AMORPHOUS ELECTROCATALYSTS FORMED BY NEAR-INFRARED-DRIVEN DECOMPOSITION

by

Danielle Aline Salvatore

B.Sc. Chemistry, McGill University, 2013

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate and Postdoctoral Studies

(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

August 2015

© Danielle Aline Salvatore, 2015
Abstract

The splitting of water into hydrogen and oxygen is widely viewed as the most sustainable option for storing energy produced by intermittent renewable energy sources such as solar or wind. Economically feasible large-scale deployment of this type of system requires the discovery of efficient electrocatalysts, particularly for the kinetically slow oxygen evolution reaction (OER). Transition metal oxides are the most durable and active water oxidation catalysts, and there is a growing body of evidence showing amorphous metal oxide films mediate the OER more efficiently than the crystalline phases of the same compositions. Notwithstanding, there is a limited set of fabrication methods available for making amorphous films, particularly in the absence of a conducting substrate. I introduce herein a scalable preparative method for accessing oxidized and reduced phases of amorphous films that involves the efficient decomposition of molecular precursors, including simple metal salts, by exposure to near-infrared (NIR) radiation. The NIR-driven decomposition process provides sufficient localized heating to trigger the liberation of the ligand from solution-deposited precursors on substrates, but insufficient thermal energy to form crystalline phases. This method provides access to state-of-the-art electrocatalyst films, as demonstrated herein for the electrolysis of water, and extends the scope of usable substrates to include non-conducting and temperature-sensitive platforms.

Because crystalline ruthenium oxide is one of the most efficient electrocatalysts in acidic media, it would be highly advantageous to be able to readily access the amorphous phase of the material. I also document two facile preparation techniques for accessing amorphous ruthenium oxide, a state-of-the-art electrocatalyst. The formation of amorphous ruthenium oxide films is triggered by the decomposition of a film of spin-cast molecular ruthenium precursors on conducting glass by either ultraviolet (UV) and near infrared (NIR) light.
Preface

Danielle A. Salvatore conducted the literature review, design of the experimental set-up, experimental data collection and analysis under the supervision of Dr. Curtis P. Berlinguette.

The material covered in Chapter 2 was published:


The material covered in Chapter 3 is under preparation for publication:

D.A. Salvatore, C.P. Berlinguette, Accessing Amorphous Ruthenium Oxide Via Controlled Processes. Energy Enviro. Sci.. (under preparation)

Danielle A. Salvatore prepared the initial and final drafts of this thesis, with revisions edited and approved by Dr. Curtis P. Berlinguette.
Table of Contents

Abstract ................................................................................................................................. ii
Preface ................................................................................................................................. iii
Table of Contents ................................................................................................................ iv
List of Tables ....................................................................................................................... v
List of Figures ...................................................................................................................... vi
List of Symbols, Abbreviations and Nomenclature ............................................................. xii
Acknowledgements .......................................................................................................... xv
Dedication ............................................................................................................................. xvi

1 Chapter 1: Introduction ................................................................................................. 1
  1.1 Solar Energy Supply & Storage ................................................................................. 1
  1.2 Water Splitting ......................................................................................................... 2
  1.3 Electrochemical Catalyst Characterization ............................................................... 4
  1.4 Amorphous Electrocatalytic Films ........................................................................... 7
  1.5 Infrared Curing ........................................................................................................ 9
  1.6 Project Outline ........................................................................................................ 11
  1.7 CREATE sustainable synthesis ............................................................................... 12

2 Chapter 2: Near-Infrared-Driven Decomposition ......................................................... 14
  2.1 Introduction ............................................................................................................ 14
  2.2 Amorphous Metal Oxide Film Formation & Characterization ............................... 16
  2.3 Access to Reduced Forms of Metal Films ................................................................. 26
  2.4 Mixed-Metal Oxides .............................................................................................. 30
  2.5 Non-conducting, UV & Heat Sensitive Materials .................................................... 34
  2.6 Conclusions ........................................................................................................... 35

3 Chapter 3: Amorphous Ruthenium Oxide .................................................................. 36
  3.1 Introduction ............................................................................................................ 36
  3.2 Ultraviolet-light Driven Decomposition .................................................................. 38
  3.3 Near Infrared Driven Decomposition ..................................................................... 41
  3.4 Electrochemical Data ............................................................................................. 42
  3.5 Conclusions ........................................................................................................... 49

4 Chapter 4: Conclusions and Future Directions ............................................................. 51
  4.1 Conclusions ........................................................................................................... 51
  4.2 Future Directions ................................................................................................... 53

5 Chapter 5: Experimental .............................................................................................. 57
  5.1 Chapter 2 ................................................................................................................ 57
      5.1.1 Materials ........................................................................................................ 57
      5.1.2 Film Syntheses .............................................................................................. 57
      5.1.3 Physical Methods ......................................................................................... 60
  5.2 Chapter 3 ................................................................................................................ 62
      5.2.1 Materials ........................................................................................................ 62
      5.2.2 Film Syntheses .............................................................................................. 62
      5.2.3 Physical Methods ......................................................................................... 64

6 References ..................................................................................................................... 66
List of Tables

Table 1.1. Cost comparison of fabrication techniques for the formation of $a$-RuO$_x$ ....... 13

Table 2.1 Benchmarked OER Activities of $a$-MO$_x$ films ................................................. 22

Table 2.2. Elemental Analysis of Amorphous Metal Oxide Films Determined by EDX. 33

Table 3.1. Relevant Benchmarking Parameters for Ruthenium Oxide OER Catalysts. ... 44
List of Figures

**Figure 1.1.** Utility load (blue) versus solar power output (black). Overlaid on the demand curve (MW) is the power output (kW) sampled every minute for a 4.6 solar PV array in north-western Arizona over the period of one day.\(^2\) .................................................. 2

**Figure 1.2.** Ragone plot of specific power density versus energy density of various storage methods.\(^1\) PHES (pumped heat electric storage), CAES (compressed air energy storage) .......................................................... 3

**Figure 1.3.** (A) electrodeposition, (B) magnetron sputtering, and (C) ultraviolet light driven decomposition schematics. .......................................................... 8

**Figure 1.4.** UV-vis-NIR absorption spectra of ruthenium complex \([\text{Ru(bpy)}_2\text{(sq)}]^+\). A LMCT transition is centered in the NIR region.\(^{34}\) ........................................... 9

**Figure 1.5.** Industrial infrared curing equipment: (A) automotive panel portable curing system\(^{37}\); (B) line conveyor oven for oil filters\(^{37}\); and (C) chain-on-edge system for glass panel\(^{37}\) ................................................................. 11

**Figure 2.1.** Scheme outlining the near-infrared driven decomposition (NIRDD) of metal precursors (e.g., FeCl\(_3\)) on a substrate (e.g., FTO) leads to the formation of amorphous metal oxide (a-MO\(_x\)) and reduced metal (a-M) films under air and nitrogen, respectively. ................................................................. 15

**Figure 2.2.** Temperature profiles of FeCl\(_3\)/FTO (purple), Fe(eh\(_3\))/FTO (blue) and bare FTO (black). Additional control measurements were also collected on a sample where Fe(eh\(_3\)) deposited directly on the copper wire of the thermocouple by the NIRDD process, denoted Fe(eh\(_3\))/thermocouple (red), as well as the bare wire of the thermocouple (green). Temperature readings were recorded with a thermocouple in 5-min increments, and indicated a rise in temperature that plateaus at a value no greater than 175 °C. These collective results confirm that a substrate temperature of 200 °C is not reached during a constant 1 h exposure to NIR radiation under our experimental conditions................................................................. 16

**Figure 2.3.** UV-vis absorption spectra, before and after being subjected to the NIRDD process, of: (A) metal halide precursor complexes on glass, FeCl\(_3\)/glass (1), NiCl\(_2\)/glass (2), and Fe\(_2\)Ni\(_3\)Cl/glass (3); and (B) coordination complexes on glass, Fe(eh\(_3\))/glass (1), Ni(eh\(_3\))/glass (2), Fe\(_2\)Ni\(_3\)(eh\(_3\))/glass (3), Ir(acac\(_3\))/glass (4) and Mn(eh\(_3\))/glass (5). Data for FeCl\(_3\)/glass and Fe(eh\(_3\))/glass following the NIRDD process in a nitrogen environment is indicated by “1/N\(_2\)” , respectively. The glass background is also shown. Note that glass was used rather than FTO to avoid interference at longer wavelengths. The film Fe\(_2\)Ni\(_3\)Cl/glass was prepared from a solution of 2 g of deionized water containing NiCl\(_2\) (0.088 g) and FeCl\(_3\) (0.039 g) that was spin-cast onto a glass substrate. The repetitive wave pattern in the 1/N\(_2\) red trace is caused by diffraction of glass as the film is very thin................................................................. 18

**Figure 2.4.** Powder XRD patterns acquired on as-prepared and annealed \(T_{\text{anneal}} = 600 \, ^\circ\text{C}\) a-FeO\(_x\) and a-Fe films prepared by applying the NIRDD process to (A) FeCl\(_3\) and (B) Fe(eh\(_3\)) deposited on FTO under air and nitrogen, respectively. Data recorded on a bare FTO substrate is also provided. **Inset:** Expanded view highlighting the region where
the reflection associated with the maghemite and hematite form of Fe$_2$O$_3$ at 35.5° is observed. This reflection is observed only for the films annealed at 600 °C under air, denoted FeO$_x$-annealed.

**Figure 2.5.** XRD patterns acquired on as-prepared and annealed ($T_{\text{anneal}} = 600$ °C) $a$-FeO$_x$ films prepared by applying the NIRDD process to (A) FeCl$_3$ and (B) Fe(eh)$_3$ deposited on FTO under air. The bars represent the Bragg reflections for the hematite form of Fe$_2$O$_3$. This reflection is observed only for the films annealed at 600 °C, denoted FeO$_x$-annealed.

**Figure 2.6.** Cyclic voltammograms for thin films of (A) $a$-FeO$_x$ and (B) $a$-Fe on FTO. Values indicate the sequence of the cycles that were recorded. The oxidative sweep of (A) $a$-FeO$_x$ leads to a sharp rise in current coincident with catalytic water oxidation and subsequent cycles led to superimposable traces. The oxidative sweep for (B) $a$-Fe featured a markedly different current profile for the first cycle; however, subsequent cycles indicated $a$-Fe was converted to $a$-FeO$_x$ upon oxidation on the basis of the superimposable scans. The differences in the reductive behavior were more stark, the cathodic peak at -0.25 V for (A) $a$-FeO$_x$ was not detected for (B) $a$-Fe prior to HER catalysis, indicating a more reduced form of iron for (B). Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s$^{-1}$; electrolyte = 0.1 M KOH (aq). 

**Figure 2.7.** Chronoamperometric measurements for thin films of $a$-FeO$_x$, prepared by the NIRDD process in air from FeCl$_3$ (blue) and Fe(eh)$_3$ (black). Blank FTO is also shown (black). The current was held at 10 mA/cm$^2$ for 7200 s. All data is collected on films deposited on FTO, and thus the slight differences in the response of the $a$-FeO$_x$ films are attributed to minor differences in film roughness or film densities. Electrochemistry conditions: Counter Electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 0.1 M KOH$_{({aq})}$; current densities were corrected for uncompensated resistance. The initial drop in current density over the first 5 minutes on blank FTO can be attributed to an initial conditioning step.

**Figure 2.8.** Cyclic voltammograms for thin films of $a$-FeO$_x$, prepared by the NIRDD process in air, and the respective precursor films from which they were derived from; Fe(NO$_3$)$_3$ (red), FeCl$_3$ (blue) and Fe(eh)$_3$ (black) precursors. All data is collected on films deposited on FTO, and thus the slight differences in the response of the $a$-FeO$_x$ films are attributed to minor differences in film roughnesses or film densities. Electrochemistry conditions: Counter Electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s$^{-1}$; electrolyte = 0.1 M KOH$_{({aq})}$; current densities were corrected for uncompensated resistance.

**Figure 2.9.** XRD patterns acquired on as-prepared films of (A) $a$-IrO$_x$, (B) $a$-NiO$_x$, and (C) $a$-MnO$_x$ on FTO. No reflections are observed other than those associated with FTO (black).

**Figure 2.10.** Cyclic voltammograms recorded on thin films of $a$-IrO$_x$ (red), $a$-NiO$_x$ (black), $a$-MnO$_x$ (green) and $a$-Fe$_2$Ni$_2$O$_x$ (blue) on FTO. Data recorded on bare FTO is also shown (grey). Electrochemistry conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s$^{-1}$; electrolyte = 1 M KOH (aq).
H$_2$SO$_4$$_{(aq)}$ for a-IrO$_x$, or 0.1 M KOH$_{(aq)}$ for a-NiO$_x$, a-MnO$_x$, a-Fe$_2$Ni$_3$O$_4$ and bare FTO. Current densities were corrected for uncompensated resistance.

**Figure 2.11.** TGA and DSC profiles for (A) FeCl$_3$ and (B) Fe(eh)$_3$ under air and N$_2$ at a ramp rate of 10 °C min$^{-1}$. The bottom plots overlay the respective percent-mass-loss profiles in air and N$_2$ to highlight the effect of the atmospheric environment. Both FeCl$_3$ and Fe(eh)$_3$ appear to lose ligands in a stepwise fashion; our tentative assignments indicate that the first ligand is excluded at ~200 °C and the last ligand is liberated at ~400 °C. The ligands are excluded from FeCl$_3$ in three distinct steps in both air and N$_2$, while data recorded on Fe(eh)$_3$ in air shows the loss of two ligands in quick succession followed by the loss of the third ligand at higher temperatures; this pattern is reversed under nitrogen. Complete decomposition is not complete until $T > 400$ °C for any of the data shown, which is much higher than the surface temperatures reached during the NIRDD process.

**Figure 2.12.** TGA and DSC profiles for (A) FeCl$_3$ and (B) Fe(eh)$_3$ brought to 200 °C and then held for 60 min. The FeCl$_3$ and Fe(eh)$_3$ precursor complexes do not decompose fully to a final mass of Fe$_2$O$_3$ during this period. Both measurements were recorded in an aerobic environment.

**Figure 2.13.** FTIR spectra of independent samples of Fe(eh)$_3$/FTO before (black traces) and after (blue traces) (A) exposure to NIR radiation for 30 min, (B) heating at 200°C in a furnace for 30 min, (C) heating at 250°C in a furnace for 30 min... 25

**Figure 2.14.** FTIR spectra for thin films of Fe(eh)$_3$ on FTO upon exposure to NIR radiation for (A) 0 (black), 4, 16, 32 and 64 (blue) min in air, and (B) 0 (black) and 60 (blue) min under nitrogen. Arrows indicate trends in the intensities of the C-H and C-O vibrational modes of 2-ethylhexanoate. 25

**Figure 2.15.** FTIR spectra of thin films of Ir(acac)$_3$/FTO, Ni(eh)$_2$/FTO, and Mn(eh)$_3$/FTO for 0 (black), 4 (red), 16 (green), 64 (blue), 128 (orange), and 256 min (navy) subjected to the NIRDD process showing the progressive loss of ligands in <2 h. Absorption bands are associated with the symmetric and asymmetric vibrations of the C-O groups of the 2-ethylhexanoate ligand and free acid.

**Figure 2.16.** X-ray photoelectron spectra for a-FeO$_x$ (red) and a-Fe (blue) on FTO. The (A) survey scan, and spectral regions corresponding to the (B) iron 2p and (C) carbon 1s regions, are shown.

**Figure 2.17.** X-ray photoelectron spectra detailing the Fe 2p$_{3/2}$ region. Sums of the fitting components for (A) a-FeO$_x$ and (B) a-Fe are shown in red. Curve fitting in A used Gupta Sen parameters based on Fe$_2$O$_3$ (blue) along with a surface peak (orange) and an Fe$^{3+}$ satellite peak (blue). Curve fitting in B used center-of-gravity peaks for Fe$^{2+}$ (green) and Fe$^{3+}$ (blue); a surface peak (orange) and a Fe$^{2+}$ satellite peak (green) are also shown. The Fe$^{3+}$ satellite peak is not shown, as it is likely superimposed with the Fe 2p$_{3/2}$ peak.

