The Pennsylvania State University
The Graduate School
Eberly College of Science

INSIGHTS INTO ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL WATER-SPLITTING

A Dissertation in
Chemistry
by
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ABSTRACT

The water-splitting reaction has been known for over a century, yet its efficient execution remains to be one of the “holy grails” for current researchers. Here, molecular water is converted to oxygen and hydrogen gas via multiple proton- and electron-transfer steps. Although the product of interest is high-purity hydrogen gas fuel, the thermodynamic and kinetic requirements of the oxygen evolution reaction (OER) are the main limiting factor. The goal of this dissertation was to develop and understand model electro- and photoelectro-catalytic systems that can address the kinetic limitations of the OER, as well as guidelines for the future development of water-splitting devices. Chapter 1 introduces the kinetic theory of heterogeneous electron-transfer reactions and how it is applied to the understanding of the water-splitting reaction. The chemical properties that make iridium oxide an ideal model electrocatalyst for the OER are discussed, as well as an overview of previous work on this material. Furthermore, the fundamentals of photo-electrochemical water-splitting are presented. Here, sunlight is used as the main driving force for producing oxygen and hydrogen.

It has been previously demonstrated that the synthesis of IrO\textsubscript{x}·nH\textsubscript{2}O colloids by alkaline hydrolysis of Ir(III) or Ir(IV) salts proceeds through iridium hydroxide intermediates. Chapter 2 is a detailed spectro-electrochemical and DFT study of such intermediates and their effect in photoelectrochemical water-splitting cells. Primarily, we have identified the monomeric nature of this hydroxide intermediates as well as their most likely chemical composition and their relative ratio between Ir(III) and Ir(IV). The results from this study address a very important, current dilemma in IrO\textsubscript{x}·nH\textsubscript{2}O–based photoelectrochemical water-splitting cells: how does the chemistry of the catalyst and its interface with the semiconductor influence the photoresponse of the cell? The careful preparation and characterization of both IrO\textsubscript{x}·nH\textsubscript{2}O catalysts and photoanodes provide reasonable explanations to previously observed discrepancies in photoelectrochemical cells that utilize IrO\textsubscript{x}·nH\textsubscript{2}O colloids as co-catalysts on the photoanode electrode.

The recent development of inexpensive electrocatalysts for the OER has suggested that efficient photoelectrochemical cells (PECs) might be constructed from terrestrially abundant materials, such as cobalt, nickel and iron. However, since these catalysts operate in aqueous buffer solutions at neutral to slightly basic pH, it is important to consider whether electrolytic cells can have low series loss under these conditions. Membranes are important components of water-splitting PECs because they prevent crossover of the cathode (e.g. hydrogen gas) products from oxygen produced at the anode. Chapter 3 is a detailed study of the resistive series losses in model electrolytic cells that utilize buffers and commercial monopolar and bipolar ion exchange membranes. Here, we have identified that long-term electrolysis of water (for periods greater than 24 hours) cannot be sustained efficiently in buffered-monopolar membrane systems due to a migration-induced concentration polarization of the electrolytic cells. In the case of buffered–bipolar membrane systems, we have determined that there is a
significant trade off between the resistivity of the membrane and the losses due to concentration gradients. However, under reverse bias conditions and in a pH-polarized electrolyte, bipolar membranes minimize the series losses of the membrane resistivity as well as those due to pH gradients. This configuration is particularly promising because it allows the de-coupling of the optimization of anode and cathode materials for overall water-splitting.

In Chapter 4 we focus again on the IrO$_x$·nH$_2$O electrocatalyst and focus on a fundamental and thorough kinetic characterization of the OER on IrO$_x$·nH$_2$O films. In a solely electrochemical study, we study the effects of temperature, pH and hydrogen/deuterium isotope on the overall OER kinetics. Preliminary results suggest that the rate of the OER in these films does not depend on the proton concentration. Interestingly, however, measurements of the hydrogen/deuterium kinetic isotope effect suggest that the mechanism in the films is rate-dependent, i.e. the kinetically-relevant surface intermediates of the OER change as a function of overpotential on IrO$_x$·nH$_2$O films.

Chapter 5 is a brief compilation of Chapters 1–4 and their implications for future research in water-splitting systems. Finally, Appendix A focuses on introducing the reader to hydrodynamic electrochemical techniques, namely rotating ring-disk electrochemistry (RRDE). Here, the characterization of N(5)-ethylflavinium ion, a fully-organic homogeneous OER catalyst, is presented and the RRDE results confirm its catalytic performance.
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LIST OF SYMBOLS AND ABBREVIATIONS

Listed below are symbols and abbreviations used throughout this dissertation. In most cases, the usage follows the recommendations of the IUPAC Commission of Electrochemistry [Parsons et al., Pure Appl. Chem. 1974, 37, 503]; however there are exceptions.

STANDARD SUBSCRIPTS

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<thead>
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<tr>
<td>a</td>
<td>anodic</td>
</tr>
<tr>
<td>b</td>
<td>backward (reverse) reaction</td>
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<td>c</td>
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GREEK SYMBOLS

<table>
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<tr>
<th>Symbol</th>
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σ conductivity \( \text{S/cm} \)

τ equilibrium time \( \text{s} \)

ϕ potential

\( \omega \) angular frequency, \( 2\pi f/60 \) \( \text{rad/s} \)

\( \omega_{0} \) pre-exponential factor \( k_{B}T/h \) \( \text{s}^{-1} \)

### ROMAN SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<td>( A )</td>
<td>electrode area</td>
<td>( \text{cm}^{2} )</td>
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<tr>
<td>( b )</td>
<td>Tafel slope</td>
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<tr>
<td>( C )</td>
<td>concentration</td>
<td>( \text{mol/L} )</td>
</tr>
<tr>
<td>( C^{*} )</td>
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<td>( \text{mol/L} )</td>
</tr>
<tr>
<td>( D )</td>
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<td>( \text{cm}^{2}/\text{s} )</td>
</tr>
<tr>
<td>( E )</td>
<td>potential</td>
<td>( \text{V} )</td>
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<tr>
<td>( \dot{E} )</td>
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<tr>
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<td>exchange current</td>
<td>( \text{A} )</td>
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<tr>
<td>( J )</td>
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<td>( \text{mol/cm}^{2} \cdot \text{s} )</td>
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<td>( k^{0} )</td>
<td>standard heterogeneous rate constant</td>
<td>( \text{cm/s} )</td>
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<tr>
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<td>Ohm</td>
</tr>
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<td>K</td>
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<tr>
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</tr>
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</tr>
<tr>
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<td>ion charge</td>
<td>none</td>
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**ABBREVIATIONS**

- AEL: anion exchange layer
- Ag/AgCl: silver-silver chloride reference electrode
- BM: bipolar membrane
- CEL: cation exchange layer
- dec: decade
- DSA®: dimensionally stable anode
- HER: hydrogen evolution reaction
- KIE: kinetic isotope effect
- NHE: normal hydrogen electrode
- OER: oxygen evolution reaction
- PEC: photoelectrochemical cell
- PEM: proton exchange membrane
- rds: rate-determining step
- SCE: standard calomel electrode
- TON: turnover number
- UV: ultraviolet
- Vis: visible
- XPS: x-ray photoelectron spectroscopy
ACKNOWLEDGEMENTS

Completing this dissertation has been an incredible journey. It is filled with amazing people that have played a major role in making sure that I complete the work presented in this manuscript.

I would like to start by thanking my advisor and mentor Tom Mallouk for teaching me that the most important question of all is: “What are we going to learn from this?” During my five years here, I have not only honed in on my electrochemistry skills, but have learned to love the process of discovery and to use my creativity to produce good science. Thank you, Tom, for giving me the flexibility to explore new research areas, as well as many places abroad. Your trust, support and guidance were indispensable during this journey.

As with any journey, it does not really always work out as planned: ten days before my dissertation was due I had an emergency appendectomy!! I would like to thank the support and consideration of my committee members Dr. Lasse Jensen, Dr. Benjamin Lear and Dr. Darrell Velegol. Thank you all for understanding and allowing me some extra time to get over the painkiller-induced “loopyness” and finish this dissertation.

One of the most valuable findings during my dissertation work was the priceless and life-long friendship I developed with soon-to-be Dr. Nick McCool and sooner-to-be Dr. Megan Strayer. I consider myself too blessed to have found such amazing people in my life; friends that are always there for me, even when I am not listening. I am sure that our journey together is only starting and there will be many more stories to write together. Dr. Emil Hernández-Pagán also makes the list of great friendships born during this journey. Emil, thank you for taking me under your wing and helping me through the process of adapting not only to grad school life, but also, life away from Home.

No matter what kind of traveling one is doing, there is always need of some currency to be able to complete it. I would like to thank the funding of the National Science Foundation – Graduate Research Fellowship Program throughout my graduate career. Moreover, the Department of Energy – Office of Basic Science provided financial support to execute the research results presented in this dissertation. Furthermore, I acknowledge the generous support of the Alfred P. Sloan Foundation – Minority Ph.D. Program Scholarship in supplementing my professional development activities during my time at Penn State University. I would like to thank the Eberly College of Science and The Graduate School at Penn State University for providing tuition and salary support during my 1st year through the Bunton-Waller Scholarship. Finally, I would like to acknowledge and thank Dr. Ronald Redwing for recruiting me to Penn State as a summer student in 2008. Ron, thank you for believing that I could succeed here at Penn State and for always making sure that I was doing okay. I would not have been here if it was not for you. Thank you.
During this trip, the number of people that have played supporting roles is immense. However, there are several that stand out and I would like to acknowledge them here: (in no particular order) Juan Callejas, Anna Bloom, Lyanne Valdez, Dr. John Swierk, Laura Ramírez, Dana Coval-Dinant, Lourdes Medina, David Sudit, Wilmarie Ríos, Rafael Díaz-Torres, Lymaris Ortiz-Rivera, Liza Díaz-Isaac, Miguel Santiago-Córdoba, Brian Conway, Inanllely Gonzalez, Isamar Ortíz, Roberto Albandoz, Ricardo Pérez, and Milton Flores-Rivera. Your unconditional support for me to follow my dream; the times you listened about the good, the bad and the ugly of my graduate career; you have all been crucial for me to achieve what I have right now. Thank you all, I could not have done it without you.

