any way inconsistent with any terms set forth in the Order Confirmation and/or in these terms and conditions or CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

8.5 The licensing transaction described in the Order Confirmation document shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such licensing transaction shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.If you have any comments or questions about the Service or Copyright Clearance Center, please contact us at 978-750-8400 or send an e-mail to info@copyright.com.

v 1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.