**Figure 2.18.** XPS data for a-CuO$_x$ (red) and a-Cu (blue) on FTO. The (A) survey scan, along with the rough fitting of the Cu LMM regions denoting (B) CuO and (C) Cu$_2$O, are shown.
Figure 2.19. XPS spectra on the copper 2p$_{3/2}$ region. The fitting of the copper 2p$_{3/2}$ region of XPS recorded on thin films of Cu(eh)$_2$ on FTO after being subjected to the NIRDD process under (A) air and (B) nitrogen, respectively; sum of the fitting components are indicated (red traces). Fitting of the data used centre-of-gravity peaks for (A) Cu(O) (green) and Cu(OH)$_2$ (orange), and (B) Cu(I)/Cu(0) (green). Signature copper(II) satellite peaks present in (A) but not (B) confirm a more reduced form of the film when prepared under nitrogen. The computed baselines are indicated in blue. ...

Figure 2.20. Images of solid samples of (A) Cu(eh)$_2$, (B) Cu(eh)$_2$ subjected to NIRDD under nitrogen, and (C) Cu(eh)$_2$ subjected to NIRDD under air. The colors of the samples in (B) and (C) indicate elemental copper and copper oxide, respectively. ...

Figure 2.21. Powder XRD patterns acquired on as-prepared and annealed ($T_{\text{anneal}} = 600$ °C) $a$-Cu$_x$O$_a$ and $a$-Cu films prepared from Cu(eh)$_2$ under (A) air and (B) nitrogen. Data recorded on bare FTO substrate is also included. Inset: Expanded view highlighting the region where the reflection associated with the crystalline form of CuO at 35.5° is observed. This signal is observed only for the films annealed at 600 °C under air and N$_2$. Cu$_O/a$-annealed and Cu-annealed. .................................................. 30

Figure 2.22. FTIR spectra of Fe$_2$Ni$_3$(eh)$_3$/FTO subjected to NIRDD for the times indicated under (A) air and (B) nitrogen to highlight the progressive loss in intensity of the bands associated with the ligand. ........................................................................ 31

Figure 2.23. XRD patterns acquired on as-prepared films of (A) $a$-Fe$_2$Ni$_3$O$_x$ and (B) $a$-Fe$_2$Ni$_3$ on FTO recorded under air and nitrogen, respectively. No reflections were observed other than those associated with FTO (black). .................................................. 32

Figure 2.24. Cyclic voltammograms for thin films of (A) $a$-Fe$_2$Ni$_3$O$_x$ and (B) $a$-Fe$_2$Ni$_3$ prepared by NIRDD under air and N$_2$, respectively. Electrochemistry conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s$^{-1}$; electrolyte = 0.1 M KOH(_aq_); current densities were corrected for uncompensated resistance. ........................................................................ 32

Figure 2.25. (A) Cyclic voltammograms for thin films of $a$-IrO$_x$/membrane (blue trace), Ir(acac)$_3$/membrane (red trace), and the membrane (black trace), where the membrane is Nafion® (B) The membrane electrode assembly was prepared by mechanically pressing a platinum mesh counter electrode, the prepared Nafion membrane, and a Toray carbon paper gas diffusion layer between two Ti plate electrodes. The catalytic current with the blank membrane is due to the titanium plates mediating the OER reaction. Electrochemistry conditions: counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s$^{-1}$; electrolyte = 0.5 M H$_2$SO$_4(_{aq})$; current densities were corrected for uncompensated resistance. ........................................... 34

Figure 2.26. (A) Full and (B) expanded FTIR spectra of Ir(acac)$_3$/membrane subjected to NIR radiation for 0 (black) and 60 (blue) min. A trace for untreated Nafion membrane (red) is also shown. The magnified spectrum in (B) is included to feature the loss in intensities of the bands associated with the ligand vibrational modes. 35

Figure 3.1. The photolytic formation of $a$-RuO$_x$ by ultraviolet-light driven decomposition (UVDD) and near-infrared driven decomposition (NIRDD) on fluorine-doped SnO$_2$-coated glass (FTO) substrates. ........................................... 38
Figure 3.2. FTIR spectra for thin films of Ru(tmhd)₂(cod) on FTO upon exposure to UV radiation for (A) 0 (black), 12 (red), 24 (blue) h under UV light (i.e., \( \lambda_{\text{max}} \) at 185 and 254 nm); and (B) 0 (black), 24 (red), 72 (blue) h under selective UV light (i.e., \( \lambda_{\text{max}} = 254 \) nm light). Arrows indicate trends in the intensities of the C-H and C-O vibrational modes for organic ligands.

Figure 3.3. UV-vis absorption spectra, before (top) and after (bottom) being subjected to the NIRDD or UVDD processes of: Ru(tmhd)₂(cod) and RuCl₃ on FTO. The FTO background is also shown. The repetitive wave pattern in the traces is caused by diffraction on the FTO substrate, as the films are very thin.

Figure 3.4. Top: Powder XRD patterns acquired on as-prepared and annealed \( \alpha \)-RuOₓ films prepared by applying the UVDD process to precursor thin films on FTO; as prepared (purple), annealed at 300°C (red), and annealed at 500°C (blue). Data recorded on a bare FTO substrate is also provided (black). Bottom: Expanded view highlighting the region where the reflection associated with the crystalline form of RuOₓ at 28° and 40° is observed. This reflection is observed only for the films annealed at 500°C.

Figure 3.5. Top: Powder XRD patterns acquired on as-prepared and annealed \( \alpha \)-RuOₓ films prepared by applying the NIRDD process to precursor thin films on FTO; as prepared (red), annealed at 300°C and annealed at 500°C (blue). Data recorded on a bare FTO substrate is also provided (black). Bottom: Expanded view highlighting the region where the reflection associated with the crystalline form of RuOₓ at 28° and 40° is observed. This reflection is observed only for the films annealed at 500°C.

Figure 3.6. Cyclic voltammograms (CVs) (A) and chronopotentiometric scans (B) for as-prepared and annealed thin films of \( \alpha \)-RuOₓ and \( c \)-RuOₓ formed by the UVDD and NIRDD; UVDD films annealed at 300°C (red) and 500°C (blue), NIRDD fresh film (purple) and annealed film at 500°C (green). Bare FTO trace is shown as a reference, note the instability in acidic environments demonstrating that the films act as protective layers. CVs: scan rate = 10 mV s⁻¹; chronopotentiometry: current density = 10 mA cm⁻² for 2 h. Electrochemical conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H₂SO₄ (aq).

Figure 3.7. Cyclic voltammograms for thin films of \( \alpha \)-RuOₓ and \( c \)-RuOₓ formed through the UVDD method and annealed at various temperatures; fresh film (purple), 100°C (red), 200°C (orange), 300°C (green), 400°C (red), 500°C (green), and 500°C (blue). Shown on the left is cycle 1 and right is cycle 3. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s⁻¹; electrolyte = 1 M H₂SO₄ (aq).

Figure 3.8. Cyclic voltammograms for thin films of \( \alpha \)-RuOₓ and \( c \)-RuOₓ formed through the NIRDD method and annealed at various temperatures; fresh film (purple), annealed films at 300°C (red), 400°C (green), and 500°C (blue). Left: cycle 1. Right: cycle 3. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s⁻¹; electrolyte = 1 M H₂SO₄ (aq).

Figure 3.9. Chronopotentiometric experiments of thin films of \( \alpha \)-RuOₓ and \( c \)-RuOₓ prepared through the UVDD method annealed at 300°C (red), 400°C (red), 500°C (blue). An FTO trace is also shown as reference (black), note the instability in acidic
environments demonstrating that the films act as protective layers. The current was held at 10 mA cm$^{-2}$ for 7200 s. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq). FTO is significantly unstable under acidic conditions.

**Figure 3.10.** Chronopotentiometric experiments of thin films of $a$-RuO$_x$ and $c$-RuO$_x$ prepared through the NIRDD method; fresh film (purple), annealed at 300°C (orange), 400°C (green), 500°C (blue). An FTO trace is also shown as reference (black), note the instability in acidic environments demonstrating that the films act as protective layers. The current was held at 10 mA cm$^{-2}$ for 7200 s. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq).

**Figure 3.11.** Relative electrochemical surface area of thin films of $a$-RuO$_x$ and $c$-RuO$_x$ formed through the UVDD and NIRDD methods and annealed films at various temperatures; UVDD films annealed at 300°C (red) and 500°C (blue), NIRDD fresh film (purple) and annealed film at 500°C (green). Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq).

**Figure 3.12.** Tafel plots for as-prepared and annealed thin films of $a$-RuO$_x$ and $c$-RuO$_x$ formed by the UVDD and NIRDD; UVDD films annealed at 300°C (red) and 500°C (blue), NIRDD fresh film (purple) and annealed film at 500°C (green). Tafel plots were acquired through staircase voltammetry (10 mV steps, 50 s intervals for the final 25 s sampled). Electrochemical conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq).

**Figure 3.13.** Cyclic voltammograms (CVs) (A) and chronopotentiometric scans (B) for Ru based films formed through the NIRDD method; $a$-RuO$_x$ (purple), $c$-RuO$_x$ (film annealed at 500°C) (blue) and $a$-RuTiO$_x$ (green), $a$-RuTaO$_x$ (red). Bare FTO is shown as reference (black), note the instability in acidic environments demonstrating that the films act as protective layers. CVs: scan rate = 10 mV s$^{-1}$; chronopotentiometry: current density = 10 mA cm$^{-2}$ for 2 h. Electrochemical conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq).

**Figure 4.1.** (A) Triangular gradient patterns are shown on the top and false color images of photocurrent are on the bottom. (B) Photograph of a scanning droplet cell. (C) Schematic drawing of the electrochemical screening apparatus showing the positions of the electrode array, O$_2$-sensing mesh, light source and camera.

**Figure 4.2.** The UVDD and NIRDD techniques implemented to form metal oxide catalysts from inkjet printed precursors followed by electrochemically automated process to characterize the catalysts.
### List of Symbols, Abbreviations and Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>$a$-Fe</td>
<td>Amorphous Iron</td>
</tr>
<tr>
<td>$a$-Fe$_2$Ni$_3$</td>
<td>Amorphous Iron Nickel</td>
</tr>
<tr>
<td>$a$-Fe$_2$Ni$_3$O$_x$</td>
<td>Amorphous Iron Nickel Oxide</td>
</tr>
<tr>
<td>$a$-FeO$_x$</td>
<td>Amorphous Iron Oxide</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>Silver / Silver Chloride Reference Electrode</td>
</tr>
<tr>
<td>$a$-IrO$_x$</td>
<td>Amorphous iridium oxide</td>
</tr>
<tr>
<td>$a$-Mn</td>
<td>Amorphous Manganese</td>
</tr>
<tr>
<td>$a$-MnO$_x$</td>
<td>Amorphous Manganese Oxide</td>
</tr>
<tr>
<td>$a$-NiO$_x$</td>
<td>Amorphous Nickel Oxide</td>
</tr>
<tr>
<td>$a$-RuO$_x$</td>
<td>Amorphous Ruthenium Oxide</td>
</tr>
<tr>
<td>$a$-RuTaO$_x$</td>
<td>Amorphous ruthenium tantalum oxide</td>
</tr>
<tr>
<td>$a$-RuTiO$_x$</td>
<td>Amorphous ruthenium titanium oxide</td>
</tr>
<tr>
<td>b</td>
<td>Tafel Slope</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>CAES</td>
<td>Compressed air energy storage</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>Cu(eh)$_2$</td>
<td>Copper(II) 2-ethylhexanoate</td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>Copper(II) Hydroxide</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>Copper(II) Oxide</td>
</tr>
<tr>
<td>CuO</td>
<td>Copper(I) Oxide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>$E_{\text{measured}}$</td>
<td>Measured cell potential</td>
</tr>
<tr>
<td>Eq</td>
<td>Equation</td>
</tr>
<tr>
<td>$E_{\text{ref}}$</td>
<td>Reference electrode potential</td>
</tr>
<tr>
<td>$E_{\text{RHE}}$</td>
<td>Potential corrected to reversible hydrogen electrode</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>$E_{\text{true}}$</td>
<td>True potential of working electrode</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe(eh)$_3$</td>
<td>Iron(III) 2-ethylhexanoate</td>
</tr>
<tr>
<td>Fe(NO$_3$)$_3$</td>
<td>Iron(III) Nitrate</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Iron(II) Oxide</td>
</tr>
<tr>
<td>Symbol</td>
<td>Compound/Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>Iron(III) Chloride</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>H$_2$</td>
<td>Hydrogen Gas</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Water</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>i</td>
<td>cell current</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>Ir</td>
<td>Iridium</td>
</tr>
<tr>
<td>Ir(acac)$_3$</td>
<td>Iridium(III) acetylacetonate</td>
</tr>
<tr>
<td>IrO$_2$</td>
<td>Iridium Oxide</td>
</tr>
<tr>
<td>j</td>
<td>Current Density</td>
</tr>
<tr>
<td>$j_0$</td>
<td>exchange current density</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>kW</td>
<td>Kilowatt</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand-to-metal charge transfer</td>
</tr>
<tr>
<td>mA</td>
<td>Milliamps</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>Mn(eh)$_3$</td>
<td>Manganese(III) 2-ethylhexanoate</td>
</tr>
<tr>
<td>Mox</td>
<td>Metal Oxide</td>
</tr>
<tr>
<td>mV</td>
<td>Millivolts</td>
</tr>
<tr>
<td>MW</td>
<td>Megawatt</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Nitrogen gas</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>Ni(eh)$_2$</td>
<td>Nickel(II) 2-ethylhexanoate</td>
</tr>
<tr>
<td>Ni(NO$_3$)$_2$</td>
<td>Nickel(II) Nitrate</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>Nickel(II) Chloride</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>NIRDD</td>
<td>Near-infrared-driven decomposition</td>
</tr>
<tr>
<td>nm</td>
<td>nanometers</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen Evolution Reaction</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton Exchange Membrane</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition/Formula</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>PHES</td>
<td>Pumped heat electric storage</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapour Deposition</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>Ru</td>
<td>Uncompensated resistance</td>
</tr>
<tr>
<td>Ru(tmdh)₂(cod)</td>
<td>( \text{bis}(2,2,6,6\text{-tetramethyl-3,5\text{-heptanediaonato})(1,5\text{-cyclooctadiene)} \text{ruthenium(II)} )</td>
</tr>
<tr>
<td>RuO₄</td>
<td>Ruthenium tetraoxide</td>
</tr>
<tr>
<td>RuOₓ</td>
<td>Ruthenium Oxide</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Sn</td>
<td>Tin</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>Ta</td>
<td>Tantalum</td>
</tr>
<tr>
<td>TaCl₅</td>
<td>tantalum (V) chloride</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>Ti(OCH₂CH₂CH₂CH₃)₄</td>
<td>Titanium (IV) butoxide</td>
</tr>
<tr>
<td>TW</td>
<td>Terawatts</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UVDD</td>
<td>Ultraviolet light driven decomposition</td>
</tr>
<tr>
<td>V</td>
<td>Volts</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Symmetry factor</td>
</tr>
<tr>
<td>( \eta )</td>
<td>overpotential</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>wavelength (nm)</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>resistance (ohms)</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>number of exchanged electrons in the reaction</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to express my deepest appreciation to my supervisor Dr. Curtis P. Berlinguette. Your enthusiasm, drive and work ethic were strong contributors to the successful completion of this thesis and to my growth as a student. I will be forever grateful for the opportunity to be a member of your research program.

Thank you to my defense committee members Dr. Naoko Ellis and Dr. Elod Gyenge for their time and critical analysis of my work.