This journey has been one in which I had to leave a lot behind. It was a very difficult decision to make: pursue my Ph.D. career in Puerto Rico and enjoy yearly beach-access within a 30-mile radius; or accept my offer from Penn State and leave Home and my Family. I admit that it was not an easy decision to make (the beaches are really nice...). But, it was the unquestionable support from my parents, Juan Vargas and Luisa Barbosa, which gave me the momentum to pursue my career. Mom, Dad, thank you for believing in me. Thank you for letting me go, even though I know that this was something very hard for you to do. This dissertation is the product of the 5 years of long-distance support that you have given me, and I would not have been able to do this without you. Thank you for your love, for smiling politely while listening to my work even though you did not really understand. For being proud of me. I love you both more than words can say.

To my younger siblings, Juan Luis, Daniel and Jessica, thank you for always making me laugh. Thank you for the perfectly timed funny jokes or pictures that made my days brighter. Your infectiously happy personalities were always there for me on the crappier days of graduate school. I want you to know that your love and encouragement have fueled my career greatly.

Finally, I would like to thank you, Wolfgang, for being that unexpected travel companion that I acquired on the way. As unlikely as it was for us to find each other, it was definitely meant to be. Thank you for being that person that completely understands me. Thank you for your long-distance love, patience and encouragement. I am excited to start the next part of our life voyage, together, filled with love and science.

I guess, this whole part can be summarized with me acknowledging

“This Lab,  
This School,  
These People”  
–NMVB (2013)
Dedicado a mi familia.
Los amo.
Chapter 1

Water-splitting via Heterogeneous Electro- and Photoelectro-catalysis

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1.1 Introduction

Since the energy crisis in the 1970’s, the search for alternate fuels for the production of electricity has been intensely pursued. Hydrogen gas (H₂) has been proposed as an alternate fuel due to its high energy density and applications in renewable technologies such as fuel cells. Also, hydrogen is widely used in the chemical industry, e.g. ammonia synthesis and carbon monoxide reduction for the production of methanol. Therefore, the production of mass quantities of hydrogen in an economically feasible manner is of great importance. Currently, the most common procedure to generate hydrogen is steam reforming, where fossil fuels are treated with gaseous water through a thermochemical reaction over a nickel-based catalyst. However, the hydrogen produced must be purified and the carbon oxide byproducts from this process are pollutants to the environment.

High purity hydrogen can be produced by means of electrolysis. Here, a current is passed through the electrodes and water is decomposed to both oxygen and hydrogen at the anode and cathode compartments, respectively (Equations 1.1.1–1.1.3, under standard conditions). The overall water-splitting reaction is thermodynamically strenuous and non-spontaneous. Furthermore, the reaction kinetics and overall mechanism involved in the coupled transfer of multiple protons and electrons is complex and poorly understood in heterogeneous systems, especially in regards of the anodic oxygen evolution reaction (OER, Equation 1.1.1).

Anode: \( 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad E^\circ = 1.229 \text{ V vs. NHE} \quad [1.1.1] \)
Cathode: \( 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2 \quad E^\circ = 0.000 \text{ V vs. NHE} \quad [1.1.2] \)
Overall: \( 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2 \quad E^\circ_{\text{rxn}} = -1.229 \text{ V vs. NHE} \quad [1.1.3] \)

Electrolyzers date back to the early 1800’s, when electricity was poorly understood and the field of electrochemistry was in its infancy. Throughout the 19th century, electrolytic cells were mainly developed for independent research that aided the development of Faraday’s laws of electrolysis, the discovery of the alkali metals and the identity and purity of the gases evolved at metal electrodes.¹⁻³

Electrolytic cells have been a cornerstone of the chemical processing industry, mainly in the production of chlorine (Cl₂), caustic soda (NaOH) and aluminum. Also, on a smaller scale they have been developed for electrosynthesis of some inorganic and organic compounds.⁴ During the early 1900’s, the infrastructure for both the chlor-alkali and water electrolysis processes was developed enough that plants in Germany, Great Britain and the United States were fully functional for the electrolysis of brine (Na⁺/K⁺ Cl⁻) and about 400 water electrolyzer units were in operation. The most commonly used materials for electrodes were carbon, lead, iron, silver and platinum, and the water electrolysis systems had working cell voltages greater that 2 V. In parallel to these advances, Butler, Volmer and Tafel were developing the kinetic theory of heterogeneous reactions at electrodes with
academic rigor.\textsuperscript{5,7} Industrial demands for making higher quantities of products with minimum costs propelled the research towards the optimization of the different components in the electrolyzers, with particular focus on the electrode materials.

Early anode materials for industrial electrolyzers were carbon, magnetite (Fe\textsubscript{3}O\textsubscript{4}) and platinum but their manufacture and upkeep costs rendered them unpractical. During the 1890’s, Acheson and Castner developed the inexpensive and reasonably efficient graphitic carbon anodes that dominated the chlor-alkali industry for more than 75 years. However, the minimal oxygen present in the anodic compartment would consume these graphitic anodes. Therefore, industry research moved to the development of better anodes that could provide higher oxidative stability and lower overall cell voltages. Initially, precious metal-plated titanium was studied and developed. Although highly catalytically active, its long-term stability remained a challenge. In the late 1960’s, Beer and De Nora moved their attention to platinum group oxides. Their research brought the development of metal oxide anodes, popularly known as Dimensionally Stable Anodes (DSA®).

The first metal oxide electrodes developed by Beer were prepared by thermal decomposition of precious metal precursors (e.g. Ir, Pt, and Ru) on Ti support.\textsuperscript{8} The initial observation was that these metal oxide anodes had higher catalytic activity and stability, although reasonable explanations for this behavior was deficient due to lack of systematic studies. De Nora tested and compared the performance of graphite and DSA® electrodes in mercury-type electrolytic cells.\textsuperscript{9} The working potential of the cells was 5 and 4 V for the graphite and DSA® electrodes, respectively. However, upon a closer look, 900 mV of that difference is a result of improved mass-transport with reduced distance between the cathode and anode electrodes. Though the catalytic improvement was minimal, it was entirely due to improved anodic activity. A new question was posed to the scientific community: why do these metal oxide materials have better capabilities for oxidizing, both chloride and water, than their purer, metallic counterparts? A new understanding of the correlations of metal oxide electrode structure, morphology and composition to electrooxidation activity was pursued.

The advent of the DSA® coincided with the 1970’s energy crisis, in which the optimization of fuel cell technology (originally discovered by William Grove in 1838)\textsuperscript{10} was revamped. A fuel cell is an electrochemical cell that utilizes chemical fuels to produce electricity. A common type of fuel cell is the proton exchange membrane (PEM) cell. Here, oxygen and hydrogen gas are the fuels for the cathode and anode compartments, respectively, to produce water and electricity in acidic electrolytes. In parallel to this work, Fujishima and Honda successfully demonstrated the photoelectrolysis of water in 1972. In this system, n-type titania served as the photoanode that, at wavelengths below 415 nm, prompted the oxidation of water to oxygen.\textsuperscript{11} From this seminal work, the efficient and cheap conversion of solar energy to chemical energy (e.g. H\textsubscript{2}, CH\textsubscript{4}, CO) has been the goal
of thousands of subsequent reports that utilize photoelectrochemical cells (PEC) for water-splitting.12-23

Fuel cells, electrolyzers and PEC require the transfer of electrons between the electrodes (or photoelectrodes in the case of PEC) and electrolyte in order to generate the desired products. So far, a brief historical perspective of these technologies has been presented. The remainder of this chapter will discuss the fundamentals and kinetic theory of heterogeneous electron transfer reactions within the scope of the water-splitting reaction. Furthermore, iridium oxide will be presented as a model electrocatalyst for the OER and the basic principles of photoelectrochemical water-splitting will be discussed.

1.2 Heterogeneous electron-transfer reactions

In an electrochemical reaction where the electrode is a solid and the electrolyte is in the liquid state, the transfer of electrons occurs precisely at the electrode/electrolyte interface. The current \(i\) measured in an electrochemical experiment is intrinsically correlated to the rate of the reaction \(v_{\text{rxn}}\), Equation 1.1.4

\[
dN/dt = v_{\text{rxn}} \text{ (mol s}^{-1} \text{ cm}^2) = i/nF/A \tag{1.2.1}
\]

where \(dN/dt\) is the number of moles electrolyzed per unit time (mol s\(^{-1}\)), \(n\), \(F\) and \(A\), are the number of electrons transferred in the electrochemical reaction, Faraday’s constant and the area of the electrode (cm\(^2\)), respectively. The magnitude of the current reflects how fast the electrochemical reaction is proceeding, i.e. higher currents, faster rates. Figure 1.1 is a generalized mechanism of all the processes near the electrode that can influence the rate of a generic, reversible heterogeneous electron-transfer reaction \(\text{O} + ne^- \rightleftharpoons \text{R}\).

![Figure 1.1 Chemical processes involved in heterogeneous electron-transfer reactions at the electrode-electrolyte interface (not to scale). The oxidized and reduced species are labeled as O and R, respectively. Adapted from Bard and Faulkner, Chapter 1. See reference 24.](image)
Each of the chemical processes identified in Figure 1.1 have specific rate constants, and the overall reaction rate is limited by the slowest step of all. Furthermore, some of the steps in the overall reaction could be potential-dependent.

When an electrochemical cell reaches equilibrium, there is no net current, and therefore little information can be extracted. The cell potential ($E_{\text{cell}}$), whether it is in equilibrium or not, is related to the standard free energy of the reaction of interest ($\Delta G^\circ_{\text{rxn}}$, Equation 1.2.2), as well as to the concentrations of the redox species involved in the reaction described by the Nernst equation (Equation 1.2.3).

$$E^\circ = -\Delta G^\circ_{\text{rxn}}/nF$$ \hspace{1cm} [1.2.2]

$$E_{\text{cell}} = E^\circ + \frac{2.303RT}{nF} \log Q$$ \hspace{1cm} [1.2.3]

where $E^\circ$ is the reaction’s thermodynamic potential of the reaction, $R$ is the gas constant, $T$ is the temperature, $n$ is the number of electrons transferred in the reaction of interest, $F$ is Faraday’s constant and $Q$ is the ratio of the concentrations of reactants and products. At the equilibrium potential of the cell ($E_{\text{cell}} = E^\circ$) there is no net current, and therefore, little kinetic information can be extracted about the redox reaction of interest. Therefore, it is common to measure $i$ as a function of applied potentials ($E_{\text{appl}}$) away from $E^\circ$. The magnitude of this deviation from $E^\circ$ is called the overpotential ($\eta$, Equations 1.2.4 and 1.2.5).

$$E_{\text{cell}} = \eta (V) = E_{\text{appl}} - E^\circ; \eta > 0 \text{ (anodic)} \text{ and } \eta < 0 \text{ (cathodic)}$$ \hspace{1cm} [1.2.4]

The phenomena that influence the magnitude of the $\eta$ are multiple, sometimes interrelated and hard to deconvolute. However, the $\eta_{\text{total}}$ can be qualitatively expressed as

$$\eta_{\text{total}} = \eta_{\text{ac}} + \eta_{\text{mt}} + \eta_{\text{IR}}$$ \hspace{1cm} [1.2.5]

where $\eta_{\text{ac}}$, $\eta_{\text{mt}}$ and $\eta_{\text{IR}}$ are the activation, mass-transport and solution resistance overpotential, respectively. The $\eta_{\text{ac}}$ is an indicator of the reaction’s kinetics, and intrinsically related to the material used as the electrode. Equation 1.2.3 highlights the crucial role of reagent and product concentrations on the cell potential (depicted in $Q$); and the flux of electroactive species to and from the surface electrode is what determines $\eta_{\text{mt}}$. The final term, $\eta_{\text{IR}}$, is related to the solution resistivity of the electrolyte, and using high supporting electrolyte concentrations can minimize its effects.