I would like to thank the many Berlinguette group members, past and present, with whom I’ve had the pleasure of working alongside. My labmates, in no particular order, Valerie Chiykowski, Rebecca Sherbo, Kevan Dettelbach, Jesse Hudkins, Cameron Kellett, Tengfei Li, Amber Blair, Molly Sung, Sarah Simon, Daniika Wheeler, Dr. Phil Schauer, Dr. Rodney Smith, Dr. Rebecca Smith, Dr. Vincent Wang, Dr. Bruno Peña Maceda and Dr. Jeffery He. These group members are not only wonderful scientists but also great people and have made every day spent in the lab enjoyable. I can always count on at least one of you at any point in time to blow off some steam. I would like to give special thanks to Kevan Dettelbach with whom I’ve worked very closely on much of the work presented in this thesis. I would also like to give special thanks to Dr. Rodney Smith and Dr. Bruno Peña Maceda for providing immense guidance and mentorship.

I would not have been able to keep sane without the many friendships I’ve enjoyed throughout my time in British Columbia. I thank all of those that have been there as running, snowboarding, hiking & cycling partners. A special mention must be given to Karen Arane & Madeleine Iafrate, I am truly grateful for your friendships.

Last, but definitely not least, I thank my family for their continued love and support. Despite being on opposite ends of the country, it was always great to hear their voices & enjoying their many visits. I would not be where I am today without their unwavering encouragement.
Dedication

To J,

Sisters by blood, friends by choice.

D
Chapter 1: Introduction

1.1 Solar Energy Supply & Storage

In 2007, the global primary energy consumption rate was 16.2 terawatts (TW, one TW equals $10^{12}$ watts, or $10^{12}$ joules per second). Conservative estimates place the global power need to be 30 TW in 2050.\(^1\) Delivering this additional power to our world is an increasingly difficult task due to the inadequacy of traditional energy sources (i.e., biomass, nuclear energy, fossil energy): biomass is limited by the low energy efficiency of photosynthesis; sites for nuclear energy cannot be built fast enough to keep up with demand; and fossil energy (oil, coal and gas) would likely triple the atmospheric CO\(_2\) concentration.\(^2\) It is therefore crucial that the global community moves to carbon-neutral energy sources.

Solar energy is an immense and effectively limitless resource. In one hour more energy from sunlight strikes the Earth than all the energy consumed on the planet in a year.\(^3\) Solar cells producing an efficiency of 10%, covering 0.1% of the earth’s surface, would be able to satisfy global energy demand.\(^3\) However, solar energy is intermittent in supply on a daily and seasonal basis. In addition to intermittent sourcing, there is a disparity between utility demand and solar energy supply curves, with demand predominantly in the evenings (Figure 1.1).\(^2\) In order to supply the demand after the sun sets, a method to store energy and account for grid fluctuations is needed.
Figure 1.1 Utility load (blue) versus solar power output (black). Overlaid on the demand curve (MW) is the power output (kW) sampled every minute for a 4.6 solar PV array in north-western Arizona over the period of one day.²

1.2 Water Splitting

Different methods for solar energy storage can be divided into four forms: (i) potential energy (pumped-hydroelectric, compressed-air, electric charge in super capacitors); (ii) kinetic energy (flywheels); (iii) chemical energy (batteries or fuels); and (iv) thermal energy (concentrated solar thermal, geothermal).¹ These technologies can be distinguished by their intrinsic power and energy densities. Fuels have the highest energy density of any storage mechanism as shown in the Ragone plot in Figure 1.2.¹ High energy density is especially important to large-scale energy storage because cost is directly correlated to the overall cost per weight of the storage technology.
Figure 1.2 Ragone plot of specific power density versus energy density of various storage methods.\(^1\) PHES (pumped heat electric storage), CAES (compressed air energy storage).

The high energy density of fuels is achieved through the storage of electrons in the two-electron bond between light elements (e.g., C-H, N-H, and H-H bonds). The challenge currently facing our society is to shift our view of chemical fuels from hydrocarbon-based energy to a sustainable and carbon neutral energy storage (e.g., hydrogen).\(^2\) Hydrogen is the lightest and most abundant element in the universe. The element is very reactive chemically and occurs as a free element only in trace amounts.\(^4\) Hydrogen gas (H\(_2\)) is not a primary fuel in the same sense as hydrocarbon based fuels: no wells produce H\(_2\) from geologically identified deposits.\(^4\) H\(_2\) is produced using other energy sources such as natural gas, coal, or electrolysis.\(^4\)

When hydrogen burns, it releases energy as heat and produces water.\(^4\) Because no carbon is involved, using hydrogen fuel produced from renewable energy would eliminate carbon monoxide and CO\(_2\) emissions.\(^4\) Currently, steam reforming is the leading technology for producing hydrogen in large quantities.\(^5\) In the steam reforming process, hydrocarbons are
catalytically split in the presence of steam at temperatures of 800-900°C producing carbon
dioxide, carbon monoxide and hydrogen.\textsuperscript{5} Natural gas is the most common feedstock and the
process proceeds in a gas-fired oven with a nickel catalyst.\textsuperscript{5}

Electrolysis, or water splitting, is an alternative and carbon-neutral method for the
production of H\textsubscript{2} gas. Water splitting involves two electrochemical reactions; the oxygen
evolution reaction (OER; Eq. 1) and the hydrogen evolution reaction (HER; Eq.2).\textsuperscript{2} The OER is
the rate limiting reaction involving four consecutive proton and electron transfer steps. (NHE is
the normal hydrogen electrode).

\[
2H\textsubscript{2}O \rightleftharpoons O_2 + 4e^- + 4H^+ \quad E^0 = 1.23 \ V - 0.059 \times pH \ (V \ vs \ NHE) \quad \text{(Eq. 1)}
\]

\[
4e^- + 4H^+ \rightleftharpoons 2H\textsubscript{2} \ E^0 = 0 \ V - 0.059 \times pH \ (V \ vs \ NHE) \quad \text{(Eq. 2)}
\]

Although a growing body of OER catalysts containing earth abundant, inexpensive
transition metals have recently appeared in the literature,\textsuperscript{6,7} the economics of hydrogen
production are governed primarily by catalytic efficiency and performance, not the cost of the
catalyst.\textsuperscript{8} A substantial market penetration of commercial electrolyzers has been hindered by the
absence of catalytic materials that exhibit high current densities (j) and low overpotentials (\(\eta\))
over prolonged time periods.

1.3 Electrochemical Catalyst Characterization

Within the framework of transition state theory, the kinetics of an electrocatalytic
reaction at an electrode can be described by the Butler-Volmer equation (Eq. 3)\textsuperscript{9}

\[
j = j_0 \left[ \exp \left( \frac{\alpha z F \eta}{R T} \right) - \exp \left( - \frac{(1-\alpha) z F \eta}{R T} \right) \right] \quad \text{(Eq.3)}
\]

where \(j\) is the current density; \(\eta\) is the overpotential; \(F\) is Faraday’s constant (9.64870 x
10\textsuperscript{4} c mol\textsuperscript{-1}); \(R\) is the gas constant (8.314 J K\textsuperscript{-1} mol\textsuperscript{-1}); \(T\) is temperature in Kelvin; \(z\) is the number
of exchanged electrons in the reaction; $j_0$ is the exchange current density and $\alpha$ is the symmetry factor. The $\eta$ is the deviation of the potential at the electrode from the equilibrium value. $j_0$, and $\alpha$ describe electron transfer kinetics at the electrode surface. The $j_0$ is the current in the absence of net electrolysis and at zero overpotential. The $\alpha$ signifies the fraction of the interfacial potential at an electrode-electrolyte interface that helps in lowering the free energy barrier for the electrochemical reaction.

The increase in current, often referred to as an electrocatalytic effect, at an electrode can be due to the structure and chemical composition of the material. The actual surface area of the electrode material has to be determined as accurately as possible in order to discriminate the real catalytic improvements from apparent effect. The Tafel equation is an equation that relates the rate of the electrochemical reaction to the overpotential. The Butler-Volmer equation can be approximated by a single exponential function with the Tafel slope, $b$, given by (Eq. 4):

$$\eta = b \times \ln\left(\frac{j}{j_0}\right)$$

(Eq. 4)

Where an electrochemical reaction occurs in two half-cell reactions on separate electrodes, the Tafel equation is applied to each electrode separately. The Tafel equation assumes that the reverse reaction rate is negligible compared to the forward reaction rate.

Activities of oxides for oxygen electrocatalysts can be obtained using cyclic voltammetry (CV) or galvanostatic measurements in a three-electrode cell consisting of a working electrode, a counter electrode, and a reference electrode. Ion-blocking membranes and separate electrode compartments connected by salt bridges are common to avoid unwanted reactions on the electrodes. For powder samples, a catalyst layer (consisting of the oxide powder, Nafion and carbon) can be deposited on conducting substrates that exhibit low OER activities (e.g., conductive glass, glassy carbon, titanium). Together, the substrate and catalyst serve as the
working electrode. The sample can be used directly as the working electrode for oxides grown
directly or electrochemically deposited on a conductive substrate. Many different reference
electrodes can be used [e.g., saturated calomel electrode, silver chloride electrode, standard
hydrogen electrode]. It is important to choose a counter electrode with a large enough surface
area such that the reaction does not limit the oxygen half-cell reaction at the working electrode.
Platinum wires are typically used as the counter electrode due to their chemical stability and high
activities for the HER.

In an electrochemical cell the potential is controlled or measured across the working and
reference electrodes, while the current is measured across the working and counter electrodes. In
the context of the OER, it is useful to convert the measured potentials to the thermodynamically
relevant scale of the reversible hydrogen electrode (RHE) through the equation (Eq. 5):

\[ E_{RHE} = E_{measured} + 0.059(pH) \]  

(Eq. 5)

The measured potentials should also be corrected for Ohmic resistances, for which the
greatest contribution is usually the uncompensated resistance of ionic conduction in the
electrolyte between the working and reference electrodes. The true potential \( E_{true} \) of the
working electrode is given by (Eq. 6):

\[ E_{true} = E_{measured} - iR_u \]  

(Eq. 6)

where \( i \) is the cell current and \( R_u \) is the uncompensated resistance.

All of the electrochemical measurements presented in this thesis were corrected for \( R_u \)
and are reported relative to the RHE. Eq. 7 is given by a combination of Eqs. 5 and 6:

\[ E_{RHE} = E_{measured} + E_{ref} + 0.059(pH) - iR_u \]  

(Eq. 7)

An Ag/AgCl (sat. KCl) reference electrode \( E_{ref} \) was calibrated regularly against a 1 mM
aqueous \( K_3[Fe(CN)_6] \) solution.
1.4 Amorphous Electrocatalytic Films

Metal oxides are the most durable and active water oxidation catalysts. Some of the catalysts with the highest activity towards the OER include IrO$_2$ and RuO$_2$, perovskites, and spinel solids. A growing body of evidence demonstrates that amorphous materials mediate the OER and HER more efficiently than do crystalline phases of the same compositions. Amorphous materials have no long-range order. It is speculated that the reaction activity of an amorphous material is higher than a crystalline electrode because the electrochemical surface area of amorphous materials in comparison to crystalline materials is larger from a greater amount of randomly oriented bonds.

These findings are particularly important in the context of efficiently storing electricity produced from intermittent and variable renewable energy sources (e.g., sunlight) as high-density fuels (e.g., hydrogen). Most amorphous metal oxide films currently reported in the literature are formed by electrodeposition and physical vapour deposition (PVD) methods. Although films prepared by these methods can demonstrate state-of-the-art electrocatalytic OER activities, these methods do not necessarily translate to every metal and may possess limitations that impede low-cost, widespread use.

Electrodeposition (Figure 1.3A) is a process that uses electrical current to form a coherent metal oxide coating on an electrode from a metal salt solution. Electrodeposition requires a conductive substrate and provides poor control of mixed-metal concentrations. PVD includes a variety of vacuum deposition methods used to deposit thin films by the condensation of a vaporized form of the desired film material onto a substrate. Some distinct variants of PVD are pulsed laser deposition, cathodic arc deposition and sputter deposition. Magnetron sputtering is a common deposition technique for the formation of amorphous metal oxide materials.
this sputtering process atoms are ejected from a solid target material due to bombardment of the target by energetic particles.\textsuperscript{26} Magnetrons are often employed at sputtering sources to induce strong electric and magnetic fields to confine charged plasma particles close to the surface of the sputter target.\textsuperscript{26} Sputtering techniques therefore require sophisticated instrumentation and the films formed are sensitive to deposition protocols.\textsuperscript{24}

![Figure 1.3](image.png)  

**Figure 1.3** (A) electrodeposition, (B) magnetron sputtering, and (C) ultraviolet light driven decomposition schematics.

The Berlinguette and Trudel groups recently introduced a facile light-based method of fabricating thin films of amorphous oxides of iridium and first row transition metals; namely, the ultraviolet light driven decomposition (UVDD, Figure 1.3C).\textsuperscript{18,28,29} The UVDD method involves the exposure of a metal precursor to ultraviolet light. Successive ligand-to-metal charge transfer (LMCT) steps are triggered by light to form a reduced metal-based film that reacts with air to form a metal oxide at room temperature.\textsuperscript{30}

In the initial report,\textsuperscript{18} UV light was utilized with bands centred at 185 and 254 nm; however, the irradiation of oxygen at 185 nm induces ozone formation.\textsuperscript{31} The ozone that is
formed can then react with certain metals (e.g., ruthenium) to form volatile and toxic by-products, (such as RuO₄). Although UVDD is a scalable, low-cost technique capable of producing catalysts with precise metal combinations, the UVDD method requires the use of photoactive precursors, has a limited substrate scope (e.g., UV sensitive materials) and has a limited ability to access all metals in the periodic table.

Given that crystalline ruthenium oxide is an efficient and robust electrocatalyst for the OER it would be highly advantageous to be able to readily access amorphous ruthenium oxide. I explored other LMCT transitions for molecular ruthenium complexes. Because ruthenium complexes not only have LMCT transitions in the UV region but also in the near-infrared (NIR) region (Figure 1.4), and the NIR region does not produce ozone, this work involves the exposure of ruthenium precursors to NIR radiation.

![UV region vs. NIR region](image)

**Figure 1.4.** UV-vis-NIR absorption spectra of ruthenium complex [Ru(bpy)₂(sq)]⁺. A LMCT transition is centered in the NIR region.

### 1.5 Infrared Curing

Infrared curing has gained increased attention from the automobile and paint industry as a result of shorter cure cycles and the possibility of smaller floor space requirements when
Infrared (IR) curing may be considered in an effort to boost performance or line speed for roll-to-roll processing systems. IR curing systems are used for a full range of coatings (e.g., liquid, powder, wax, adhesives) and can be useful for heat sensitive substrates.

Unlike convection, which first heats air to transmit energy to the part, IR energy may be absorbed directly by the coating. In order to achieve cure IR radiation can be absorbed by the coating or transmitted to the substrate. Because IR energy is radiant, this curing process is known to have line-of-sight limitations: The photons can only be absorbed by the substrate that is facing the source since light can only travel in a straight line. This result decreases the amount of energy required for cure because infrared targets the coating specifically instead of heating the entire object.

In order to reduce the curing time from minutes to seconds there has been increased use of infrared curing in coating processes. This reduction in processing time is extremely important for energy consumption because optimizing the uptake of energy by the coating system and reduction energy consumption during coating processes is vital. Although infrared curing systems are widely used for the paint coating industry, there is no current application in electrocatalytic coatings or films.
1.6 Project Outline

I set out to develop a scalable method for preparing a wide variety of amorphous metal and mixed-metal oxides across the periodic table. With the collective knowledge that ruthenium complexes have LMCT transitions in NIR region\(^\text{34}\) and there is existing infrastructure related to NIR curing,\(^\text{38}\) I exposed spin-coated metal precursor films to NIR light.

*Chapter 2* outlines the recently reported near-infrared driven decomposition (NIRDD) method to successfully fabricate thin films of amorphous oxides of iridium (\(a\text{-IrO}_x\)) and first row transition metals (\(a\text{-FeO}_x, a\text{-IrO}_x, a\text{-MnO}_x\)) in both oxidized and reduced phases.\(^\text{39}\) This method also enables deposition on temperature and UV-sensitive substrates as documented by amorphous metal oxide film formation interfaced with Nafion. Films of \(a\text{-FeO}_x, a\text{-IrO}_x, a\text{-NiO}_x, \text{and } a\text{-MnO}_x\) were formed when the corresponding metal compounds were subjected to NIR radiation. The electrocatalytic properties of \(a\text{-IrO}_x\) in 1 M H\(_2\)SO\(_4\) are consonant with literature values, as are those for \(a\text{-FeO}_x, a\text{-NiO}_x\) and \(a\text{-MnO}_x\) in alkaline conditions.

*Chapter 3* outlines two protocols to provide access to amorphous ruthenium oxide (\(a\text{-RuO}_x\)). The first is the exposure to near-infrared light, which allows the efficient decomposition of a ruthenium salt. The second, by irradiating with exclusively 254 nm light, we successfully
converted the photoactive precursor Ru(tmhd)$_2$(cod) to a thin film of $a$-RuO$_x$. The onsets of catalysis, Tafel slopes and potentials required to reach 10 mA cm$^{-2}$ for the $a$-RuO$_x$ films prepared herein were 70-90 mV, ~46-53 mV dec$^{-1}$, 150-270 mV, respectively, which is consistent with films prepared by previously documented methods. Moreover, the $a$-RuO$_x$ catalysts are favourable when compared to the prepared crystalline counterparts, $c$-RuO$_x$, with an onset overpotential cathodically shifted ~50 mV.

The overall conclusions and suggestions for future work are found in Chapter 4 while Chapter 5 contains experimental procedures and methods.

1.7 CREATE sustainable synthesis

The work reported in this dissertation was supported through the NSERC collaborative research and training experience (CREATE) Sustainable Synthesis (SusSyn) program. This program involves collaboration between the departments of Chemical and Biological Engineering, Pharmaceutical Sciences and Chemistry. The CREATE SusSyn training objective aims to prepare industry ready graduates to contribute to globally competitive clean technologies and sustainable manufacturing solutions of industrial relevance to manufacturers. Sustainable manufacturing relies upon catalysis to efficiently and cleanly achieve chemical transformations while minimizing waste generation and toxic by-products. Scientists focusing on discovery must collaborate with engineers to further develop technologies into viable industrial processes to realize innovative solutions to address on-going manufacturing challenges.

The near-infrared-driven decomposition process presented herein represents an applicable industrially relevant technique to manufacture catalysts at scale. Manufacturing electrolyser catalysts at scale involves the ability to deposit catalysts on large sized surfaces
This process compares favourably to other techniques in terms of energy (kwh) and subsequent energy cost ($) to form equivalent catalysts. Taking \textit{a-RuO}_x as an example, there is currently four potential methods for making catalyst films; electrodeposition,\textsuperscript{23} sputtering,\textsuperscript{23} and NIRDD (presented herein). A summary of the energy (and cost of gas; if necessary) is summarized in Table 1.1. The values for power, time & gas flow are from the relevant represented reported procedures.

\textbf{Table 1.1.} Cost comparison of fabrication techniques for the formation of \textit{a-RuO}_x

<table>
<thead>
<tr>
<th>technique</th>
<th>ref.</th>
<th>power (W)\textsuperscript{a}</th>
<th>flow (sscm)</th>
<th>time (h)</th>
<th>energy consumed (kWh)</th>
<th>energy cost ($0.10 per kWh)\textsuperscript{b}</th>
<th>Ar gas cost ($0.0029 per cm\textsuperscript{3})\textsuperscript{c}</th>
<th>total cost per catalyst film (3x3 cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodeposition</td>
<td>23</td>
<td>8 (potentiostat) 230 (furnace)\textsuperscript{d}</td>
<td>1</td>
<td>0.008</td>
<td>0.001</td>
<td>$0.15</td>
<td>$0.41</td>
<td>$0.04</td>
</tr>
<tr>
<td>Sputtering</td>
<td>23</td>
<td>200 (RF source) 4.5 (Ar)</td>
<td>0.5</td>
<td>0.01</td>
<td>0.010</td>
<td></td>
<td></td>
<td>$0.41</td>
</tr>
<tr>
<td>NIRDD \textit{this work}</td>
<td></td>
<td>175 (NIR lamp)</td>
<td>2</td>
<td>0.350</td>
<td>0.035</td>
<td></td>
<td></td>
<td>$0.04</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Instrument power is taken as maximum possible output. \textsuperscript{b}Based on current average canadian electricity costs. \textsuperscript{c}Based on current Ar costs from Praxair. \textsuperscript{d}Electrodeposited catalysts require 2 h annealing at 300°C.
Chapter 2: Near-Infrared-Driven Decomposition

2.1 Introduction

Amorphous metal-based films are pervasive in a myriad of applications [e.g.,
transistors,\textsuperscript{40,41} and flexible electronics\textsuperscript{42}], including schemes that involve the electrocatalytic oxidation of water into clean hydrogen fuels. Indeed, there is a growing body of evidence showing that amorphous films mediate the OER\textsuperscript{6,17,18,22} and hydrogen evolution reaction HER\textsuperscript{19,20} more efficiently than do crystalline phases of the same compositions. These findings are particularly important in the context of efficiently storing electricity produced from intermittent and variable renewable energy sources (e.g., sunlight and wind) as high-density fuels (e.g., hydrogen).\textsuperscript{1,2}

Most amorphous metal oxide films reported in the literature are formed by electrodeposition,\textsuperscript{6,17,18,22} sputtering,\textsuperscript{24} thermal decomposition,\textsuperscript{42,43} or ultraviolet (UV) light-driven decomposition\textsuperscript{18} of metal precursors. Although films prepared by these methods can demonstrate state-of-the-art electrocatalytic OER activities,\textsuperscript{7,28,29,44} the syntheses are not necessarily amenable to scalable manufacture because of sensitivities of metal work functions, reaction media, or prohibitively expensive precursors. Consequently, accessing specific compositions of amorphous metal oxides for commercial applications is not trivial, particularly when complex metal compositions are desired.\textsuperscript{18,42} Moreover, the isolation of amorphous metals is substantially more challenging because single-element metallic films typically require sophisticated protocols.\textsuperscript{15}
Figure 2.1. Scheme outlining the near-infrared driven decomposition (NIRDD) of metal precursors (e.g., FeCl₃) on a substrate (e.g., FTO) leads to the formation of amorphous metal oxide (a-MOₓ) and reduced metal (a-M) films under air and nitrogen, respectively.

We report here a previously untested method for generating amorphous-metal based films, in the reduced and oxidized phases, that relies merely on the exposure of transition metal salts [e.g., MClₓ and M(NO₃)ₓ] (M = Fe, Ni, Mn, Ir) to near-infrared (NIR) radiation under inert and aerobic environments, respectively (Figure 2.1). This method is distinctive from the UV-driven photochemical decomposition of metal complexes in that NIRDD is ultimately a thermally driven process and therefore does not require photoactive precursors. Notwithstanding, this NIR-driven decomposition (NIRDD) process furnishes amorphous metal oxide films that display properties commensurate with films prepared by more complex methods and precursors, yet is amenable to curing techniques widely used in large-scale manufacturing processes, including roll-to-roll processing. We therefore contend that NIRDD represents a significant advance toward a solar fuel economy, which will invariably require electrocatalysts to efficiently mediate small-molecule transformations. Moreover, NIRDD provides access to reduced phases of amorphous films using moderate experimental conditions. We demonstrate the broad use of this fabrication technique herein by examining the formation of amorphous oxide films containing metals of relevance to the OER reaction [for example iron, iridium, manganese, nickel, and copper]. We also provide evidence that NIRDD, which works despite substrate temperatures not reaching 200°C (Figure 2.2), can also be extended to
substrates that are not conducting and sensitive to temperature and UV radiation by documenting amorphous metal oxide film formation interfaced with Nafion.

Figure 2.2, Temperature profiles of FeCl$_3$/FTO (purple), Fe(eh)$_3$/FTO (blue) and bare FTO (black). Additional control measurements were also collected on a sample where Fe(eh)$_3$ deposited directly on the copper wire of the thermocouple by the NIRDD process, denoted Fe(eh)$_3$/thermocouple (red), as well as the bare wire of the thermocouple (green). Temperature readings were recorded with a thermocouple in 5-min increments, and indicated a rise in temperature that plateaus at a value no greater than 175 °C. These collective results confirm that a substrate temperature of 200 °C is not reached during a constant 1 h exposure to NIR radiation under our experimental conditions.

2.2 Amorphous Metal Oxide Film Formation & Characterization

The formation of amorphous metal oxide films upon exposure of metal salts to NIR radiation was confirmed by placing FeCl$_3$ spin-cast on FTO, FeCl$_3$/FTO, under a 175-W NIR lamp for 120 min in an aerobic environment. The colour change from yellow to light brown upon irradiation supported the formation of iron oxide (UV-vis spectra are provided in Figure 2.3), whereas the absence of reflections in the powder X-ray diffraction (XRD) patterns indicated the amorphous nature of the material (Figures 2.4 and 2.5). (A signature Bragg reflection of hematite is apparent at $2\theta = 35.9^\circ$ only after annealing the same film in air for 1 h at 600°C.) The
electrochemical behaviour of this amorphous film, $a$-FeO$_x$, in aqueous media was also consistent with previous accounts of amorphous iron oxide (Figure 2.6 and Table 2.1). These films demonstrated oxidative stability at a current density of 10 mA/cm$^2$ over a 2-hour period (Figure 2.7). An extensive electrochemical analysis indicated that $a$-FeO$_x$ could be readily produced from other iron compounds [for example Fe(NO$_3$)$_3$ and Fe(eh)$_3$; eh = 2-ethylhexanoate] (Figure 2.8) and that the NIRDD method translated effectively to other metals: Films of $a$-IrO$_x$, $a$-NiO$_x$, and $a$-MnO$_x$ were also formed when the corresponding metal compounds were subjected to NIR radiation (Figures 2.9 and 2.10). The electrocatalytic properties of $a$-IrO$_x$ in 1 M H$_2$SO$_4$ are consonant with literature values, as are those for $a$-NiO$_x$ and $a$-MnO$_x$ in alkaline conditions (Table 2.1).
Figure 2.3. UV-vis absorption spectra, before and after being subjected to the NIRDD process, of: (A) metal halide precursor complexes on glass, FeCl$_3$/glass (1), NiCl$_2$/glass (2), and Fe$_2$Ni$_3$Cl/glass (3); and (B) coordination complexes on glass, Fe(eh)$_3$/glass (1), Ni(eh)$_3$/glass (2), Fe$_2$Ni$_3$(eh)$_3$/glass (3), Ir(acac)$_3$/glass (4) and Mn(eh)$_3$/glass (5). Data for FeCl$_3$/glass and Fe(eh)$_3$/glass following the NIRDD process in a nitrogen environment is indicated by “1/N$_2$”, respectively. The glass background is also shown. Note that glass was used rather than FTO to avoid interference at longer wavelengths. The film Fe$_2$Ni$_3$Cl/glass was prepared from a solution of 2 g of deionized water containing NiCl$_2$ (0.088 g) and FeCl$_3$ (0.039 g) that was spin-cast onto a glass substrate. The repetitive wave pattern in the 1/N$_2$ red trace is caused by diffraction of glass as the film is very thin.
Figure 2.4 Powder XRD patterns acquired on as-prepared and annealed ($T_{\text{anneal}} = 600 \, ^\circ\text{C}$) $a$-FeO$_x$ and $a$-Fe films prepared by applying the NIRDD process to (A) FeCl$_3$ and (B) Fe(eh)$_3$ deposited on FTO under air and nitrogen, respectively. Data recorded on a bare FTO substrate is also provided. *Inset:* Expanded view highlighting the region where the reflection associated with the maghemite and hematite form of Fe$_2$O$_3$ at 35.5° is observed. This reflection is observed only for the films annealed at 600 °C under air, denoted $FeO_x$-annealed.

Figure 2.5. XRD patterns acquired on as-prepared and annealed ($T_{\text{anneal}} = 600 \, ^\circ\text{C}$) $a$-FeO$_x$ films prepared by applying the NIRDD process to (A) FeCl$_3$ and (B) Fe(eh)$_3$ deposited on FTO under air. The bars represent the Bragg reflections for the hematite form of Fe$_2$O$_3$. This reflection is observed only for the films annealed at 600 °C, denoted $FeO_x$-annealed.
Figure 2.6. Cyclic voltammograms for thin films of (A) \( a-\text{FeO}_x \) and (B) \( a-\text{Fe} \) on FTO. Values indicate the sequence of the cycles that were recorded. The oxidative sweep of (A) \( a-\text{FeO}_x \) leads to a sharp rise in current coincident with catalytic water oxidation and subsequent cycles led to superimposable traces. The oxidative sweep for (B) \( a-\text{Fe} \) featured a markedly different current profile for the first cycle; however, subsequent cycles indicated \( a-\text{Fe} \) was converted to \( a-\text{FeO}_x \) upon oxidation on the basis of the superimposable scans. The differences in the reductive behavior were more stark, the cathodic peak at -0.25 V for (A) \( a-\text{FeO}_x \) was not detected for (B) \( a-\text{Fe} \) prior to HER catalysis, indicating a more reduced form of iron for (B). Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s\(^{-1}\); electrolyte = 0.1 M KOH (aq).

Figure 2.7 Chronoamperometric measurements for thin films of \( a-\text{FeO}_x \), prepared by the NIRDD process in air from FeCl\(_3\) (blue) and Fe(eh)\(_3\) (black). Blank FTO is also shown (black). The current was held at 10 mA/cm\(^2\) for 7200 s. All data is collected on films deposited on FTO, and thus the slight differences in the response of the \( a-\text{FeO}_x \) films are attributed to minor differences in film roughness or film densities. Electrochemistry conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 0.1 M KOH\(_{(aq)}\); current densities were corrected for uncompensated resistance. The initial drop in current density over the first 5 minutes on blank FTO can be attributed to an initial conditioning step.
Figure 2.8 Cyclic voltammograms for thin films of \textit{a-FeO}_x, prepared by the NIRDD process in air, and the respective precursor films from which they were derived from; Fe(NO\textsubscript{3})\textsubscript{3} \textit{(red)}, FeCl\textsubscript{3} \textit{(blue)} and Fe(eh)\textsubscript{3} \textit{(black)} precursors. All data is collected on films deposited on FTO, and thus the slight differences in the response of the \textit{a-FeO}_x films are attributed to minor differences in film roughnesses or film densities. Electrochemistry conditions: Counter Electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s\textsuperscript{-1}; electrolyte = 0.1 M KOH\textsubscript{(aq)}; current densities were corrected for uncompensated resistance.

Figure 2.9 XRD patterns acquired on as-prepared films of (A) \textit{a-IrO}_x, (B) \textit{a-NiO}_x and (C) \textit{a-MnO}_x on FTO. No reflections are observed other than those associated with FTO \textit{(black)}.
Figure 2.10. Cyclic voltammograms recorded on thin films of \textit{a-IrO}_x (red), \textit{a-NiO}_x (black), \textit{a-MnO}_x (green) and \textit{a-Fe}_2Ni_3O_x (blue) on FTO. Data recorded on bare FTO is also shown (grey). Electrochemistry conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s\(^{-1}\); electrolyte = 1 M H\(_2\)SO\(_4\) (aq) for \textit{a-IrO}_x, or 0.1 M KOH (aq) for \textit{a-NiO}_x, \textit{a-MnO}_x, \textit{a-Fe}_2Ni_3O_x and bare FTO. Current densities were corrected for uncompensated resistance.