Under conditions in which a steady-state current ($i_{\text{ss}}$) is achieved at a specific $\eta$, the magnitude of $i_{\text{ss}}$ will be limited by the rate-determining step (rds) of the overall reaction. Indeed, at steady-state conditions, the rates of all the steps in an electrochemical reaction are equal to the rate constant of the rds. Moreover, the
correlation of overpotentials and steady state currents is part of the basis of the kinetic theory of electrochemical electron-transfer.

1.3 Kinetic theory of electrochemical electron-transfer reactions (4,24,25)

The theory that describes electron-transfer kinetics is based on transition state theory, proposed simultaneously by Eyring, Evans and Polanyi in the early 1930’s,26,27 The application of transition state theory to heterogeneous electron-transfer reactions was developed by Erdey-Grúz and is thoroughly described by Gileadi, Bard and Faulkner.24,25,28

Briefly, in order to proceed between reactants and products, and vice versa, an intermediate activated complex (or transition state, ‡) must be attained. This transition state can only be reached with additional energy beyond that of the standard free energy ($\Delta G^{\circ}\text{rxn}$), namely the activation energy ($E_a$) (Figure 1.2A). In the electrochemical community, $E_a$ and $\Delta G^{\circ}\text{rxn}$ are often described in terms of the $\eta$ and standard redox potential of the reaction ($E^\circ$), respectively (Figure 1.2B).

\[ \text{Figure 1.2 } A \text{ simplified reaction profile for a heterogeneous non-spontaneous oxidation reaction at an electrode. The oxidation reaction } A \rightarrow A^\ast + e^- \text{ proceeds from left to right via a transition state (A‡). (A) In order for the reaction to proceed, the standard reaction energy (}$\Delta G^{\circ}\text{rxn}$\text{) and additional activation energy (}$E_a$\text{) are required. (B) In the electrochemical community, }E_a\text{ and }\Delta G^{\circ}\text{rxn}\text{ are usually presented in terms of the overpotential (}$\eta$\text{) and the standard potential of the reaction (}$E^\circ$\text{), respectively. Figure with the help and courtesy of Nick McCool.} \]

\[ \text{Note that the activation energy symbol } E_a \text{ is usually used to describe the standard enthalpy of activation at constant pressure. Also, the symbol } \Delta H^{\ddagger} \text{ describes the standard enthalpy of activation at constant volume. However, since neither the volume nor the pressure change significantly in a typical electrochemical experiment, both terms are used interchangeably. The term } E_a \text{ will be used throughout the rest of the text to describe the energy required to attain the transition state in an electrochemical reaction.} \]
There are three main assumptions when transition state theory is applied to any chemical reaction:

1. the reaction rate \( v_{\text{rxn}} \) is proportional to the concentration of the activated complex;
2. the activated complex is in quasi-equilibrium with the reactant; and
3. the activated complex behaves classically, i.e. the energy levels of the transition state are so close to each other that it seems like a continuum.

In accordance to Arrhenius’ empirical evidence, that for most solution-phase reactions, the natural log of the rate constant \( k \), namely \( \ln k \), varies linearly with the inverse of temperature; the rate constants in transition state theory are described in an Arrhenius form

\[
k = \kappa \frac{k_B T}{h} \exp \left[ \frac{E_a}{RT} \right]
\]

where \( \kappa \), \( k_B \) and \( h \) are the transmission coefficient, Boltzmann’s and Planck’s constants, respectively. The pre-exponential factor is a consequence of assumption (3), outlined above. Based on the previous definition of \( k \), we can now describe the reaction rate \( v_{\text{rxn}} \) for A \( \Leftrightarrow \) A\(^\dagger\) \( \rightarrow \) A\(^+\) + e\(^-\) at quasi-equilibrium as

\[
v_{\text{rxn}} = k_f C_A = k_b C_A^{\dagger}
\]

where the subscripts ‘f’ and ‘b’ refer to the forward and backward reactions, and \( C_A \) and \( C_A^{\dagger} \) are the concentrations of the reactant (A) and transition state intermediate (A\(^\dagger\)), respectively. We can now describe the constant \( (K^{\dagger}) \) for the A \( \Leftrightarrow \) A\(^\dagger\) equilibrium as

\[
C_{A^{\dagger}}/C_A = K^{\dagger} = \exp[-\Delta G^{\dagger}/RT]
\]

and

\[
\Delta G^{\dagger} = E_a - \beta F \eta
\]

Here, \( \Delta G^{\dagger} \) is the standard free energy to reach the transition state \textit{via} the oxidation, and \( \beta E_a \) is the standard activation energy to reach the transition state for the oxidation (anodic) reaction at the standard thermodynamic redox potential \( (E^\circ) \), \( \eta \) is the overpotential and \( \beta \) is the symmetry factor.

This new parameter \( \beta \) can only range from zero to unity and is related to the shape of the potential energy profiles at the transition state, as well as the position of the transition state along the reaction coordinate. Empirical data suggests that for simple one-electron transfer reactions this value is \( \frac{1}{2} \), and it is common practice in
the electrochemical community to assume this is the case for all electron-transfer reactions. However, it should be noted that this is a valid assumption if and only if the mechanism for the forward and backward reactions is the same, i.e. the transition state and \( rds \) are the same for the anodic and cathodic reaction of the one-electron transfer reaction under study.

The schematic of the reaction profile shown in Figure 1.2 is a simplification of the potential energy profiles of the reactants and products. Indeed, two parabolas that intersect at some point in the reaction coordinate better describe the potential energy of reactants and products in a reaction (Figure 1.3). Furthermore, Figure 1.3 depicts schematically the qualitative effect of \( \beta \) on the potential energy profiles for this reaction.

\[
\beta = \frac{1}{2} \\
\beta < \frac{1}{2} \\
\beta > \frac{1}{2}
\]

Figure 1.3 Potential energy diagram for a one-electron oxidation reaction via a high-energy transition state (\( A^\dagger \)). The middle and right-hand schemes show the effect of \( \beta \) on the potential energy profiles.

The overpotential variable (\( \eta \)) and its relevance to the transition state were introduced in Equation 1.3.4. Figure 1.4 depicts the effect of an anodic overpotential on the potential energy diagram for a simple, one-electron oxidation. The overpotential induces changes on the relative energy levels of the reagents and products, and therefore, affects the energetics of the transition state. Since the overpotential is an anodic one, it lowers the potential barrier to reach the products (the oxidized species) by a factor of \( \beta F \eta \). Note that because the potential energy requirements of the transition state are affected, the activation energy is also changed; in this particular example, it has been lowered (\( E'_a < E_a \) in Figure 1.4). Since the measured current of an electrochemical reaction can be related to its rate, it is possible to determine the activation energy of an electrochemical reaction by measuring the current at different temperatures and preparing an Arrhenius plot. Figure 1.5 shows overpotential-dependent Arrhenius plots that clearly demonstrate the effect of the overpotential on the activation energy, namely its decrease (smaller slopes) with increasing, favorable overpotential.\(^{25}\)
Figure 1.4 Schematic of the effect of an anodic overpotential on the potential energy diagram for a one-electron oxidation reaction ($\beta = 0.5$). The applied anodic overpotential induces a shift in the relative energies of the potential energy parabola such that the activation energy for the oxidation is less than under standard conditions. Adapted from reference 24.

Figure 1.5 Arrhenius plots showing the variation of the activation energy (calculated from the slope of the straight lines) as a function of overpotential. All lines extrapolate to the same value at infinite temperature, showing that the entropy of activation is independent of potential. Adapted from reference 25.
Now, we can establish relationships between the current and overpotential of the oxidation of reagent A with its kinetics. From Equations 1.2.1, 1.3.1–1.3.3 follows

\[ i = nFv_{rea} = nFC_A \omega \exp \left( \frac{-\alpha E_{a,a}}{RT} \right) \exp \left( \frac{\beta F\eta}{RT} \right) \]  \[ \text{[1.3.5]} \]

where \( \omega \) is the constant, pre-exponential factor \( \kappa k_B T/h \) and Equation 1.3.5 can now be reduced to

\[ i = nFC_A k^o \exp \left( \frac{\beta F\eta}{RT} \right); k^o = \omega \exp \left( \frac{-\alpha E_{a,a}}{RT} \right) \]  \[ \text{[1.3.6]} \]

This is now an explicit correlation between the current and overpotential of the reaction, with a new rate constant, namely the standard heterogeneous rate constant \( k^o \) in units of cm/s. \( k^o \) is a measure of how reversible an electrochemical reaction is, i.e. large values of \( k^o \) (> 0.02 cm/s) are typical of highly reversible couples. For example, \( k^o \) for \([\text{Ru(NH}_3\text{)}_6]^{2+}\) equals 9 cm/s, whereas for irreversible reactions \( k^o \) is below \( 10^{-5} \) cm/s.