Table 2.1 Benchmarked OER Activities of \textit{a-MO}_x films

<table>
<thead>
<tr>
<th>sample (^\ast)</th>
<th>(\eta_{\text{onset}}) (V) (^\dagger)</th>
<th>Tafel slope (mV dec(^{-1}))</th>
<th>(\eta_{10 \text{mA/cm}^2}) (V) (^\dagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{a-FeO}_x</td>
<td>0.32</td>
<td>35</td>
<td>0.42</td>
</tr>
<tr>
<td>\textit{a-NiO}_x</td>
<td>0.21</td>
<td>62</td>
<td>0.36</td>
</tr>
<tr>
<td>\textit{a-Fe}_2Ni_3O_x</td>
<td>0.19</td>
<td>34</td>
<td>0.33</td>
</tr>
<tr>
<td>\textit{a-MnO}_x</td>
<td>0.22</td>
<td>167(^\ddagger)</td>
<td>0.43(^\dagger)</td>
</tr>
<tr>
<td>\textit{a-IrO}_x</td>
<td>0.08</td>
<td>47</td>
<td>0.26</td>
</tr>
</tbody>
</table>

\(^\ast\) \textit{O}_x is broadly defined as oxo/oxyl/hydroxo. \(^\dagger\)Overpotential required for onset of catalysis (i.e.; low overpotential regime of Tafel plot). \(^\ddagger\)Overpotential required to reach 10 mA/cm\(^2\), unless otherwise indicated, without correcting for mass transport. \(^\dagger\)Overpotential required to reach 1 mA/cm\(^2\); we are not aware of any value reported at 10 mA/cm\(^2\). \(^\ddagger\)Corresponds to FeNiO\(_x\). \(^\ddagger\)The Tafel slope of MnO\(_x\) is higher than expected due to instability with MnO\(_x\) on FTO, annealing may be required.

The discovery that NIRDD could drive \textit{a-MO}_x formation was not expected given the low absorptivity’s of the films at \(\lambda > 600\) nm (Figure 2.3). We therefore contend that the efficacy of the process is due to localized heating of the film rather than a photochemical effect. This
assessment is validated by the observations that: (i) substrates do not exceed 200°C under our experimental conditions (Figure 2.2); (ii) bulk samples of FeCl₃ do not decompose to a mass corresponding to Fe₂O₃ until > 300 °C (Figures 2.11 and 2.12); (iii) samples of precursors on FTO exposed to 1 h of constant irradiation yielded complete decomposition, whereas six successive 10-min segments of exposure separated by 5-min periods in the dark did not; and (iv) films of precursors on FTO did not show the same rates of decomposition when placed in an oven set to 200°C (Figure 2.13). The temporal resolution of the NIRDD process was evaluated by tracking the formation of a-FeOₓ during the NIR irradiation of Fe(eh)₃, which contains reporter ligands that can be tracked by Fourier transform IR (FTIR) spectroscopy, and indicated complete ligand loss within 1 hour in both air and N₂ (Figure 2.14). The absorption spectra (Figure 2.3), lack of powder XRD reflections (Figures 2.4 and 2.5), and electrochemical data (Table 2.1) collectively support the assignment of the as-prepared films as a-FeOₓ. Films of a-MOₓ (M = Ir, Ni, Mn) derived from Ir(acac)₃ (acac = acetylacetonate), Ni(eh)₂, or Mn(eh)₂, were each formed quantitatively within 4 h of irradiation (Figure 2.15).
Figure 2.11. TGA and DSC profiles for (A) FeCl$_3$ and (B) Fe(eh)$_3$ under air and N$_2$ at a ramp rate of 10 °C min$^{-1}$. The bottom plots overlay the respective percent-mass-loss profiles in air and N$_2$ to highlight the effect of the atmospheric environment. Both FeCl$_3$ and Fe(eh)$_3$ appear to lose ligands in a stepwise fashion; our tentative assignments indicate that the first ligand is excluded at ~200 °C and the last ligand is liberated at ~400 °C. The ligands are excluded from FeCl$_3$ in three distinct steps in both air and N$_2$, while data recorded on Fe(eh)$_3$ in air shows the loss of two ligands in quick succession followed by the loss of the third ligand at higher temperatures; this pattern is reversed under nitrogen. Complete decomposition is not complete until $T > 400$ °C for any of the data shown, which is much higher than the surface temperatures reached during the NIRDD process.
Figure 2.12. TGA and DSC profiles for (A) FeCl$_3$ and (B) Fe(eh)$_3$ brought to 200 °C and then held for 60 min. The FeCl$_3$ and Fe(eh)$_3$ precursor complexes do not decompose fully to a final mass of Fe$_2$O$_3$ during this period. Both measurements were recorded in an aerobic environment.

Figure 2.13. FTIR spectra of independent samples of Fe(eh)$_3$/FTO before (black traces) and after (blue traces) (A) exposure to NIR radiation for 30 min, (B) heating at 200°C in a furnace for 30 min, (C) heating at 250°C in a furnace for 30 min.

Figure 2.14. FTIR spectra for thin films of Fe(eh)$_3$ on FTO upon exposure to NIR radiation for (A) 0 (black), 4, 16, 32 and 64 (blue) min in air, and (B) 0 (black) and 60 (blue) min under nitrogen. Arrows indicate trends in the intensities of the C-H and C-O vibrational modes of 2-ethylhexanoate.\textsuperscript{25}
Figure 2.15. FTIR spectra of thin films of Ir(acac)$_3$/FTO, Ni(eh)$_2$/FTO, and Mn(eh)$_3$/FTO for 0 (black), 4 (red), 16 (green), 64 (blue), 128 (orange), and 256 min (navy) subjected to the NIRDD process showing the progressive loss of ligands in <2 h. Absorption bands are associated with the symmetric and asymmetric vibrations of the C-O groups of the 2-ethylhexanoate ligand and free acid.

2.3 Access to Reduced Forms of Metal Films

The formation of $a$-FeO$_x$ from FeCl$_3$ signalled that oxygen was derived from the aerobic environment, thus raising the possibility that reduced forms of the films could be accessed merely by carrying out NIRDD in an inert atmosphere. This hypothesis was tested by irradiating a film of FeCl$_3$ on FTO under nitrogen, which yielded a light gray film, denoted $a$-Fe, that did not produced any Bragg reflections (Figures 2.4 and 2.5). Moreover, the electrochemistry of $a$-Fe on FTO in 0.1 M KOH was consistent with a lower average iron valency than that of $a$-FeO$_x$ (Figure 2.3). An oxidative sweep of $a$-FeO$_x$ leads to a sharp rise in current at 1.55 V coincident with catalytic OER (Figure 2.3 A), and subsequent cycles over the 1.0-1.8 V range led to superimposable traces. The oxidative sweep for $a$-Fe featured a markedly different current profile (Figure 2.3B); however, subsequent cycles indicated that $a$-Fe was converted to $a$-FeO$_x$ upon oxidation in aqueous media on the basis of the superimposable scans. The differences in the reductive behaviour was more stark because the cathodic peak at -0.25 V for $a$-FeO$_x$ was not detected for $a$-Fe before HER catalysis at ca. -0.50 V. The two films could be interconverted:
holding \(a-\text{FeO}_x\) at -0.68 V for 10 min yields a colour change that matches that of \(a-\text{Fe}\) (gray), whereas maintaining \(a-\text{Fe}\) at 1.92 for 10 min drives a colour change toward that of \(a-\text{FeO}_x\) (brown).

Evidence for the oxidized and reduced forms of the films formed under aerobic and nitrogen environments, respectively, is further supported by the different absorption (Figure 2.2) and x-ray photoelectron (XPS; Figures 2.16 and 2.17) data. The XPS data for \(a-\text{FeO}_x\) contain a signature iron(III) satellite signal at 719 eV that is not observed for \(a-\text{Fe}\), and iron 2p\(_{3/2}\) envelope that could be accurately modeled using peak parameters corresponding to Fe\(_2\)O\(_3\).\(^{49}\) The 2p\(_{3/2}\) envelope of \(a-\text{Fe}\) was fit to a combination of iron(III), iron(II), and iron(0), where the zero valency was implicated by the low-energy shoulder. Although these results confirm that \(a-\text{Fe}\) exists in a more reduced form, the high susceptibility of the films to aerial oxidation prevented confirmation that elemental iron was being formed in exclusivity during the NIRDD process. We therefore analyzed surrogate films of \(a-\text{CuO}_x\) and \(a-\text{Cu}\) prepared by applying the NIRDD process to Cu(eh)\(_2\) on FTO under air and nitrogen, respectively, in view of elemental copper oxidizing less readily to Cu\(_2\)O and, in turn, CuO.\(^{50}\) XPS data recorded on these samples did indeed yield different spectroscopic signatures (Figure 2.18 and 2.19): The copper 2p\(_{3/2}\) envelope for \(a-\text{CuO}_x\) showed a mixture of CuO and Cu(OH)\(_2\), whereas the same envelope for \(a-\text{Cu}\) shows a single peak corresponding to zero- or mono-valent copper sites. The Cu LMM peak indicated the presence of Cu\(_2\)O, possibly due to aerial oxidation (Figure 2.18). Visible inspection of the samples prepared by NIRDD in an inert atmosphere indicated a color consistent with elemental copper (Figure 2.20), with XRD measurements ruling out formation of crystalline domains (Figure 2.21), lending credence to the samples existing in a reduced form, and potentially metallic phase, when prepared under nitrogen.
Figure 2.16. X-ray photoelectron spectra for \( \textit{a-FeO}_x \) (red) and \( \textit{a-Fe} \) (blue) on FTO. The (A) survey scan, and spectral regions corresponding to the (B) iron 2p and (C) carbon 1s regions, are shown.

Figure 2.17 X-ray photoelectron spectra detailing the Fe 2p\(_{3/2}\) region. Sums of the fitting components for (A) \( \textit{a-FeO}_x \) and (B) \( \textit{a-Fe} \) are shown in red. Curve fitting in A used Gupta Sen parameters based on Fe\(_2\)O\(_3\) (blue) along with a surface peak (orange) and an Fe\(^{3+}\) satellite peak (blue). Curve fitting in B used centre-of-gravity peaks for Fe\(^{2+}\) (green) and Fe\(^{3+}\) (blue); a surface peak (orange) and a Fe\(^{2+}\) satellite peak (green) are also shown. The Fe\(^{3+}\) satellite peak is not shown, as it is likely superimposed with the Fe 2p\(_{1/2}\) peak.
Figure 2.18. XPS data for \( a\text{-}\text{CuO}_x \) (red) and \( a\text{-}\text{Cu} \) (blue) on FTO. The (A) survey scan, along with the rough fitting of the Cu LMM regions denoting (B) CuO and (C) \( \text{Cu}_2\text{O} \), are shown.

Figure 2.19. XPS spectra on the copper 2p\(_{3/2} \) region. The fitting of the copper 2p\(_{3/2} \) region of XPS recorded on thin films of Cu(oh)\(_2 \) on FTO after being subjected to the NIRDD process under (A) air and (B) nitrogen, respectively; sum of the fitting components are indicated (red traces). Fitting of the data used centre-of-gravity peaks for (A) Cu(O) (green) and Cu(OH)\(_2 \) (orange), and (B) Cu(I)/Cu(0) (green). Signature copper(II) satellite peaks present in (A) but not (B) confirm a more reduced form of the film when prepared under nitrogen. The computed baselines are indicated in blue.
Figure 2.20. Images of solid samples of (A) Cu(eh)$_2$, (B) Cu(eh)$_2$ subjected to NIRDD under nitrogen, and (C) Cu(eh)$_2$ subjected to NIRDD under air. The colors of the samples in (B) and (C) indicate elemental copper and copper oxide, respectively.

Figure 2.21. Powder XRD patterns acquired on as-prepared and annealed ($T_{\text{anneal}} = 600 \, ^\circ\text{C}$) $a$-$\text{CuO}_x$ and $a$-$\text{Cu}$ films prepared from Cu(eh)$_2$ under (A) air and (B) nitrogen. Data recorded on bare FTO substrate is also included. Inset: Expanded view highlighting the region where the reflection associated with the crystalline form of CuO at 35.5° is observed. This signal is observed only for the films annealed at 600 °C under air and N$_2$, $\text{CuO}_x$-annealed and Cu-annealed.

2.4 Mixed-Metal Oxides

Mixed metal oxides are known to exhibit superior electrocatalytic behaviour in basic media,\textsuperscript{29} which prompted us to synthesize the binary solid, $a$-$\text{Fe}_2\text{Ni}_3\text{O}_x$, by subjecting a mixture of iron precursors [for example, Fe(eh)$_3$, FeCl$_3$, or Fe(NO$_3$)$_3$] and nickel precursors [Ni(eh)$_2$,
NiCl₂, or Ni(NO₃)₂] (mol Fe/ mol Ni 2:3) spin-cast on FTO to the NIRDD process (Figure 2.22). The resultant films were amorphous according to powder XRD measurements (Figure 2.23), and the energy dispersive x-ray spectroscopy (EDX) measurements recorded on different regions of the films confirmed uniform metal distributions across the substrates (Table 2.2). The electrochemical behaviour, including OER catalytic activity, also matches films of similar compositions prepared by other methods (Figure 2.24 and Table 2.1), including the absence of an oxidative peak at $E_p \approx 1.45$ that is present in pure phases of NiOₓ.¹⁷

Intrigued by the potential to access amorphous metal alloys, we set out to prepare the binary film $a$-$Fe_2Ni_3$ in the same manner as $a$-$Fe_2Ni_3O_x$, but under nitrogen. The electrocatalytic behaviour of the films indicated a more reduced phase compared to that of $a$-$Fe_2Ni_3O_x$ (Figure 2.6B). The film contained a uniform distribution of metals within the solid (Table 2.2). Although the film was found not to be a state-of-the-art HER electrocatalyst, it is superior to pure phases of $a$-$Fe$ and $a$-$Ni$, this highlighting that metal cooperativity with other metal combinations may unearth superior catalysts in future studies.¹⁷,²⁹

![Figure 2.22. FTIR spectra of Fe₂Ni₅(oh)₃/FTO subjected to NIRDD for the times indicated under (A) air and (B) nitrogen to highlight the progressive loss in intensity of the bands associated with the ligand.](image-url)
Figure 2.23. XRD patterns acquired on as-prepared films of (A) $a$-$\text{Fe}_2\text{Ni}_3\text{O}_x$ and (B) $a$-$\text{Fe}_2\text{Ni}_3$ on FTO recorded under air and nitrogen, respectively. No reflections were observed other than those associated with FTO (black).

Figure 2.24 Cyclic voltammograms for thin films of (A) $a$-$\text{Fe}_2\text{Ni}_3\text{O}_x$ and (B) $a$-$\text{Fe}_2\text{Ni}_3$ prepared by NIRDD under air and $N_2$, respectively. Electrochemistry conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s$^{-1}$; electrolyte = 0.1 M KOH$_{(aq)}$; current densities were corrected for uncompensated resistance.
### Table 2.2. Elemental Analysis of Amorphous Metal Oxide Films Determined by EDX.

#### $a$-Fe$_2$Ni$_3$O$_x$

<table>
<thead>
<tr>
<th></th>
<th>area</th>
<th>%Fe</th>
<th>%Ni</th>
<th>%Fe</th>
<th>%Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>38.86</td>
<td>61.14</td>
<td>38.45</td>
<td>61.55</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>41.35</td>
<td>58.65</td>
<td>40.63</td>
<td>59.37</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>39.32</td>
<td>60.68</td>
<td>39.99</td>
<td>60.01</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>39.84</td>
<td>60.16</td>
<td>39.69</td>
<td>60.31</td>
</tr>
<tr>
<td></td>
<td>(at.%)</td>
<td>±1.32</td>
<td>±1.32</td>
<td>±1.12</td>
<td>±1.12</td>
</tr>
<tr>
<td></td>
<td>nominal (at.%)</td>
<td>43.34</td>
<td>56.66</td>
<td>43.34</td>
<td>56.66</td>
</tr>
<tr>
<td></td>
<td>difference</td>
<td>-3.50</td>
<td>+3.50</td>
<td>-3.65</td>
<td>+3.65</td>
</tr>
</tbody>
</table>

Based on the relative molar ratios of metal nitrate ($a$-Fe$_2$Ni$_3$O$_x$) precursors; †EDX data was recorded on catalyst films deposited on FTO glass; error bars represent the standard deviation between the three different areas of measurement on the surface.