Equation 1.3.6 is only applicable in situations where mass-transport is not limiting the current, i.e. that the currents measured are only due to the intrinsic kinetic limitations of the reaction. Or, in other words, \( \eta = \eta_{ac} \). Furthermore, Equation 1.3.6 only describes the oxidation reaction \( A \rightarrow A^+ + e^- \). An equation of the same form is obtained when the reverse reaction is studied, in which the negative sign in the exponent results from Equation 1.2.2

\[ i_c = nFC_A k^o \exp \left( -\frac{\beta F\eta}{RT} \right) \]  \[ \text{[1.3.7]} \]

Now, the net current measured during an electrochemical reaction will be the difference of the anodic and cathodic currents measured simultaneously, and since \( \beta \) can only range from zero to unity, for the cathodic reaction we can express this parameter as \( 1 - \beta \)

\[ i = nFC_A k^o \exp \left( \frac{\beta F\eta}{RT} \right) - nFC_A k^o \exp \left( -\frac{(1 - \beta)F\eta}{RT} \right) \]  \[ \text{[1.3.8]} \]

If we consider the system to be in equilibrium \( (\eta = 0; \ k^o_a = k^o_c) \) then

\[ i_o = nFC_A k^o_a = nFC_A k^o_c \]  \[ \text{[1.3.9]} \]
where \( i_o \) is the exchange current, it is proportional to \( k^o \) and it reflects the intrinsic rates of electron transfer between the analyte and an electrode at zero overpotential. The exchange current is usually reported normalized to the area of the electrode \( (j_o, \text{A/cm}^2) \) and is often used to compare the catalytic activity of electrode materials. Substitution of 1.3.9 in 1.3.8 we obtain

\[
i = i_o \left( \exp \left( \frac{\beta F \eta}{RT} \right) - \exp \left( \frac{-(1 - \beta) F \eta}{RT} \right) \right)
\]  

[1.3.10]

Note that the measured current \( (i) \) will depend on \( \eta \) as well as \( C_A \) and \( C_A^+ \) (both of these are embedded in \( i_o \)). Furthermore, since for this example \( n = 1 \), it has been omitted from the exponential term. Equation 1.3.10 is a form of the Butler-Volmer equation and it is always applied when understanding of electrode kinetics is required.

### 1.3.1 Tafel equation and Tafel plots

Named after Julius Tafel due to his early studies on interfacial dynamics, Tafel plots establish an exponential relationship between the current and the applied overpotential (Equation 1.3.11).

\[
\eta = a - b \log i
\]  

[1.3.11]

The Tafel equation is a special case of Equation 1.3.10, that of high \( \eta \), in which only one of the redox reactions is driven at a measurable rate. Because of this reason, Tafel plots are particularly useful for studying the kinetics of irreversible systems. Tafel established this equation empirically in 1905 from his studies of hydrogen evolution on mercury electrodes.\(^6\) The intercept \( a \) from the Tafel equation gives \( i_o \) (as we show below) and the Tafel slope \( b \) can provide information about the mechanism (see section 1.3.2) If we consider an anodic reaction, e.g. \( \eta \) is greater than 200 mV, Equation 1.3.11 is reduced to only to the anodic term

\[
i = i_o \exp \left( \frac{\beta F \eta}{RT} \right)
\]  

[1.3.12]

and applying the logarithmic function we obtain

\[
\log i = \log i_o + \left( \frac{\beta F}{2.303RT} \right) \eta
\]  

[1.3.13]

and rearranging to fit Tafel’s empirical equation
\[ \eta = \left( \frac{2.303RT}{\beta F} \right) \log i - \left( \frac{2.303RT}{\beta F} \right) \log i_0 \]  \hfill [1.3.14]

where \( \beta \) is \( (2.303RT/\beta F) \), the “Tafel slope”) and the intercept \( a \) provides us the exchange current density of the reaction. A Tafel plot is traditionally presented with \( \log i \) and \( \eta \) in the \( x \)- and \( y \)-axis, respectively (Figure 1.6).

**Figure 1.6** Modeled Tafel plot for various symmetry factor (\( \beta \)) values and no mass-transport effects. \( i_0 = 1 \) \( \mu \)A/cm\(^2\), \( T = 298 \) K. Note that all plots converge to the same \( i_0 \) because \( \beta \) does not influence the rate of the reaction, only its mechanism. Adapted from reference 24.

### 1.3.2 Multielectron mechanisms and Tafel slopes as mechanistic criteria

Tafel slopes are the electrochemist’s main tool for identifying the mechanism and \( rds \) of an electron transfer reaction. However, Tafel slopes can only be applied as mechanistic criteria when a thorough mechanism has been proposed for the reaction under scrutiny, as we demonstrate below. Let us consider the arbitrary redox reaction

\[ A + ne^- \Leftrightarrow Z \]  \hfill [1.3.15]

and write all the proposed chemical transformations and electron-transfer steps following the approach developed by Parsons,\(^{30} \) where we consider the forward and backwards part of the \( rds \) independently. This approach makes the \( rds \) appear irreversible in both directions.
\[ A + e^- \rightleftharpoons B \quad \text{(pre-step 1, electron-transfer step)} \]  
\[ B \rightleftharpoons C \quad \text{(pre-step 2, chemical step)} \]  
\[ \vdots \]  
\[ \vdots \]  
\[ Q + e^- \rightleftharpoons R \quad \text{(pre-step } n_p\text{, electron-transfer step)} \]  
\[ R + n_q e^- \rightleftharpoons S \quad \text{(rds)} \]  
\[ S \rightleftharpoons T \quad \text{(post-step 1, chemical step)} \]  
\[ T + e^- \rightleftharpoons U \quad \text{(post-step 2, electron-transfer step)} \]  
\[ \vdots \]  
\[ \vdots \]  
\[ Y + e^- \rightleftharpoons Z \quad \text{(post-step } n_r\text{, electron-transfer step)} \]  

where \( n_p \) is the number of electrons transferred prior to the rds, \( n_r \) is the number of electrons transferred after the rds, and \( n_q \) is the number of electrons transferred during the rds. Since we are restricting the mechanism to uni-molecular steps, the total number of electrons transferred is

\[ n = n_p + n_r + n_q \]  

and \( n_q \) (the number of electrons transferred in the rds) can only be zero or unity.

Looking back to the previously derived current-overpotential relationship (Equation 1.3.10), it must be modified to accommodate multiple electron-transfer steps (since \( \beta \) is only valid for a one-electron reaction).

\[ i = i_o \left( \exp \left( \frac{\alpha_f F \eta}{RT} \right) - \exp \left( \frac{\alpha_b F \eta}{RT} \right) \right) \]  

where \( \alpha \) is the unitless transfer coefficient and is defined as \( \alpha_f \) and \( \alpha_b \) for the forward and backward reaction, respectively and

\[ \alpha_f = n_p + n_q \beta \]  

\[ \alpha_b = n_r + n_q (1 - \beta) \]
Although related, $\beta$ and transfer coefficients are very different parameters. The symmetry factor describes the rate-determining step on a single electron-transfer reaction. On the other hand, the transfer coefficients describe the overall kinetics of a multi-step, many-electron reaction. Furthermore, it should be underscored that the $\beta$ ranges from zero to unity, whereas the sum of the transfer coefficients is

$$\alpha_f + \alpha_t = n$$  \[1.3.27\]

and not necessarily equal to unity. In addition to this, in systems where the rds of the forward and backward reaction are not the same the sum of $\alpha_f + \alpha_t$ have no particular diagnostic value. Conventionally, $\alpha_f$ and $\alpha_t$ correspond to the anodic and cathodic reactions, respectively, such that the current–overpotential equation is now

$$i = i_o \left( \exp \left( \frac{\alpha_f F \eta}{RT} \right) - \exp \left( \frac{\alpha_t F \eta}{RT} \right) \right)$$  \[1.3.28\]

Sometimes, the sum of transfer coefficients can be estimated by

$$\alpha_a + \alpha_c = n/\nu$$  \[1.3.29\]

where $\nu$ is the stoichiometric number. The stoichiometric number indicates how many times the rds needs to occur in order to complete the overall reaction once. The value of $\alpha$ can be determined experimentally using a Tafel plot. Based on the transformations to accommodate a more complex electrochemical reaction, the Tafel slope $b$ for the forward (anodic) reaction, for example, is now defined as

$$b = 2.303RT/\alpha_a F$$  \[1.3.30\]

and makes extraction of $\alpha$ for a particular reaction, in this case the forward reaction, straightforward. Because we have a good grasp of the parameters that affect the current-overpotential equation, we can now consider a multi-step, multi-electron reaction and predict its Tafel slope. Let us consider a simple proposed mechanism for the hydrogen evolution reaction (HER, Equation 1.1.2)

$$\text{H}_3\text{O}^+ + \text{M} (e^-) \rightarrow \text{M} - \text{H}_{\text{ads}} + \text{H}_2 \quad \text{[step 1, proton discharge]}$$  \[1.3.31\]

$$\text{M} - \text{H}_{\text{ads}} + \text{M} - \text{H}_{\text{ads}} \rightarrow 2\text{M} + \text{H}_2 \quad \text{[step 2, hydrogen gas discharge]}$$  \[1.3.32\]

Since the HER is a reduction reaction, we consider only the cathodic branch of the current–overpotential equation. If we consider step 1 to be the rds,

$$i = -i_o \exp \left[ -\frac{\alpha_f F \eta}{RT} \right]$$  \[1.3.33\]
Rearranging
\[ \eta = \left( \frac{2.303RT}{\alpha_c F} \right) \log i - \left( \frac{2.303RT}{\alpha_c F} \right) \log i_o \] \[\text{[1.3.34]}\]

and taking the derivative, i.e. extracting the slope
\[ b_{\text{step 1}} = \frac{\partial \eta}{\partial \log i} = \frac{2.303RT}{\alpha_c F} \] \[\text{[1.3.35]}\]

where the 2.303 factor arises from switching from natural log to a base-10 logarithmic function. If we assume that \( \alpha_c = 0.5 \), then the predicted Tafel slope for step 1 is 120 mV/decade. The physical interpretation of this slope is that if the overpotential is increased cathodically by 120 mV, the measured current will increase ten-fold. If under experimental conditions where the HER is monitored a Tafel slope of 120 mV/dec is measured, step 1 is confirmed as the \( \text{rds} \).