#### $a$-Fe$_2$Ni$_3$

<table>
<thead>
<tr>
<th></th>
<th>area</th>
<th>%Fe</th>
<th>%Ni</th>
<th>%Fe</th>
<th>%Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>41.55</td>
<td>58.45</td>
<td>39.87</td>
<td>60.13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>37.95</td>
<td>62.05</td>
<td>40.37</td>
<td>59.61</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>41.88</td>
<td>58.12</td>
<td>37.31</td>
<td>62.69</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>40.46</td>
<td>59.54</td>
<td>39.18</td>
<td>60.81</td>
</tr>
<tr>
<td></td>
<td>(at.%)</td>
<td>±2.18</td>
<td>±2.18</td>
<td>±1.65</td>
<td>±1.65</td>
</tr>
<tr>
<td></td>
<td>nominal (at.%)</td>
<td>43.34</td>
<td>56.66</td>
<td>43.34</td>
<td>56.66</td>
</tr>
<tr>
<td></td>
<td>difference</td>
<td>-2.88</td>
<td>+2.88</td>
<td>4.15</td>
<td>+4.15</td>
</tr>
</tbody>
</table>

*Based on the relative molar ratios of metal nitrate ($a$-Fe$_2$Ni$_3$) precursors; †EDX data was recorded on catalyst films deposited on FTO glass; error bars represent the standard deviation between the three different areas of measurement on the surface.*
2.5 Non-conducting, UV & Heat Sensitive Materials

We tested the viability of this synthetic method for situations where the substrate is non-conducting or sensitive to high temperatures (for example, interfacial layers in solar cells and carbon-based substrates). Proof-of-principle experiments of relevance to electrolysis were designed where an 180-µm-thick film of Nafion was coated with Ir(acac)₃ and subjected to the NIRDD process. The exclusive formation of amorphous IrOₓ interfaced with the Nafion was found within 120 min of irradiation, with no damage to the membrane according to electrochemical and FTIR data (Figures 2.25 and 2.26). These results show that NIRDD may have the potential to efficiently coat three-dimensional substrates which may prove to be particularly important in contemporary electrolysers.

![Figure 2.25](image.png)

**Figure 2.25.** (A) Cyclic voltammograms for thin films of \(a\)-IrOₓ/membrane (blue trace), Ir(acac)₃/membrane (red trace), and the membrane (black trace), where the membrane is Nafion®. (B) The membrane electrode assembly was prepared by mechanically pressing a platinum mesh counter electrode, the prepared Nafion membrane, and a Toray carbon paper gas diffusion layer between two Ti plate electrodes. The catalytic current with the blank membrane is due to the titanium plates mediating the OER reaction. Electrochemistry conditions: counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s⁻¹; electrolyte = 0.5 M H₂SO₄(aq); current densities were corrected for uncompensated resistance.
Figure 2.26. (A) Full and (B) expanded FTIR spectra of \textit{Ir(acac)}$_{3}$/membrane subjected to NIR radiation for 0 \textit{(black)} and 60 \textit{(blue)} min. A trace for untreated Nafion membrane \textit{(red)} is also shown. The magnified spectrum in (B) is included to feature the loss in intensities of the bands associated with the ligand vibrational modes.

2.6 Conclusions

Amorphous metal (oxide) films can be prepared by merely exposing metal salts (\textit{e.g.}, FeCl$_3$) to NIR radiation. This method offers the opportunity to prepare films on various substrates, and offers the opportunity to manufacture state-of-the-art electrocatalysts and other thin-film applications using infrastructure requirements similar to those used in curing processes currently used in industry. Moreover, the NIRDD method provides strikingly easy access to complex compositions of alloys and metal oxide films in the amorphous phases, and offers a much broader substrate scope than is available to other commonly used methods. The NIRDD method also appears to provide facile access to more reduced phases of the films by merely avoiding the presence of oxygen.
Chapter 3: Amorphous Ruthenium Oxide

3.1 Introduction

The electrolysis of water is a proven method for storing electricity produced from intermittent and variable renewable energy sources. The efficiency of this process is inherently sensitive to the performance of the catalyst responsible for negotiating the oxygen evolution reaction (OER; Eq.1), thus driving a broad effort to develop new metal oxide materials that are compatible with commercial electrolyser systems. The development of OER catalysts that consist of inexpensive transition metals is important to realizing a scalable clean energy economy, but the economics of hydrogen production are governed primarily by catalytic performance and stability, and not the cost of the catalyst. It is for this reason that crystalline ruthenium oxide ($\text{c-RuO}_2$), a highly active electrocatalyst, is widely used in electrosynthesis industries, including commercial alkaline electrolyser systems. While $\text{c-RuO}_2$ is one of the most efficient catalysts for mediating the OER, it can form chemically unstable $\text{RuO}_4$ at strongly oxidizing potentials over prolonged periods in the absence of stabilizing agents (e.g., Ta, Sn). Notwithstanding, the relatively high activity in tandem with the higher relative stability of ruthenium in acid positions these materials as particularly useful candidates for use in emergent proton exchange membrane (PEM) electrolyser systems, which can display markedly higher current densities than conventional electrolyers.

There is a growing body of evidence showing that amorphous metal oxides mediate the OER more efficiently than crystalline phases of the same composition. It is speculated that the reaction activity of an amorphous material is higher than a crystalline electrode because the electrochemical surface area of amorphous materials in comparison to crystalline materials is larger from a greater amount of randomly oriented bonds. This claim has also been made for ruthenium-based catalyst films. While it can be more challenging to make $\text{a-RuO}_x$ because of...
the requisite lower temperatures required during the synthesis, electrodeposition\textsuperscript{23,61,62} and sputter deposition\textsuperscript{23,27,61} techniques have been demonstrated to yield said films. While there has been a more significant effort in studying hydrous $a$-$\text{RuO}_x$ for supercapacitor applications,\textsuperscript{21,27,62} there are several groups that have demonstrated the excellent electrocatalytic activities of $a$-$\text{RuO}_x$ towards the OER. Nakato \textit{et al.} studied the OER activity of electrodeposited and sputtered $a$-$\text{RuO}_x$ films and found the onset overpotentials were cathodically shifted by 30-60 mV from those for the rutile crystalline samples.\textsuperscript{61} A broad comparative study of 26 electrocatalysts by Jaramillo, Peters and coworkers found $a$-$\text{RuO}_x$ to deliver superior performance.\textsuperscript{23} The state-of-the-art electrocatalytic activities of these amorphous phases are important, but accessing said phase of ruthenium oxides through scalable methods is not trivial given the inherent sensitivity to deposition protocols and infrastructure costs.\textsuperscript{29,41}

We recently introduced two facile light-based methods of fabricating thin films of amorphous metal oxides; namely, the ultraviolet-light driven decomposition (UVDD)\textsuperscript{18} and the near-infrared driven decomposition (NIRDD)\textsuperscript{39} processes (Scheme 1). Both synthetic protocols have been previously shown to furnish amorphous transition metal oxide films upon exposure of spin-cast molecular precursors to UV and NIR light, respectively. In this report, it is demonstrated that these two light-induced decomposition processes can also be tailored to form films of $a$-$\text{RuO}_x$. Our previously reported UVDD protocol utilizing UV light ($\lambda = 185$ and 254 nm) could not be used to produce ruthenium films because the precursors [e.g., Ru(acac)$_3$, Ru(tmhd)$_2$(cod), Ru(eh)$_3$] were volatilized as ruthenium tetroxide (RuO$_4$).\textsuperscript{32} \textbf{CAUTION: RuO$_4$ is a toxic, volatile compound and should not be inhaled!} The films could be produced by the UVDD method, however, by using a more selective UV light source that prevents the formation of ozone; i.e., irradiation at wavelengths that bypass the formation of ozone in an aerobic
environment. The use of the NIRDD method to form \textit{a-RuO}_x also proved challenging given that many ligands of precursors that are effective for other transition metals can make ruthenium susceptible to sublimation.\textsuperscript{39} This study demonstrates that the NIRDD of RuCl\textsubscript{3}, a precursor that does not sublime at temperatures below 200 °C successfully yields the desired film (Figure 3.1). The films produced by both of these methods demonstrate electrocatalytic efficiencies in aqueous acid media (1 M H\textsubscript{2}SO\textsubscript{4}) consonant with other ruthenium-based electrocatalysts, and thus offers promising alternatives for depositing \textit{a-RuO}_x films on electrode surfaces.

![Figure 3.1](image.png)

**Figure 3.1.** The photolytic formation of \textit{a-RuO}_x by ultraviolet-light driven decomposition (UVDD) and near-infrared driven decomposition (NIRDD) on fluorine-doped SnO\textsubscript{2}-coated glass (FTO) substrates.

### 3.2 Ultraviolet-light Driven Decomposition

The UVDD method subjects a spin-coated metal precursor film on a substrate to UV light.\textsuperscript{18} Successive ligand-to-metal charge transfer (LMCT) steps are triggered by light to form a reduced metal-based film that reacts with air to form a metal oxide at moderate temperatures.\textsuperscript{30} Our previous studies have utilized UV light with emission bands centered at \textit{ca.} 185 and 254 nm;\textsuperscript{18,28,29} however, the irradiation of oxygen with 185-nm light induces the formation of ozone that can react with ruthenium to form volatile and toxic RuO\textsubscript{4}.\textsuperscript{32} **CAUTION: RuO\textsubscript{4} is a toxic, volatile compound and should not be inhaled!** Consequently, the ruthenium precursor is liberated from
the substrate as a gaseous product during photolysis (Figure 3.2a). We therefore took steps to avoid the formation of RuO₄ by irradiating the films with UV light with a selective 254-nm light source that bypasses the formation of ozone that can otherwise occur upon irradiation with 185-nm light.

The choice of the UVDD precursor, Ru(tmhd)₂(cod), was selected based on its proven utility in photolithography applications. Thin films of the precursor were prepared by spin-coating a hexanes solution of the precursor onto fluorine-doped tin oxide (FTO) glass followed by irradiation with 245-nm light. Photolysis at this wavelength successfully converted the photoactive precursor to \( \alpha \)-RuOₓ within three days. The course of the reaction was indicated by a colour change from yellow to dark grey (Figure 3.3), and a loss in ligand-based vibrational modes with concomitant growth of a broad signal corresponding to surface hydroxyl species (Figure 3.2b). The non-crystalline nature of the \( \alpha \)-RuOₓ is claimed here on the basis that there is a lack of Bragg reflection peaks associated with crystalline phases of ruthenium oxide in the X-ray diffraction (XRD) patterns (Figure 3.4), where the same films heated to 500 °C did yield diffraction peaks at 28.0° (110) and 40.0° (200) consistent with \( \text{c-RuO}_x \) (rutile structure). Efforts to convert precursors of ruthenium(III)acetylacetonate \([\text{Ru(acac)}_3]\) and ruthenium(II)2-ethylhexanoate \([\text{Ru(eh)}_3]\) to \( \alpha \)-RuOₓ by UVDD at 254 nm were not successful based on colour changes and vibrational spectroscopy despite three weeks of irradiation. We note that the labile metal-ligand bond of Ru(tmhd)₃ has been invoked for chemical vapour deposition protocols, a property that may help facilitate UVDD of Ru(tmhd)₂(cod).
Figure 3.2. FTIR spectra for thin films of Ru(tmhd)$_2$(cod) on FTO upon exposure to UV radiation for (A) 0 (black), 12 (red), 24 (blue) h under UV light (i.e., $\lambda_{\text{max}}$ at 185 and 254 nm); and (B) 0 (black), 24 (red), 72 (blue) h under selective UV light (i.e., $\lambda_{\text{max}} = 254$ nm light). Arrows indicate trends in the intensities of the C-H and C-O vibrational modes for organic ligands.

Figure 3.3. UV-vis absorption spectra, before (top) and after (bottom) being subjected to the NIRDD or UVDD processes of: Ru(tmhd)$_2$(cod) and RuCl$_3$ on FTO. The FTO background is also shown. The repetitive wave pattern in the traces is caused by diffraction on the FTO substrate, as the films are very thin.
3.3 Near Infrared Driven Decomposition

The NIRDD method subjects a metal precursor, a coordination complex or metal halide salt, to NIR light. The film reaches moderate temperatures to avoid crystalline domain formation (<200°C), but with sufficient thermal energy to drive thermal decomposition. Volatile ruthenium coordination complexes that we tested for the UVDD method, as well as documented CVD precursors, such as Ru(tmhd)₂(cod), were not suitable for NIRDD because they vaporized prior to conversion to the oxide. RuCl₃ proved to be an effective molecular precursor for the NIRDD process because it is not volatile at 200°C. Thin films were therefore prepared by spin coating a MeOH solution of the halide salt onto FTO glass, and then irradiated with NIR light. The lack of distinctive ligand vibrational modes precluded the use of FTIR spectroscopy to track
the decomposition process, but the change in colour of the film from orange to grey within two hours suggested the formation of $a$-RuO$_x$ (Figure 3.2), which is supported by the electrochemical analysis (vide infra). The XRD amorphous nature of the films were confirmed following the same protocol as the films prepared by UVDD (Figure 3.5).

![Figure 3.5](image)

**Figure 3.5** Top: Powder XRD patterns acquired on as-prepared and annealed $a$-RuO$_x$ films prepared by applying the NIRDD process to precursor thin films on FTO; as prepared (red), annealed at 300°C and annealed at 500°C (blue). Data recorded on a bare FTO substrate is also provided (black). **Bottom:** Expanded view highlighting the region where the reflection associated with the crystalline form of RuO$_x$ at 28° and 40° is observed. This reflection is observed only for the films annealed at 500°C.

### 3.4 Electrochemical Data

Cyclic voltammograms (CVs) were recorded in 1 M H$_2$SO$_4$ on $a$-RuO$_x$ fabricated by both the UVDD and NIRDD methods (Figure 3.6). The as-prepared $a$-RuO$_x$ films prepared by the UVDD method were exceedingly unstable: The films started to dissolve during the oxidative scan prior to water oxidation. This instability has been previously reported for electrodeposited
ruthenium films, and ascribed to poor adhesion with the FTO. Films of a-RuOₓ prepared by UVDD on FTO were therefore annealed at 100, 200, 300, 400, and 500°C, respectively, given that annealing has been found to increase film stabilities of other metals. Films annealed at 100°C (UVDD₁₀₀°C) were liberated from the surface at 1.3 V vs RHE, a potential that corresponds roughly to the onset of water oxidation catalysis (Figure 3.7). Films annealed at 200°C (UVDD₂₀₀°C) were stabilized enough to observe the onset of water oxidation catalysis, but the films were still unstable at current densities of ~20 mA/cm² (Figure 3.7). Annealing steps at higher temperatures (UVDD₄₀₀°C and UVDD₅₀₀°C) yielded more stable films, but are less catalytically active due to a phase transition to less active c-RuO₂ (Figures 3.6 and 3.7). An annealing temperature of 300°C (UVDD₃₀₀°C) seemed to provide the best balance of stability and catalytic activity, although some activity is still lost upon successive cycling as is expected for purely ruthenium films (Figures 3.6 and 3.7).

CVs recorded on as-prepared a-RuOₓ films formed by NIRDD yielded films with OER catalytic activities comparable to the films formed by the UVDD method (Figures 3.6 and 3.8). An oxidative sweep of the as-prepared a-RuOₓ films (NIRDD) displayed a high catalytic activity on the first scan consonant with that of the UVDD₃₀₀°C films, but there was also a loss in activity after subsequent cycling. Films formed by NIRDD were also annealed at 300, 400 and 500 °C (denoted as NIRDD₃₀₀°C, NIRDD₄₀₀°C and NIRDD₅₀₀°C, respectively), and all displayed slightly higher activity towards the OER in comparison to the as-prepared film (Figure 3.8).