Similarly, we can consider step 2 to be the \( \text{rds} \) and predict its Tafel slope. Here, the surface coverage (\( \theta \)) of adsorbed hydrogen (H\(_{\text{ads}}\)) will be the rate-limiting factor, such that
\[ v_{\text{step 2}} = k_{\text{step 2}} \theta_{\text{H}_{\text{ads}}}^2 \] \[\text{[1.3.36]}\]

However, since this a slow step, excess H\(_{\text{ads}}\) accumulates at the surface of the electrode, and consequently can get re-oxidized to establish equilibrium with step 1
\[ \text{H}_3\text{O}^+ + \text{M}(\varepsilon^-) \rightleftharpoons \text{M–H}_{\text{ads}} + \text{H}_2\text{O} \quad \text{(step 1 at equilibrium)} \] \[\text{[1.3.37]}\]

Applying the Nernst equation for the equilibrium on Equation 1.3.37,
\[ E_{\text{cell}} = E_{\text{o}}^o + \frac{RT}{F} \ln \left[ \frac{C_{\text{H},\theta^o}}{\theta_{\text{H}_{\text{ads}}}} \right] \] \[\text{[1.3.38]}\]

where the concentration of adsorbed protons on the metal surface, namely [M–H\(_{\text{ads}}\)], is presented as the coverage (\( \theta_{\text{H}_{\text{ads}}} \)), which is the ratio of sites occupied by the total sites available. Solving for \( \theta_{\text{H}_{\text{ads}}} \) we obtain:
\[ \theta_{\text{H}_{\text{ads}}} = C_{\text{H},\theta^o} \exp \left[ -\left( \frac{E_{\text{cell}} - E_{\text{o}}^o}{RT} \right) \right] \] \[\text{[1.3.39]}\]
Under highly acidic conditions, *i.e.* pH < 1, it is okay to assume that the proton concentration does not change significantly. Since \( C_{H^+}, F, R, T \) are constants, and the \( \eta \) is negative for a cathodic reaction we obtain

\[
\theta_{H_{ads}} = K_{H_{ads}} \exp \left( \frac{F \eta}{RT} \right) \tag{1.3.40}
\]

Substituting into the rate equation for step 2

\[
v_{\text{step } 2} = k_{\text{step } 2} \left( K_{H_{ads}} \exp \left( \frac{F \eta}{RT} \right) \right) \tag{1.3.41}
\]

and since two electrons are exchanged in the process, the current produced will be given by Equation 1.2.1 (assuming a 1 cm\(^2\) electrode area)

\[
i = 2Fv_{\text{step } 2} \tag{1.3.42}
\]

\[
i = 2Fk' \exp \left( \frac{2F\eta}{RT} \right) ; k' = k_{\text{step } 2} K_{H_{ads}}^2 \tag{1.3.43}
\]

solving for the overpotential and taking its derivative with respect to log \( i \) we obtain the Tafel slope

\[
b_{\text{step } 2} = -\frac{2.303RT}{2F} = 30 \text{ mV/dec (under standard conditions)} \tag{1.3.44}
\]

These predicted Tafel slope values could now be used to compare experimental Tafel plots and assess the effect of substrate on the kinetics and mechanism of the HER. Figure 1.7 presents digitized Tafel plots for various metals tested for the HER in acid.
At a glance, it is clear that the substrate has a significant effect on the kinetics of the reaction as evidenced by the different Tafel slopes and the varying magnitudes of current density they range. Pt, with a Tafel slope of 30 mV/dec, is the material for which minimal increases in overpotential result in 10-fold current increases. This makes Pt the benchmark in all HER electrocatalysis, however from an application and device development perspective this is not viable due to the high costs of pure Pt and fast poisoning of the catalyst under reaction conditions.

The Tafel slope of Pt suggests that the recombination of two hydrogen atoms (Equation 1.3.31) is the \( rds \) in Pt wire electrodes. However, detailed work by Ross and coworkers demonstrate that the exposed crystallographic axis of Pt surfaces influences the \( rds \).\(^{38}\) In particular, for the Pt(110) the recombination of two \( M-H_{ads} \) is rate-limiting (\( b = 2.303RT/2F \approx 30 \) mV/dec), whereas on Pt(100) electrochemical discharge of \( H_2 \) is the \( rds \) with a Tafel slope of \( 2(2.303RT/F) \), \( ca. \) 120 mV/dec:

\[
M-H_{ads} + H_3O^+ + e^- \rightarrow M + H_2 + H_2O \tag{1.3.45}
\]

For energy application purposes, the HER reaction is of great relevance, since \( H_2 \) can be used as a high energy density fuel. Many researchers have focused on the design, optimization and characterization of HER electrocatalysts that incorporate...
Earth-abundant elements, offer high stability and perform as close as possible to the Pt benchmark. However, the HER is only a half-reaction of the overall water-splitting reaction. Indeed, commercial electrolyzers are limited, for the most part, by the sluggish oxygen evolution reaction (OER). In order to design and develop novel materials for more efficient OER catalysts, a better general understanding on the kinetics and mechanism of the OER is needed.

1.4 Kinetics and mechanism of the oxygen evolution reaction (OER)

In the particular case of the OER, Bockris proposed, predicted and compiled the Tafel slopes of several mechanisms that could describe this reaction. Most of the mechanistic research of the OER that followed the 1950’s is based on and extends from the systems presented on Table 1.1. As a first impression, we can see that as the number of transferred electrons in an electrochemical reaction increases, the number of possible mechanisms and rds increases dramatically. Note that Table 1.1 presents a small survey of proposed mechanisms for the OER. Indeed, there are many other possible mechanisms that can describe the OER.

In Table 1.1 we can also identify some of the problems in utilizing Tafel slopes as mechanistic criteria. Firstly, there are multiple mechanisms that share the same predicted slope! Moreover, there are instances in which the Tafel slope for a particular step is coverage-dependent (e.g. Kobbussen’s path). This change in Tafel slope implies that at some point during the electrochemical experiment, namely at some specific overpotential range, the Tafel slope will shift its value. Therefore, the unambiguous determination of reaction pathways for complex multi-electron reactions using electrochemical techniques, by themselves, is difficult.

A common, alternate approach to determine the mechanism and kinetically relevant intermediates in the OER has been to study homogeneous catalysts that incorporate the catalytic metals of heterogeneous materials. In the particular case of Ru-based homogeneous catalysts significant work has been done by Meyer, Thummel, Llobet, and Sun. Crabtree and coworkers have focused their efforts in understanding the Mn,Ca-based oxygen evolving complex in photosystem II and Ir-based homogeneous catalysts. The drawback to these studies is that the correlation of their results to heterogeneous systems is not straightforward.
Table 1.1 Proposed mechanisms, rds and predicted Tafel slopes for the oxygen evolution reaction

<table>
<thead>
<tr>
<th>Rate-determining step (rds)</th>
<th>ν</th>
<th>Tafel slope, $\partial \eta / \partial \ln i$ (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 $\neq$ 0</td>
<td>0 $\neq$ 1</td>
</tr>
<tr>
<td><strong>1. Bockris’ oxide path</strong>&lt;sup&gt;46,47&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a. OH$^-$ + M $\rightarrow$ M-OH + e$^-$</td>
<td>4</td>
<td>2RT/F</td>
</tr>
<tr>
<td>1b. 2M-OH $\rightarrow$ M-O + M + H$_2$O</td>
<td>2</td>
<td>RT/2F</td>
</tr>
<tr>
<td>1c. 2M-O $\rightarrow$ 2M + O$_2$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td><strong>2. Bockris’ electrochemical oxide path</strong>&lt;sup&gt;46,47&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a. OH$^-$ + M $\rightarrow$ M-OH + e$^-$</td>
<td>2</td>
<td>2RT/F</td>
</tr>
<tr>
<td>2b. M-OH + OH$^-$ $\rightarrow$ M-O + H$_2$O + e$^-$</td>
<td>2</td>
<td>2RT/3F</td>
</tr>
<tr>
<td>2c. 2M-O $\rightarrow$ 2M + O$_2$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td><strong>3. Hydrogen peroxide path</strong>&lt;sup&gt;45&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a. OH$^-$ + M $\rightarrow$ M-OH + e$^-$</td>
<td>4</td>
<td>2RT/F</td>
</tr>
<tr>
<td>3b. 2M-OH $\rightarrow$ M-(H$_2$O)$_2$ + M</td>
<td>1</td>
<td>RT/2F</td>
</tr>
<tr>
<td>3c. M-OH + M(H$_2$O)$_2$ $\rightarrow$ M-OOH + H$_2$O</td>
<td>1</td>
<td>RT/3F</td>
</tr>
<tr>
<td>3d. 2M-OOH + M-OH $\rightarrow$ 2M + H$_2$O + O$_2$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td><strong>4. Electrochemical metal peroxide path</strong>&lt;sup&gt;45&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a. OH$^-$ + M $\rightarrow$ M-OH + e$^-$</td>
<td>2</td>
<td>2RT/F</td>
</tr>
<tr>
<td>4b. 2M-OH $\rightarrow$ H$_2$O + M-O</td>
<td>1</td>
<td>RT/2F</td>
</tr>
<tr>
<td>4c. M-O + M-OH $\rightarrow$ M-OOH</td>
<td>2</td>
<td>2RT/5F</td>
</tr>
<tr>
<td>4d. 2M-OOH $\rightarrow$ H$_2$O + M-O + M + O$_2$</td>
<td>1</td>
<td>RT/6F</td>
</tr>
<tr>
<td><strong>5. Metal Peroxide path</strong>&lt;sup&gt;35&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a. OH$^-$ + M $\rightarrow$ M-OH + e$^-$</td>
<td>4</td>
<td>2RT/F</td>
</tr>
<tr>
<td>5b. 2M-OH $\rightarrow$ H$_2$O + M-O</td>
<td>1</td>
<td>RT/2F</td>
</tr>
<tr>
<td>5c. M-O + M-OH $\rightarrow$ M-OOH</td>
<td>1</td>
<td>RT/3F</td>
</tr>
<tr>
<td>5d. M-OOH + M-OH $\rightarrow$ H$_2$O + O$_2$ + 2M</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td><strong>6. Krasil'shchikov's path</strong>&lt;sup&gt;69&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6a. M + OH$^-$ $\rightarrow$ M-OH + e$^-$</td>
<td>2</td>
<td>2RT/F</td>
</tr>
<tr>
<td>6b. M-OH + OH$^-$ $\rightarrow$ M-O + H$_2$O</td>
<td>2</td>
<td>RT/3F</td>
</tr>
<tr>
<td>6c. M-O $\rightarrow$ M-O + e$^-$</td>
<td>2</td>
<td>2RT/3F</td>
</tr>
<tr>
<td>6d. 2M-O $\rightarrow$ 2M + O$_2$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td><strong>7. O’Grady’s path</strong>&lt;sup&gt;70&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7a. M$^+$ + OH$^-$ $\rightarrow$ M$^+$OH + e$^-$</td>
<td>2</td>
<td>2RT/F</td>
</tr>
<tr>
<td>7b. M$^+$OH $\rightarrow$ M$^{+1}$OH + e$^-$</td>
<td>2</td>
<td>2RT/3F</td>
</tr>
<tr>
<td>7c. 2M$^{+1}$OH + 2OH$^-$ $\rightarrow$ 2M$^+$ + H$_2$O + O$_2$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td><strong>8. Kobussen's Path</strong>&lt;sup&gt;71,72&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8a. M + OH$^-$ $\rightarrow$ M-OH + e$^-$</td>
<td>1</td>
<td>2RT/F</td>
</tr>
<tr>
<td>8b. M-OH + OH$^-$ $\rightarrow$ M-O + H$_2$O + e$^-$</td>
<td>1</td>
<td>2RT/3F</td>
</tr>
<tr>
<td>8c. M-O + OH$^-$ $\rightarrow$ M-OOH</td>
<td>1</td>
<td>RT/2F</td>
</tr>
<tr>
<td>8d. M-OOH$^-$ + OH$^-$ $\rightarrow$ M-OO$^-$ + H$_2$O + e$^-$</td>
<td>1</td>
<td>2RT/5F</td>
</tr>
<tr>
<td>8e. M-OO$^-$ $\rightarrow$ O$_2$ + e$^-$</td>
<td>1</td>
<td>2RT/7F</td>
</tr>
</tbody>
</table>

Notes: All mechanisms are proposed under alkaline conditions. θ refers to that of the adsorbed species at each step, and follow Langmuirian behavior. All Tafel slopes assume a value of $a_0 = \frac{1}{2}$. 


Recently, Lyons and coworkers have focused on studying and describing the mechanism of heterogeneous OER on metal oxides by predicting Tafel slopes for possible surface intermediates that resemble those determined on recent work in homogeneous OER catalysts. Here, the surface-active metal site $M$ is envisioned as an octahedrally coordinated moiety ($\text{surf}_\text{aq}$ group) that incorporates some heterogeneous and homogeneous character (Figure 1.8). These anionic surface groups can be in equilibrium with the electrolyte and allows the model to include changes in the surface chemistry of the catalyst as a function of pH. This opposes the previous ambiguous picture of a single site $M$ with unknown chemical properties that make it active (see all proposed mechanisms in Table 1.1, except O'Grady’s).

![Figure 1.8 Schematic representation of surface active site in heterogeneous metal oxide catalysts, where $M$ represents the metal and the $z$ superscript is its oxidation state. Adapted from reference 75.](image)

Another approach to understanding the kinetics and mechanism of the OER in heterogeneous catalysts is to utilize in-situ and ex-situ characterization techniques. Recent developments in spectroscopic techniques have allowed researchers to identify kinetically-relevant intermediates and propose catalytic cycles for the OER. For example, Nocera and coworkers have elucidated the OER mechanism in cobalt-phosphate ($\text{Co-P}_i$) thin films by combining electron paramagnetic resonance (EPR), in-situ electrochemical–synchrotron x-ray absorption (XAS), and nuclear magnetic resonance (NMR) spectroscopies to identify the underlying cubane structure of the amorphous Co-P$_i$ films, and correlate it to its activity for the OER. These spectroscopic results in combination with rigorous electrochemical characterization and H/D isotopic experiments suggest that a proton-coupled electron-transfer equilibrium precedes the rate-limiting molecular oxygen bond formation. Frei and coworkers have focused on understanding the mechanism of visible-light photochemically driven OER on iridium oxide colloids utilizing in-situ infrared spectroscopy. Results from $^{18}$O-labeled water and hydrogen/deuterium-labeled hydrated iridium oxide colloids demonstrate the formation of a stable, kinetically relevant surface iridium intermediate $\text{Ir}^{3+}–\text{OOH}$. Finally, theoretical methods have proven very useful in guiding experimental researchers to focus on specific
chemical properties in materials that could render them good OER electrocatalysts. In this regard, the work of Norskov and coworkers has been particularly innovative. 18,85-88

Chapter 4 builds from this previous literature and presents a detailed electrochemical study of the effects of temperature, pH and hydrogen/deuterium isotope effects in a specific OER electrocatalyst. Tafel slopes and the temperature-dependence of isotope effects are used as diagnostic criteria to attempt to understand the mechanism of the OER in colloidal iridium oxide films.

1.5 Iridium oxide as a model electrocatalyst for the OER

Among the many electrocatalysts available for OER, iridium oxide is particularly interesting because it outperforms every other metal oxide in stability and activity at a wide range of pH values. Historically, researchers have found useful assessing the activity of materials in volcano plots, where an empirical property related to the activity of a material is correlated to an intrinsic property of that material. Figure 1.9 shows one of such plots in which the overpotential for the OER (empirical property) is correlated to the enthalpy of formation of a higher oxide from a lower one (intrinsic property) on various metal oxide materials. 89

![Figure 1.9 Volcano plot for the electrocatalytic activity for OER, shown by the overpotential, as a function of the enthalpy of the transition from a lower to a higher oxidation state. The open and filled markers indicate the overpotential in alkaline and acidic media, respectively. Note that RuO\(_2\) and IrO\(_2\) fall near the peak of the volcano plot, indicating intermediate binding of oxide intermediates that result in low overpotentials for the OER. Digitized data from reference 89.](image)

Here, it is shown qualitatively that the overpotential for OER changes with the energy required for a material to form a higher oxidation state from a lower one.
Materials with low $\Delta H^\circ$ are oxidized with difficulty and are not very active because intermediates absorb to weakly, e.g. PbO$_2$. On the other hand, metal oxides that are easily oxidized (high $\Delta H^\circ$) are also not very active because the intermediates bind too strongly (e.g. Fe$_3$O$_4$). IrO$_2$ and RuO$_2$ fall in an intermediate range for $\Delta H^\circ$ and show the lowest overpotentials for OER. This is an indication that highly active catalysts for OER stabilize higher oxidation state intermediates that allow the formation of oxygen without entirely blocking the surface and hindering the reaction.

Recent work by McCrory et al. have focused on establishing a standard protocol for assessing the viability, stability and activity of electrodeposited heterogeneous catalysts for both OER and HER. In their work, iridium oxide is by far the only material that meets their stability criteria in acidic media (maintains an overpotential below 0.36 V at a constant current density of 10 mA/cm$^2$ for up to 2 hours). Under long-term alkaline conditions, IrO$_2$ corrodes and its stability is a big issue. However, when IrO$_2$ is used for laboratory-scale testing and short electrolysis time (less than 1 h), the degradation of the electrode is negligible and fundamental understanding of the OER electrocatalysis can be attained.

### 1.5.1 Iridium oxide

Elemental iridium has an electronic structure of [Xe] 4$f^{14}$ 5$d^7$ 6$s^2$ and can form stable compounds that range from $-\text{III}$ to $+\text{VI}$ oxidation states. As a metal, iridium has a face-centered cubic structure, however IrO$_2$, its most stable and well-characterized oxide, crystalizes in the rutile structure. IrO$_2$ is part of the transition metal oxide group that has near metallic conductivities with reported electrical resistivities between 50 – 60 $\mu\Omega\cdot\text{cm}$ at 300 K. The metallic behavior can be explained by the metal–metal $d$–$d$ orbital overlap because of the close proximity in edge sharing octahedral environment, leading to a broad $5d$ band and delocalization of the occupying $d$–electrons. This high electronic conductivity is one of the main reasons for its extensive use as an electrocatalyst for various reactions, microelectrodes in electrophysiology and microelectronic devices and pH sensors.

The theoretical, thermodynamic-electrochemical and pH-dependent stability of iridium oxide is depicted as a Pourbaix diagram in Figure 1.10. A Pourbaix diagram is a phase diagram that presents the possible thermodynamically stable species of a solvent–metal system at specific pH and potential conditions. The reactions considered to generate Figure 1.10 are

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E = 0.000 - 0.0591\text{pH} \quad (1) \quad [1.5.1]$$

$$\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad E = 1.229 - 0.0591\text{pH} \quad (2) \quad [1.5.2]$$
\[
\text{Ir}^0 + 2\text{H}_2\text{O} \rightarrow \text{IrO}_2 + 4\text{H}^+ + 4e^- \quad E = 0.926 - 0.0591\text{pH} \quad (3) \quad [1.5.3]
\]

\[
\text{IrO}_2 + 2\text{H}_2\text{O} \rightarrow \text{IrO}_4^{2-} + 4\text{H}^+ + 2e^- \quad E = 2.057 - 0.1128\text{pH} \quad (4) \quad [1.5.4]
\]

**Figure 1.10** Pourbaix diagram for the iridium–water system at 25°C. Adapted from reference 102.

In Figure 1.10, the region between equilibrium lines 1 and 2 shows the potential-pH range in which liquid water is thermodynamically stable. Within this water-stable region, equilibrium line 3 is present, which indicates the wide thermodynamic stability of iridium oxide in water. This wide pH-potential stability is a very fortuitous property for an OER catalyst. During the process of converting water to oxygen, four protons are released in close proximity to the surface of the electrode and locally reduce the pH. The accumulation of high concentrations of protons (either because of poor mass-transport away from the electrode or high kinetics) can induce pH gradients large enough to start dissolving the electrocatalysts. This pH-dependent stability is particularly problematic for 1st row transition metal-based OER catalysts. This issue can be partially mitigated by using buffering electrolytes. However, the implementation of high concentration buffer electrolytes produces system-level losses in model water-splitting electrolytic cells.\textsuperscript{103} This is discussed in more depth in Chapter 3.

Finally, equilibrium line 4 in Figure 1.10 shows the equilibrium for corrosion of IrO\textsubscript{2}. The corrosion of iridium oxide to iridates under alkaline conditions has been studied,\textsuperscript{104,105} and could limit its implementation in long-term alkaline commercial devices.
1.5.2 Synthesis of iridium oxide

There is a plethora of synthetic approaches to produce IrO$_2$ in a variety of shapes and structured on different length scales. Iridium metal decomposes to rutile IrO$_2$ under an O$_2$ stream at temperatures greater than 1100 °C. Single crystals of IrO$_2$ can be grown in a similar manner with a vapor-transport, temperature-gradient approach. The protocols for the preparation of IrO$_2$ thin films is varied and includes sputtering, pulsed-laser, chemical vapor, spray pyrolysis, sol-gel, and electrochemical deposition methods.

The preparation of iridium oxide nanoparticles is based on a century old protocol of alkaline hydrolysis of hexachloroiridate precursors to produce 1 to 2 nm blue colloids. The characterization implementation of nanoparticles as catalysts is advantageous due to the increased surface area available for the reaction of interest as well as facility in performing spectroscopic kinetic studies. Adapted hydrolysis-based methods have been developed for functionalization of the iridium oxide colloids with ligands that allow for stabilization and chemical attachment to photoelectrodes for applications in light-driven photoelectrochemical systems. These ligand-based methods are seldom quantitative, but can yield colloids within the 2–70 nm diameter range with various catalytic activities depending on the preparation method.