In order to probe the stabilities of the catalyst films under working conditions, chronopotentiometric scans were performed with the current held at 10 mA/cm² for 2 h (Figures 3.6b, 3.9 and 3.10). All of the annealed films prepared by UVDD were demonstrated to be stable over a 2-h time period after an initial conditioning step. The film annealed at 300°C was
characterized by an overpotential that was 70 mV lower than the films annealed at 500°C. All of the NIRDD films were also stable over the 2-h time period after an initial conditioning step, with OER activities that were not significantly different. Indeed, the data seems to indicate that the \textit{a-RuO}_x films formed by both methods displayed very similar activities, with any differences most likely due to differences in electrochemical surface areas (Figure 3.11). The catalytic onset overpotential, Tafel slope and overpotential of the films at 10 mA/cm$^2$ corresponds to reported literature values for \textit{a-RuO}_x (Table 3.1 and Figure 3.12).

**Table 3.1. Relevant Benchmarking Parameters for Ruthenium Oxide OER Catalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset $\eta$ (V)</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>$\eta_{10\text{mA/cm}^2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{a-RuO}_x/UVDD$^{300\degree}$C</td>
<td>0.07</td>
<td>46</td>
<td>0.27</td>
</tr>
<tr>
<td>\textit{c-RuO}_x/UVDD$^{500\degree}$C</td>
<td>0.14</td>
<td>78</td>
<td>0.34</td>
</tr>
<tr>
<td>\textit{a-RuO}_x/NIRDD</td>
<td>0.09</td>
<td>53</td>
<td>0.15</td>
</tr>
<tr>
<td>\textit{c-RuO}_x/NIRDD$^{500\degree}$C</td>
<td>0.14</td>
<td>79</td>
<td>0.17</td>
</tr>
<tr>
<td>\textit{a-RuO}_x$^{61,23}$</td>
<td>0.08$^{61,23}$</td>
<td>33$^{61,23}$</td>
<td>0.28$^{61,23}$</td>
</tr>
<tr>
<td>\textit{c-RuO}_x$^{61}$</td>
<td>0.13$^{61,23}$</td>
<td>84$^{61,23}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Electrochemical conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq). All potentials are expressed versus a reversible hydrogen electrode (RHE).

*Overpotential required to reach 10 mA/cm$^2$ at t=0. \| Value reported vs Ag|AgCl, extrapolated vs RHE. \§Electrochemical experiments carried out in 0.1M deoxygenated HClO$_4$ (pH 1.3). \| Overpotential required for onset of catalysis (i.e.; low overpotential regime of Tafel plot)
Figure 3.6. Cyclic voltammograms (CVs) (A) and chronopotentiometric scans (B) for as-prepared and annealed thin films of \( a\)-RuO\(_x\) and \( c\)-RuO\(_x\) formed by the UVDD and NIRDD; UVDD films annealed at 300°C (red) and 500°C (blue), NIRDD fresh film (purple) and annealed film at 500°C (green). Bare FTO trace is shown as a reference, note the instability in acidic environments demonstrating that the films act as protective layers. CVs: scan rate = 10 mV s\(^{-1}\); chronopotentiometry: current density = 10 mA cm\(^{-2}\) for 2 h. Electrochemical conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H\(_2\)SO\(_4\) (aq).

Figure 3.7. Cyclic voltammograms for thin films of \( a\)-RuO\(_x\) and \( c\)-RuO\(_x\) formed through the UVDD method and annealed at various temperatures; annealed films at 100°C (purple), 200°C (orange), 300°C (red), 400°C (green), and 500°C (blue). Shown on the left is cycle 1 and right is cycle 3. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s\(^{-1}\); electrolyte = 1 M H\(_2\)SO\(_4\) (aq).
Figure 3.8. Cyclic voltammograms for thin films of $a$-RuO$_x$ and $c$-RuO$_x$ formed through the NIRDD method and annealed films at various temperatures; fresh film (purple), annealed films at 300°C (red), 400°C (green), and 500°C (blue). Left: cycle 1. Right: cycle 3. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); scan rate = 10 mV s$^{-1}$; electrolyte = 1 M H$_2$SO$_4$ (aq).

Figure 3.9. Chronopotentiometric experiments of thin films of $a$-RuO$_x$ and $c$-RuO$_x$ prepared through the UVDD method annealed at 300°C (red), 400°C (red), 500°C (blue). An FTO trace is also shown as reference (black), note the instability in acidic environments demonstrating that the films act as protective layers. The current was held at 10 mA cm$^{-2}$ for 7200 s. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq). FTO is significantly unstable under acidic conditions.
Figure 3.10. Chronopotentiometric experiments of thin films of \textit{a-RuO}_x and \textit{c-RuO}_x prepared through the NIRDD method; fresh film (purple), annealed at 300°C (orange), 400°C (green), 500°C (blue). An FTO trace is also shown as reference (black), note the instability in acidic environments demonstrating that the films act as protective layers. The current was held at 10 mA cm$^{-2}$ for 7200 s. Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq)

Figure 3.11. Relative electrochemical surface area of thin films of \textit{a-RuO}_x and \textit{c-RuO}_x formed through the UVDD and NIRDD methods and annealed films at various temperatures; UVDD films annealed at 300°C (red) and 500°C (blue), NIRDD fresh film (purple) and annealed film at 500°C (green). Experimental conditions: Counter-electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq)
Figure 3.12. Tafel plots for as-prepared and annealed thin films of $a$-RuO$_x$ and $c$-RuO$_x$ formed by the UVDD and NIRDD; UVDD films annealed at 300°C (red) and 500°C (blue), NIRDD fresh film (purple) and annealed film at 500°C (green). Tafel plots were acquired through staircase voltammetry (10 mV steps, 50 s intervals for the final 25 s sampled). Electrochemical conditions: Counter electrode = Pt mesh; reference electrode = Ag/AgCl, KCl (sat’d); electrolyte = 1 M H$_2$SO$_4$ (aq).

3.5 Ruthenium Mixed Metal Systems

Ruthenium oxide electrocatalysts are known to be unstable over long time periods in acidic environments, but the films can be stabilized by tantalum or titanium. To prove the ease in manufacturing mixed-metal oxide films using the NIRDD method, binary films of $a$-RuTiO$_x$ and $a$-RuTaO$_x$ were fabricated by photolyzing spin-cast mixtures of RuCl$_3$ with either Ti(OCH$_2$CH$_2$CH$_2$CH$_3$)$_4$ (mol Ru/mol Ti 1:1) or TaCl$_5$ (mol Ru/mol Ta 1:1) dissolved in MeOH. The films of $a$-RuTaO$_x$ and $a$-RuTiO$_x$ displayed a lower initial activity (Figure 3.13a) compared to the $a$-RuO$_x$ films formed through NIRDD, the films showed improved stability and lower overpotentials over a 2 h time period (Figure 3.13b), with $a$-RuTaO$_x$ showing the lowest overpotential (0.52 V) of all the films after 2 h of testing.
3.5 Conclusions

We have demonstrated two effective methods of fabrication $a$-$\text{RuO}_x$ electrocatalysts that act as effective OER catalysts. In order to circumvent the reaction of Ru with ozone, the modified UVDD method uses solely 254 nm light for the light driven decomposition of a molecular precursor, Ru(tmhd)$_2$(cod). The NIRDD method utilizes a thermal decomposition process of a RuCl$_3$ salt. The $a$-$\text{RuO}_x$ films prepared herein compare agreeably to those prepared by alternate methods, such as electrodeposition and sputter deposition methods.$^{23,61}$ The onsets of catalysis, Tafel slopes and potentials required to reach 10 mA cm$^{-2}$ for the $a$-$\text{RuO}_x$ films prepared herein were 70-90 mV, $\sim$46-53 mV dec$^{-1}$, 150-270 mV, respectively, which are consonant with films prepared by previously documented methods. Moreover, the $a$-$\text{RuO}_x$ catalysts are favourable when compared to $c$-$\text{RuO}_x$, with a $\sim$30-70 mV savings in overpotential.
required to reach 10 mA cm$^{-2}$. In addition, the UVDD and NIRDD methods provide strikingly easy access to complex compositions metal oxide films in the amorphous phases. Both methods present the opportunity to prepare films on various substrates, and offer the ability to manufacture state-of-the-art ruthenium based electrocatalysts at scale.
Chapter 4: Conclusions and Future Directions

4.1 Conclusions

Amorphous metal oxides have gained prominence in the contemporary field of water oxidation catalysis because of their superior catalytic behaviour relative to their crystalline counterparts. The superior catalytic behaviour was demonstrated herein with \( a\text{-RuO}_x \) catalysts outperforming \( c\text{-RuO}_x \) (e.g., a lower onset overpotential, tafel slope overpotential required to reach \( 10 \text{ mA cm}^{-2} \)). Notwithstanding, there are very few techniques that provide access to a wide variety of catalyst film compositions. While several high-impact publications have used electrodeposition to form amorphous metal oxide films,\(^6\),\(^7\),\(^61\) this technique does not translate effectively to all metals and is not amenable to making films with a uniform distribution of different metals.\(^25\) Moreover, these methods do not work on non-conducting substrates, which are desirable for next-generation electrolyzers, and optoelectronic applications.\(^41\)

The work described in this thesis provides a facile solution to these problems that is a step-change improvement for fabrication of amorphous films: The exposure of metal salts to NIR radiation forms amorphous oxides.\(^39\) This finding was not expected, but is an important discovery for various applications that rely on films. Moreover, this method can be used to make amorphous metal alloys, a class of materials far less developed than the oxides because extreme conditions (e.g., high vacuum and/or ultra-low temperatures) are generally required.\(^15\)

In Chapter 2 the recently reported near-infrared driven decomposition method is outlined. The NIRDD method is a scalable preparative method for accessing oxidized and reduced phases of amorphous films that involves efficient decomposition of molecular precursors, including metal halide and nitrate salts, by exposure to NIR radiation. The NIRDD process provides sufficient localized heating to trigger the liberation of the ligands from solution-deposited precursors on substrates, but insufficient thermal energy to form crystalline phases. This method
provides access to state-of-the-art electrocatalyst films, as demonstrated for the electrolysis of water, and extends the scope of usable substrates to include non-conducting and temperature-sensitive platforms.

In Chapter 3 I demonstrated two distinctive methods of fabrication of $a$-RuO$_x$ electrocatalysts, which are commercially relevant OER catalysts. In order to circumvent the reaction of Ru with ozone, the modified UVDD method uses UV light that bypasses the formation of ozone during the light driven decomposition of a molecular precursor, Ru(tmhd)$_2$(cod), to avoid volatizing the ruthenium films and producing ruthenium oxide films in quantitative yields.

The NIRDD method utilizes a thermal decomposition process of a RuCl$_3$ salt. The $a$-RuO$_x$ films prepared herein compare agreeably to those prepared by alternate methods, such as electrodeposition and sputter deposition methods. The onsets of catalysis, Tafel slopes and potentials required to reach 10 mA cm$^{-2}$ for the $a$-RuO$_x$ films prepared herein were 70-90 mV, ~46-53 mV dec$^{-1}$, 150-270 mV, respectively, which are consonant with films prepared by previously documented methods. Moreover, the $a$-RuO$_x$ catalysts are favourable when compared to the prepared crystalline counterparts, $c$-RuO$_x$, with an onset overpotential cathodically shifted ~50 mV, a ~20 mV dec$^{-1}$ lower tafel slope and ~30-70 mV savings in overpotential required to reach 10 mA cm$^{-2}$. In addition, the UVDD and NIRDD methods provide strikingly easy access to complex compositions metal oxide films in the amorphous phases. These methods present the opportunity to prepare films on various substrates, and offer the ability to manufacture state-of-the-art ruthenium based electrocatalysts at scale.
4.2 Future Directions

High-Throughput Combinatorial Testing of $a$-MO$_x$ Materials

One of the most powerful attributes of the NIRDD and UVDD methods are that they offer the unprecedented ability to make mixed-metal oxides with precise stoichiometric control.$^{18,39}$ These approaches therefore provide access to a wide range of compositions, a parameter space where previously documented fabrication methods were distinctly lacking. These methods produce amorphous films for a wide variety of metals without adjusting the procedure for each element and without the need for special conditions.$^{18,39}$ One large bottleneck to catalyst development is the inherently wide sample space for discovery. The newfound ability to effortlessly make mixed-metal compositions of amorphous oxides leads to a myriad of previously unknown metal combinations that need to be tested. Since computational methods are currently unable to predict the behaviour of such complex systems and the number of possible catalyst compositions far exceeds the number that can be manually tested, a high-throughput combinatorial method must be developed to synthesize and screen catalysts prepared by the newly reported techniques.

The Berlinguette and Trudel groups fabricated a preliminary series of 21 amorphous mixed-metal oxide films with a mixture of Fe, Co and Ni metals using the UVDD technique.$^{29}$ This series of catalysts, prepared in a labour-intensive fashion, showed distinct trends in catalytic activity with changing composition of the film. The proposed project is a high-throughput combinatorial screening of the electrocatalytic performance of materials prepared by the photochemical technique. A high-throughput screening will allow the efficient introduction of other first and second row transition metals, for example Mo and Ti, into the well-studied and catalytically efficient binary mixtures of Fe and Ni. This study can then be extended further to adding a quaternary metal into the array.
High-throughput search strategies for crystalline metal oxide electrocatalysts and photoelectrocatalysts have been prevalent for the past couple decades. Parkinson and coworkers use a materials printer to deposit an overlapping triangular gradient pattern of ternary and quaternary metal oxides (Figure 4.1A). To screen the photoelectrocatalysts a false colour image of photoactivity is produced with a scanning laser system by measuring the photocurrent as the laser scans over the sample. The Gregoire group prints a combinatorial template with an inkjet printer and measures the photoelectrocatalysts with a scanning droplet cell. In the scanning droplet cell a drop of electrolyte at the bottom of the cell contacts the working electrode, an internal fiber optic illuminates the electrode and the photocurrent is measured (Figure 4.1B). Stahl and coworkers have developed an O$_2$-sensitive fluorescence-quenching assay for high throughput discovery. In the electrochemical cell configuration of the assay a stainless steel mesh coated with O$_2$ sensitive fluorescence paint is placed above an array of metal-oxide electrocatalysts. While under operation the cell is irradiated with light and the fluorescence, indicative of the amount of O$_2$ evolved, is captured by a digital camera (Figure 4.1C). While these techniques have enabled discovery of new catalysts for the OER and HER, many current high throughput synthesis strategies are aimed at crystalline metal oxides and many electrochemical testing strategies are aimed at photoelectrocatalysts. There is a large research gap for high throughput methodology for amorphous electrocatalysts.
Figure 4.1. (A) Triangular gradient patterns are shown on the top and false color images of photocurrent are on the bottom.\textsuperscript{66} (B) Photograph of a scanning droplet cell.\textsuperscript{68} (C) Schematic drawing of the electrochemical screening apparatus showing the positions of the electrode array, O$_2$-sensing mesh, light source and camera.\textsuperscript{69}

The UVDD and NIRDD techniques can be incorporated into a high-throughput process by changing the method of depositing precursor solutions. The precursor solutions will be inkjet printed on a conductive substrate using a combinatorial template design. The patterned substrate will then be photolyzed with UV or NIR light to form metal oxide catalysts. A potential challenge with this project is the deposition of the precursor solutions on the substrates. To overcome it, a higher viscosity solvent may be used as well as modification of the substrate to be more hydrophilic or hydrophobic depending on solvent choice. The electrocatalytic performance of each catalyst in the printed pattern template will be measured using an automated three-electrode scanning process (Figure 5.1). A custom made well plate was designed in order to modify a CH instruments 1550A Solution Dispenser. Under each well is a unique composition of printed catalyst that acts as the working electrode. An Ag/AgCl Reference Electrode and a platinum wire counter electrode will be attached to the moving arm of the device that can be moved in the x-y-z direction.
Ideally, a high throughput combinatorial scanning process using the UVDD and NIRDD techniques will not only open up an entire new research area with the ability to discover new efficient electrocatalytic materials, which can then be implemented in photoelectrochemical cells, but can also open up the possibility of discovering catalysts combinations with unexplored metals for the OER. This was showcased recently by the discovery of two distinct regions with efficient OER catalysis upon a combinatorial study of Fe-Co-Ni-Ce oxides.\textsuperscript{70}

\textbf{Figure 4.2.} The UVDD and NIRDD techniques implemented to form metal oxide catalysts from inkjet printed precursors followed by electrochemically automated process to characterize the catalysts.
Chapter 5: Experimental

5.1 Chapter 2

5.1.1 Materials

Iron(III) 2-ethylhexanoate (Fe(eh)$_3$, 50% w/w in mineral spirits), iridium (III) acetylacetonate (Ir(acac)$_3$), nickel(II) 2-ethylhexanoate (Ni(eh)$_2$, 78% w/w in 2-ethylhexanoic acid), manganese(III) 2-ethylhexanoate (Mn(eh)$_3$, 40% w/w in 2-ethylhexanoic acid), and copper(II) 2-ethylhexanoate (Cu(eh)$_2$) were purchased from Strem Chemicals. Nafion® N117 proton exchange membranes (177.8 μm thick) were purchased from Ion Power, ferric chloride (98% anhydrous) (FeCl$_3$) was purchased from Aldrich, iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) and nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) were purchased from Fischer Scientific. All reagents were used without further purification.