Murray and coworkers were the first to report the synthesis and electrochemical characterization of stable ligand-free iridium oxide nanocolloids for electrocatalytic water oxidation as free-diffusing redox mediators. On average, the colloids were 2 nm in diameter and exhibited excellent electrocatalytic activity for the OER at pH 13. From these colloids, they later reported the preparation of stable iridium oxide films by electro-flocculation. The method of electro-flocculation allows the iridium oxide colloid to be adhered to the surface of the electrode as a thin film while retaining its size and electrocatalytic properties by applying a constant anodic potential. Harriman and coworkers have reported an alternative method to alkaline hydrolysis by radiolytic means. Here, an aerated aqueous solution of [IrCl$_6$]$_{3-}$ is irradiated with a γ-source and clusters of ~5 Ir atoms per iridium oxide nanoparticle are formed and isolated by filtration. Titration experiments of these colloids suggest that the resting oxidation state of the colloid is 3.2, a mixture of Ir$^{III}$ and Ir$^{IV}$.

Recently, Mallouk and coworkers identified a colorless iridium hydroxide intermediate in the synthesis of hydrous iridium oxide colloids (IrO$_x$·nH$_2$O) by alkaline hydrolysis. This iridium hydroxide intermediate is proposed to be a stable precursor for the formation of iridium oxide colloids. A detailed UV-Vis study demonstrates that this molecule is present at all pH values (λ$\text{max}$ 313 nm) and the concentration of iridium hydroxide precursor increases as a function of pH. From these results, an acidic condensation mechanism is proposed for the formation of these IrO$_x$·nH$_2$O colloids (Figure 1.11). Thin films of IrO$_x$·nH$_2$O can be prepared by electro-flocculation on various substrates from both the colloids and the iridium
hydroxide intermediate.\textsuperscript{129} Colloidal iridium oxide films prepared from the iridium hydroxide precursor are highly active as OER electrocatalysts, however, they pose severe problems when incorporated in metal oxide semiconductors for photoelectrochemical OER. Chapter 2 presents a detailed characterization of this iridium hydroxide intermediate and its effects in photoelectrochemical cells that utilize iridium oxide colloids as co-catalysts.

\textbf{Figure 1.11} UV-Vis spectra of iridium oxide colloidal solutions prepared by acidic condensation and then adjusted to different pH values.\textsuperscript{128} The reaction scheme depicts the pH-dependent equilibrium of iridium hydroxide intermediates and the iridium oxide colloids immediately after alkaline hydrolysis of a hexachloroiridate precursor. Note that the higher concentration of iridium oxide colloids (absorbance band at 580 nm) is obtained at low pH values. Consequently, the higher concentration of iridium hydroxide intermediate (absorbance at 310 nm) occurs at high pH.

\textbf{1.5.3 Electrochemistry of iridium oxide}

The electrochemistry of iridium oxide had been extensively studied particularly because it shows an electrochromic behavior, rendering it useful of applications in the development of polymer electrolytes for “smart window” applications.\textsuperscript{130-133} A characteristic pH-dependent cyclic voltammogram (CV) of colloidal iridium oxide films is shown in Figure 1.12, where redox peaks for the two one-electron reactions of Ir\textsuperscript{III} \rightleftharpoons Ir\textsuperscript{IV} and Ir\textsuperscript{IV} \rightleftharpoons Ir\textsuperscript{V} are present, prior to the exponential increase in current, which indicates catalytic water oxidation. These peaks are also pH-dependent because they involve the insertion/release of a proton or hydroxide ion. At greater anodic potentials, the current increases exponentially and indicates the onset of the OER.
Figure 1.12 pH-dependent cyclic voltammograms of colloidal iridium oxide films prepared via electroflocculation from an iridium hydroxide precursor. The circles indicate the overpotential for the onset of OER at 1.5 mA/cm² and are used to generate the Pourbaix diagram on the right. The solid line in the Pourbaix diagram represents the equilibrium line for the H₂O/O₂ couple and the dashed line is provided as a guide. The average overpotential for the OER at 1.5 mA/cm² is 203 ± 32 mV. Adapted from reference 129.

1.6 Basics of photoelectrochemical water-splitting

The working principle of water-splitting photoelectrochemical cells (PEC) is based on charge-transfer processes in semiconductor–liquid junctions. Figure 1.13 illustrates the effect of contact between an n-type semiconductor and a liquid electrolyte that contains a redox couple in the dark and under illumination.

Figure 1.13 Junction formation between an n-type semiconductor and an electrolyte solution containing a redox couple O/R (A) prior to contact in the dark; (B) after contact in the dark and electrostatic equilibrium. The band gap \( E_g \) is defined as the potential difference between the valence band (VB) and conduction band (CB) of the semiconductor. (C) Same junction as (B) but depicting the extent of the space-charge region (SCR) and band bending induced by electron transfer from the semiconductor to the electrolyte to attain electrostatic equilibrium, and (D) same junction under illumination. Adapted from reference 24.
Upon contact of the semiconductor and the electrolyte, electrostatic equilibrium is obtained only when the Fermi energy of both the semiconductor and the electrolyte are equal. This equilibrium occurs as a result of charge transfer between the semiconductor and liquid phases. In the particular case of Figure 1.12, the Fermi energy of the semiconductor lies higher than that of the redox couple. Therefore, electrons will flow from the semiconductor to the liquid electrolyte. The excess positive charge in the semiconductor does not reside at the surface, but rather is distributed in a space-charge region (SCR, also known as the depletion layer). The positive-charge accumulation-induced electric field within the space-charge region results in changes of the electrochemical energy of the electrons. Thus, the positive charge in the SCR causes the bands energies to become more negative with increasing distance towards the bulk semiconductor (or more positive with increasing distance towards the electrolyte). This effect is termed band bending and when the semiconductor is more positive than the liquid electrolyte, the bands bend upward with respect to their level at the field free bulk semiconductor (Figure 1.13C). When the semiconductor–liquid electrolyte junction is exposed to light of appropriate energy ($h\nu > E_g$, where $E_g$ is the energy difference between the valence band and the conduction band of the semiconductor) charge carriers (electron–hole pairs) are generated (Figure 1.13D). For the $n$-type semiconductor–liquid junction in Figure 1.13D, the holes generated in the valence band (from light-excited electrons moving into the conduction band) migrate to the surface of the semiconductor and oxidize the reduced species $R$ in the electrolyte. These light-generated charge carriers are used to drive photoelectrochemical reactions.

**Figure 1.14** Overall light-driven water-splitting under acidic conditions (A) with an ideal semiconductor that has a band gap ($E_g$) that straddles the reduction potentials of both the hydrogen evolution reaction ($H_2/H^+$) and the oxygen evolution reaction ($O_2/H_2O$). Here, the light-induced electrons in the conduction band (CB) reduce protons to hydrogen gas, and the holes in the valence band (VB) oxidize water to molecular oxygen. (B) Buried-junction single absorber photoelectrochemical cell in which an $n$-type semiconductor (SC) is the photoanode and a dark metal cathode electrocatalyze the oxygen evolution and hydrogen evolution reactions, respectively. (C) Buried-junction, dual-absorber photoelectrochemical cell that, like (B) uses an $n$-type SC for the photoanode, and a $p$-type SC for driving the hydrogen evolution reaction. Here, the $n$-type and $p$-type SC photoelectrodes are connected in series. Adapted from reference 16.
For a water-splitting photoelectrochemical cell (PEC) with a single-absorber the \( E_g \) of the semiconductor must straddle the reduction potentials of both the OER and HER reactions (Figure 1.14A). This criterion is quite stringent and limits the number of semiconductors that can be used efficiently in PEC. Therefore, as developed originally by Fujishima and Honda, one of the reactions is driven photoelectrochemically and the other uses a dark electrode to close the circuit (Figure 1.14B). An alternate approach incorporates dual-absorbers (Figure 1.14C), such that the HER and OER are de-coupled and the materials developed for each reaction are optimized independently.

The kinetics of the overall water-splitting reaction in photoelectrochemical cells can be improved by introducing electrocatalysts (also referred to as co-catalysts) on the surface of the photoabsorbers. In this configuration, the co-catalysts help shuttle the light-generated charge carriers and lower the overpotential for the overall reaction. Bard and coworkers have studied the photoelectrochemical activity of various co-catalysts in BiVO₄-based photoabsorbers using scanning electrochemical microscopy.⁹⁴⁹⁵ In their work, they have identified that good electrocatalytic materials do not always improve the performance of a PEC. Recent work by Lin and Boettcher elegantly probed the junction between photoabsorbers and co-catalysts and demonstrated its dynamic behavior as a function of the oxidation state of the co-catalyst.⁹⁶ Chapter 2 of this dissertation studies the role of monomeric intermediates in the formation of colloidal IrOₓ·nH₂O nanoparticles and their effect in water-splitting PEC.

1.7 Summary and dissertation outline

The water-splitting reaction is a very promising way to generate high-purity hydrogen gas fuel. However, its thermodynamic and mostly kinetic hindrances make it a big challenge for researchers. This dissertation focuses on providing some fundamental insights that can guide researchers to more efficient materials and devices. In Chapter 2, the chemical characterization of monomeric iridium intermediates is presented, as well as their role in the efficiency of PEC that incorporate colloidal iridium oxide nanoparticles as co-catalysts. In a more device-development driven approach, Chapter 3 explores and quantifies the series losses that arise when buffer electrolytes and commercial membranes are used in model water-splitting PEC. Expanding of previous research on the kinetics and mechanism of the OER, Chapter 4 presents preliminary results in a solely electrochemical study of this reaction in which temperature, pH and hydrogen/deuterium kinetic isotope effects are explored in colloidal iridium oxide electrocatalytic films. In Chapter 5 an overall summary of the work presented on this dissertation is discussed and the possible directions it may be directed towards. Finally, Appendix A presents the technique of rotating ring-disk electrochemistry and its usefulness in the characterization of a fully organic homogenous OER electrocatalyst.
Chapter 2

Understanding the effect of monomeric iridium(III/IV) aquo complexes on the photoelectrochemistry of \( \text{IrO}_x \cdot n\text{H}_2\text{O} \)–catalyzed water-splitting systems

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2.1 Introduction

Photoelectrochemical cells (PECs) utilize sunlight to drive electrochemical reactions. In solar fuel applications of PECs, the anode reaction is typically the oxygen evolution reaction (OER). The efficiency of PECs is strongly dependent on efficient catalysis of the OER because of the complex four-electron, four-proton mechanism of the reaction. Many catalysts have been studied including those based on precious metals\(^{48,119,120,126,128,137,138}\) and Earth-abundant elements.\(^{39,139-144}\) The incorporation of these catalysts into photoabsorbers and onto the surfaces of oxide semiconductors has been well studied.\(^{136,145-149}\)

Iridium oxide is a highly active OER catalyst, and has been recently benchmarked by McCrory et al. as the only known solid electrocatalyst for the OER that is highly active and stable in acidic electrolytes.\(^{90}\) The overpotential for water oxidation at iridium oxide is low over a broad range of pH,\(^{126}\) although it is less active and unstable under strongly alkaline conditions. Amorphous iridium oxide nanoparticles (IrO\(_x\)·nH\(_2\)O) have been used successfully to improve the OER efficiency of both PECs\(^{145,150,151}\) and molecular photochemical systems.\(^{152,153}\)

Recently, Bard and coworkers used scanning electrochemical microscopy to probe the photoelectrochemical activity of \(n\)-type BiVO\(_4\).\(^{134,135}\) In characterizing the effects of metal and metal oxide electrocatalysts on tungsten-doped BiVO\(_4\) photoanodes, they found rather surprisingly that the photocurrent was dramatically reduced by incorporating IrO\(_x\)·nH\(_2\)O into the photoelectrode, whereas other catalysts such as cobalt oxide increased the photocurrent.