5.1.2 Film Syntheses

*a-FeO$_x$* on FTO (or glass). To a 20-mL beaker containing 0.58 g of Fe(eh)$_3$ (0.60 mmol) was added to 1.07 g hexanes (12.4 mmol). The solutions were then spin-cast onto FTO (or glass) at 3000 rpm for 1 min. The resultant film, Fe(eh)$_3$/FTO (or Fe(eh)$_3$/glass), was left under a NIR lamp for 30 min. The following conditions for this “NIRDD” process were used for each experiment unless otherwise stated: the samples were placed underneath a Phillips 175 W NIR lamp, where the bottom of the lamp was positioned 2 cm above the substrate that was set on an aluminum foil surface to help dissipate the heat; the face of the active film was positioned towards the lamp for this process. We caution that unoptimized spacing of the lamp may lead to sufficiently high temperatures to yield crystalline phases. *Alternative methods:* Films were also be prepared from FeCl$_3$ (0.24 g) or Fe(NO$_3$)$_3$ (0.11 g) in deionized water (2 g), that were spin-cast on FTO to form FeCl$_3$/FTO and Fe(NO$_3$)$_3$/FTO, respectively, and subject to the NIRDD
process described above to form $a$-FeO$_x$. Samples prepared on glass were prepared using the same protocol as those prepared on FTO.

**$a$-Fe on FTO (or glass).** The films were prepared following the same protocol as $a$-FeO$_x$, except the subsequent photolysis step being carried out in an MBraun Labmaster 130 glove box filled with nitrogen.

**$a$-FeO$_x$-annealed.** Films of $a$-FeO$_x$ on FTO were annealed in a furnace at 600 °C for 60 min.

**$a$-Fe-annealed.** Films of $a$-Fe on FTO were annealed for 60 min on a hot plate set at 600 °C inside the glove box. The temperature of the hot plate was confirmed with a Fluke 52 thermocouple.

**$a$-IrO$_x$ on FTO (or glass).** To a 20-mL beaker containing 0.09 g of Ir(acac)$_3$ (0.3 mmol) was added 1.48 g chloroform. The solution was spin-cast onto the substrates (glass or FTO) at 3000 rpm for 1 min. The resultant film, Ir(acac)$_3$/FTO, was subject to the NIRDD process for 2 h to ensure the reaction was completed.

**$a$-NiO$_x$ on FTO (or glass).** To a 20-mL beaker containing 0.27 g of Ni(eh)$_2$ (0.61 mmol) was added to 1.26 g hexanes (14.6 mmol). The solutions were then spin-cast onto the substrates (glass or FTO) at 3000 rpm for 1 min. The resultant film, Ni(eh)$_2$/FTO, was subject to the NIRDD process until the reaction was complete (~60 min). **Alternative methods:** Films could
also be prepared from NiCl$_2$ (0.17 g) or Ni(NO$_3$)$_2$ (0.14 g) in deionized water (2 g), that were spin-cast on FTO to form NiCl$_2$/FTO and Ni(NO$_3$)$_3$/FTO, respectively, and then subject to the NIRDD process to form $a$-NiO$_x$ on FTO (~30 min).

$a$-MnO$_x$ on FTO (or glass). To a 20-mL beaker containing 0.55 g of Mn(\textit{eh})$_3$ (0.64 mmol) was added to 1.06 g of hexanes (12.3 mmol). The solutions were then spin-cast onto FTO at 3000 rpm for 1 min. The resultant film, Mn(\textit{eh})$_3$/FTO, was then subject to the NIRDD process to form $a$-MnO$_x$ on FTO (~30 min).

$a$-CuO$_x$ on FTO (or glass). To a 20 mL beaker containing 0.21 g of Cu(\textit{eh})$_2$ (0.65 mmol) was added to 1.62 g ethanol (35.2 mmol). The solutions were then spin-cast onto FTO at 3000 rpm for 1 min. The resultant film, Cu(\textit{eh})$_2$/FTO, was then subject to the NIRDD process to form $a$-CuO$_x$ on FTO (~30 min).

$a$-Fe$_2$Ni$_3$O$_x$ on FTO (or glass). To a 20-mL beaker containing 0.23 g of Fe(\textit{eh})$_3$ (0.24 mmol) and 0.16 g of Ni(\textit{eh})$_2$ (0.36 mmol) was added 1.28 g of hexanes (14.9 mmol). The mixture was spin-cast onto FTO at 3000 rpm for 1 min. The resultant film, FeNi(\textit{eh})/FTO, was then subject to the NIRDD process to form $a$-Fe$_2$Ni$_3$O$_x$ on FTO (~30 min). Alternative methods: Films could also be prepared from a solution of NiCl$_2$ (0.088 g) [or Ni(NO$_3$)$_2$ (0.105 g)] and FeCl$_3$ (0.039 g) [or Fe(NO$_3$)$_3$ (0.097 g)] in deionized water (2 g) spin-cast on FTO and subject to the NIRDD process as described above to form $a$-Fe$_2$Ni$_3$O$_x$. 

59
\(a\text{-Fe}_2\text{Ni}_3\) on FTO (or glass). Films of \(a\text{-Fe}_2\text{Ni}_3\) on FTO were prepared in the same fashion as \(a\text{-Fe}_2\text{Ni}_3\text{O}_x\), but the photolysis step was carried out in a glove box.

\(a\text{-IrO}_x\text{/membrane}\). Nafion membranes were cut into squares with geometric surface areas of 6.25 cm\(^2\) and then submerged in a bath of 3% w/w H\(_2\)O\(_2\) stirring at 800 rpm for ~5 min. The membranes were then left to stand in a bath of stirring 0.5 M H\(_2\)SO\(_4\) at 150\(^\circ\) C for 60 min. The membranes were dehydrated in a vacuum oven (room temperature, 0.8 atm) for at least 5 h. Excess acid was removed before dehydration with compressed nitrogen. A solution containing 0.004 g of Ir(acac)\(_3\) (0.009 mmol) in 0.9 ml chloroform was then spray-coated on the surface of the dehydrated Nafion to form \(\text{Ir(acac)}_3\text{/membrane}\). The resultant film was then subjected to the NIRDD process to form \(a\text{-IrO}_x\text{/membrane}\) (~120 min).

5.1.3 Physical Methods

Electrochemical measurements were performed on a C-H Instruments Workstation 660D potentiostat. The Ag/AgCl (sat. KCl) reference electrode (\(E_{\text{ref}}\)) was calibrated regularly against a 1-mM aqueous K\(_3\)[Fe(CN)\(_6\)] solution. Cyclic voltammograms were acquired at a 10 mV s\(^{-1}\) scan rate unless otherwise indicated. All potentials were corrected for uncompensated resistance (\(R_u\)) and are reported relative to the reversible hydrogen electrode (vs RHE), \(E_{\text{RHE}} = E + E_{\text{ref}} + 0.059(\text{pH}) - iR_u\). Tafel plots were acquired through staircase voltammetry (10 mV steps, 50 s intervals for the final 25 s sampled). Chronopotentiometric experiments were held at 10mA/cm\(^2\) for 7200 s. For the metal oxide and metal films on FTO, all experiments were carried out using 0.1 M KOH as an electrolyte, unless otherwise noted, in a standard three-compartment electrochemical cell. A Luggin capillary connects the reference and working electrodes while a porous glass frit connects the working electrode to the platinum mesh counter electrode. All
experiments involving Nafion were carried out in 0.5 M H₂SO₄. Membranes were hydrated in 0.2 M H₂SO₄ prior to electrochemical experiments. Measurements were performed in a customized three-electrode test cell using the above Ag/AgCl reference electrode. All potentials were corrected for $R_u$. The membrane electrode assembly (MEA) was prepared by mechanically pressing a platinum mesh counter electrode (Aldrich), the prepared Nafion membrane, and a Toray carbon paper gas diffusion layer (Ion Power) between two Ti plate electrodes (McMaster Carr). No aggregation was induced on the test cell besides that from evolved gaseous products.

FTIR spectroscopy was recorded on a Bruker alpha spectrometer with a transmission accessory. Thin films were prepared as described above, the disappearance of the vibrations associated with the ligand were followed during photolysis. Powder X-ray diffraction (XRD) data was recorded with a Bruker D8 Advance diffractometer using Cu Kα radiation. Data was collected between $2\theta$ angles of 5° and 90° with a step size of 0.04°. The step time was 0.6 s unless otherwise indicated. Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC) measurements were collected simultaneously with a PerkinElmer Simultaneous Thermal Analyzer (STA) 6000. These measurements were carried out under both air and N₂ at a 20-mL min⁻¹ flow rate. Starting from a temperature of 50 °C, the temperature was ramped up (10 °C min⁻¹) until 100 °C where it was held for one minute. It was then ramped at 10 °C min⁻¹ until a final temperature of 500 °C was reached and held for an additional minute. For constant temperature measurements, the temperature was ramped up (10 °C min⁻¹) until 200 °C where it was held for 60 minutes. UV-vis absorption spectroscopy on fresh and on metal oxide films was performed using a Perkin Elmer Lambda 35 UV-vis spectrometer with a solid sample holder accessory. Baseline scans were performed with clean glass. The films examined were prepared from 0.3 M precursor solutions of 1-5. X-ray photoelectron spectroscopy (XPS) measurements
were collected on a Leybold MAX200 spectrometer using Al K-alpha radiation. The pass energy used for the survey scan was 192 eV while for the narrow scan it was 48 eV. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements were carried out on a FEI Helios NanoLab 650 dual beam scanning electron microscope with an EDAX Pegasus system with EDS detector. The magnification was set to 2000X, the accelerating voltage was set to 2.0 KeV, the current was set to 51 nA and the working distance was 9 mm.

The temperature of the substrates was tracked with a Fluke 52 thermocouple attached to a multimeter. For the FTO measurements, constant contact of the tip of the detector was maintained throughout the experiment. For the thermocouple measurements, the tip of the detector was dipped in Fe(eh)$_3$. The substrate & thermocouple was placed 2 cm from the lamp. Temperature values were recorded every 5 min.

5.2 Chapter 3

5.2.1 Materials

The reagents $\text{bis}(2,2,6,6$-tetramethyl-$3,5$-heptanediaonato)(1,5-cyclooctadiene)ruthenium(II) ([Ru(tmhd)$_2$(cod)]) were purchased from Strem Chemicals, ruthenium (III) chloride hydrate was purchased from Pressure Chemicals, tantalum (V) chloride and titanium (IV) butoxide were purchased from Sigma-Aldrich, and FTO glass was purchased from Hartford Glass. All reagents were used without further purification.

5.2.2 Film Syntheses

$a$-$\text{RuO}_x$ on FTO (UVDD). To a 20-mL beaker containing 0.055 g of Ru(tmhd)$_2$(cod) was added 0.327 g hexanes. The solutions were then spin-cast onto FTO at 3000 rpm for 1 min.
The resultant film, Ru(tmhd)$_2$(cod)/FTO, were left under a UV lamp for 72 hrs. The following conditions for this UVDD process were used for each experiment unless otherwise stated: The samples were placed underneath a Atlantic Ultraviolet 5.8W 254 nm, where the bottom of the lamp was positioned 1 cm above the substrate; the face of the active film was positioned towards the lamp for this process. The entire lamp is encased in a stainless steel box for safety considerations.

**UVDD**$^T$ °C where T is 100°C , 200°C, 300°C, 400°C, and 500 °C. Films of $a$-$\text{RuO}_x$ (UVDD) on FTO were annealed in a furnace at 100°C, 200°C, 300°C, 400°C, and 500°C for 60 min.

**$a$-$\text{RuO}_x$ on FTO (NIRDD).** To a 20-mL beaker containing 0.052 g of RuCl$_3$ was added 1.45 g MeOH. The solutions were then spin-cast onto FTO at 3000 rpm for 1 min. The resultant film, RuCl$_3$/FTO, were left under a NIR lamp for 2 hrs. The following conditions for this NIRDD process were used for each experiment unless otherwise stated: The samples were placed underneath a Phillips 175 W NIR lamp, where the bottom of the lamp was positioned 1 cm above the substrate that was set on an aluminum foil surface to help dissipate the heat; the face of the active film was positioned towards the lamp for this process.

**NIRDD**$^T$ °C where T is 100°C, 200°C, 300°C, 400°C and 500 °C. Films of $a$-$\text{RuO}_x$ (NIRDD) on FTO were annealed in a furnace at 100°C, 200°C, 300°C, 400°C and 500°C for 60 min.
**a-RuTiOₓ on FTO (NIRDD).** To a 20-mL beaker containing 0.0784 g of RuCl₃ and 0.105 g Ti(OCH₂CH₂CH₂CH₃)₄ was added 1.578 g MeOH. The solutions were then spin-cast onto FTO at 3000 rpm for 1 min. The resultant film was left under a NIR lamp for 2 hrs.

**a-RuTaOₓ on FTO (NIRDD).** To a 20-mL beaker containing 0.078 g of RuCl₃ and 0.12 g TaCl₅ was added to 1.578 g ethanol. The solutions were then spin-cast onto FTO at 3000 rpm for 1 min. The resultant film was left under a NIR lamp for 2 hrs.

### 5.2.3 Physical Methods

Electrochemical measurements were performed on a C-H Instruments Workstation 660D potentiostat. The Ag/AgCl (sat. KCl) reference electrode (E<sub>ref</sub>) was calibrated regularly against a 1-mM aqueous K₃[Fe(CN)₆] solution. Cyclic voltammograms were acquired at a 10 mV s⁻¹ scan rate unless otherwise indicated. All potentials were corrected for uncompensated resistance (R<sub>u</sub>) and are reported relative to the reversible hydrogen electrode (vs RHE), \( E_{\text{RHE}} = E + E_{\text{ref}} + 0.059(\text{pH}) - iR_u \). Tafel plots were acquired through staircase voltammetry (10-mV steps, 50-s intervals for the final 25 s sampled). Chronopotentiometric experiments were held at 10 mA/cm² for 7200 s. All experiments were carried out using 1 M H₂SO₄ as an electrolyte, unless otherwise noted, in a standard three-compartment electrochemical cell. A Luggin capillary connects the reference and working electrodes while a porous glass frit connects the working electrode to the platinum mesh counter electrode. FTIR spectroscopy was recorded on a Bruker Alpha Spectrometer with a transmission accessory. Powder XRD data was recorded with a Bruker D8 Advance diffractometer using Cu Kα radiation. Data was collected between 2θ angles of 5° and 90° with a step size of 0.04°. The step time was 0.6 s unless otherwise indicated. UV-vis absorption spectroscopy on precursor films and on metal oxide films was performed using a
Perkin Elmer Lambda 35 UV-vis spectrometer with a solid sample holder accessory. Baseline scans were performed with clean FTO. The films examined were prepared from 0.3 M precursor solutions.
References


775.