Alkaline hydrolysis of Ir(III) or Ir(IV) salts produces a soluble intermediate that condenses in acid to form catalytically active, ligand-free IrO\(_x\)·nH\(_2\)O nanoparticles.\(^{128}\) In this preparation of IrO\(_x\)·nH\(_2\)O colloids there are distinct features in UV-Vis spectra that suggest the presence of a low nuclearity and possibly monomeric anion. A strong absorption band centered at 313 nm is observed, most likely from a ligand-to-metal charge transfer absorption of a hydroxyiridate species. At concentrations below 0.5 mM, no visible absorption bands are observable and there is minimal light scattering by the solution. At higher concentrations, a weak 580 nm band appears along with light scattering that is typical of blue IrO\(_x\)·nH\(_2\)O colloids. Both absorption features are pH-dependent, and the 313 nm absorbance in strong in very basic solutions. This suggests a reversible acid condensation of the hydroxyiridate monomer to form IrO\(_x\)·nH\(_2\)O colloids.

We report here a systematic spectroscopic, electrochemical, and computational study to identify the monomeric iridium complexes formed in this reaction. Interestingly, we find that these anions adsorb strongly not only to ligand-free IrO\(_x\)·nH\(_2\)O colloids but also to TiO\(_2\) and other oxide semiconductor surfaces. The adsorption-desorption equilibrium of these previously unrecognized electroactive anions significantly complicate the photoelectrochemistry of oxide photoanodes.
that are functionalized with IrO\textsubscript{x}\cdot nH\textsubscript{2}O catalyst particles. By removing the monomer, blocking its path to the electrode back contact, or using alternative attachment chemistries for the IrO\textsubscript{x}\cdot nH\textsubscript{2}O colloids, the photoelectrochemical performance of these catalyzed electrodes is dramatically improved.

2.2 Experimental Methods

2.2.1 Low-temperature ligand-free IrO\textsubscript{x}\cdot nH\textsubscript{2}O nanoparticle synthesis

0.2 mmol K\textsubscript{2}IrCl\textsubscript{6} was dissolved in 90 mL of 8 mM aqueous NaOH. The solution was heated rapidly to 75 °C with strong stirring. The solution was immediately cooled in an ice bath where it remained stirring for ca. 64 h. The pH was closely monitored and maintained at 11.9 units by addition of 1 M NaOH throughout the reaction. The final solution volume was adjusted to 100 mL with nanopure water. The colloidal solutions prepared by this low-temperature method are denoted hereafter as LT-IrO\textsubscript{x}\cdot nH\textsubscript{2}O. For comparison purposes, ligand-free IrO\textsubscript{x}\cdot nH\textsubscript{2}O nanoparticles reported by Murray and coworkers\textsuperscript{126} were also synthesized and are referred to as LF-IrO\textsubscript{x}\cdot nH\textsubscript{2}O. Separation of both kinds of ligand-free colloidal particles from adsorbed anionic Ir complexes was accomplished by precipitating the colloids in twice the volume of isopropanol and then re-dispersing in the desired solvent. The precipitated colloids can be re-dispersed in nanopure water, dimethyl sulfoxide, tetrahydrofuran and dimethylformamide.

2.2.2 Ligand-capped IrO\textsubscript{x}\cdot nH\textsubscript{2}O nanoparticle synthesis

2-carboxyethylphosphonic acid (PCOOH)–capped IrO\textsubscript{x}\cdot nH\textsubscript{2}O nanoparticles were synthesized as previously described.\textsuperscript{20} Briefly, 0.3 mmol PCOOH and 0.05 mmol K\textsubscript{2}IrCl\textsubscript{6} were dissolved in 50 mL of nanopure water and the pH was adjusted to 5.0 with concentrated NaOH. The solution was refluxed at 90 °C for 1 h until it turned colorless. The solution was allowed to cool to 80 °C and the pH was monitored and adjusted to 7.5 until the solution turned clear blue and the absorbance peak at ca. 580 nm was stable (ca. 8 hours). The nanoparticles were purified to remove excess ligand and iridium-containing monomers using a DOWEX 1X8-50 anion exchange resin that was pre-treated with NaOH for 10 minutes and washed until neutral with nanopure water.

2.2.3 Hydroxyiridate monomer solution synthesis

1 mM solutions of hydroxyiridate monomers were prepared as previously reported\textsuperscript{129} and were diluted to the appropriate concentrations for adsorption experiments. Briefly, 0.05 mmoles of K\textsubscript{2}IrCl\textsubscript{6} were dissolved in 50 mL of 6 mM aqueous NaOH, and the solution was heated rapidly to 70 °C, followed by immediate cooling in an ice bath. The final pH of these solutions was between 7 and 8 pH units. To prepare 100 µM solutions, 0.005 mmoles of K\textsubscript{2}IrCl\textsubscript{6} were dissolved in 50 mL of standardized 0.1008 M NaOH solutions and heated to 70 °C
until colorless, clear solutions were obtained. The solution was immediately cooled in an ice bath and kept in a refrigerator at 2 °C until used.

2.2.4 Photoanode preparation

Mesoporous TiO$_2$ electrodes were prepared by doctor-blading a TiO$_2$ paste directly unto fluorine-doped tin oxide (FTO)-coated glass slides masked with three layers of scotch tape (ca. 10 µm total thickness). The mesoporous TiO$_2$ paste and rutile-TiO$_2$ vertical nanorod electrodes were prepared following previously published procedures.$^{154,155}$ Tungsten-doped bismuth vanadate (W-BiVO$_4$) electrodes were prepared as described by Bard and coworkers.$^{135}$ The bismuth, vanadium and tungsten precursors used were Bi(NO$_3$)$_3$·5H$_2$O, VCl$_3$ and (NH$_4$)$_10$W$_{12}$O$_{41}$, respectively. The Bi, V and W precursors were mixed in a molar ratio of 4.5:5:0.5 in ethylene glycol to attain a 10 mM total concentration of precursors. 100 µL of this precursor solution was deposited on a fluorine-doped tin oxide (FTO)–coated glass slide (1.5 cm by 1.5 cm) followed by a slow annealing step where the temperature was ramped at a 1 °C/min rate to 500 °C and held at this temperature for 3 hours in air to produce films ca. 400 nm thick.

2.2.5 Time-dependent density functional theory (TDDFT) methodology

All calculations presented in this work were performed using a local version of the Amsterdam Density Functional (ADF) program package.$^{156-158}$ The geometries were optimized using a TZ2P basis set and the OPBE functional. The OPBE functional was chosen as it has been shown to provide a good description of spin-states.$^{159}$ Solvent effects were accounted for using COSMO$^{160}$ and scalar relativistic effects were included using the zeroth-order regular approximation (ZORA).$^{161,162}$ Excitation energies were calculated using the long-range corrected LCY-BP86 functional based on the Yukawa potential with a range separation parameter of 0.34.$^{163}$

2.2.6 Measurements and Characterization

Electrochemical measurements and colloid deposition on glassy carbon (GC) rotating disk electrodes (RDE) were performed with a BAS 100B electrochemical workstation. Photoelectrochemical measurements were done using a 150 mW Xe lamp with AM1.5 filter. UV-Vis spectra were recorded on a Varian Cary 6000i spectrophotometer.

Spectroelectrochemical experiments were performed using a Honeycomb quartz cell (Pine Research Instruments) with gold honeycomb working and counter electrodes, and a homemade standard calomel electrode (SCE) as a reference. The dimensions of the cell and the diffusivity of electroactive species determined the time needed to acquire the spectrum after each potential step. The diffusion timescale ($\tau$) in a spectroelectrochemical cell is given by Equation 2.2.1:
Here, \( \delta \) (in cm) is the longest distance that electroactive species have to travel to reach the electrode surface in the honeycomb-working electrode and \( D \) is the diffusion coefficient (in \( \text{cm}^2/\text{s} \)). In our experiments, \( \delta \) was 0.05 cm, the width of the honeycomb channels, and \( D \) was estimated as \( 5 \times 10^{-6} \text{ cm}^2/\text{s} \), so \( \tau \) was about 250 s. UV-Vis spectra were collected approximately 30 min after each potential step in order to ensure adequate time for diffusion of oxidized and reduced monomeric anions.

Transmission electron microscopy (TEM) images were obtained using a JEOL JM-2010 microscope with a LaB\(_6\) electron source at an accelerating voltage of 200 keV. Samples were prepared by drop-casting the nanoparticle solution onto a lacey carbon-coated copper grid. The samples were dried at room temperature before use. EPR measurements were carried out at cryogenic temperatures on a Bruker ESP300 CW X-Band spectrometer (operating at approx. 9.48 GHz) equipped with a rectangular cavity (TE102) and a continuous-flow cryostat (Oxford 910) with a temperature controller (Oxford ITC 503). The EPR spectrum of the monomer solution was obtained after subtraction of the spectrum of a 0.1 M NaOH solution. Spin quantitation was performed relative to a 256.25 \( \mu \text{M} \) Cu\(^{2+}\)-EDTA standard.

### 2.3 Results and Discussion

#### 2.3.1 Characterization of hydroxyiridate anions

Although the alkaline hydrolysis of K\(_2\)IrCl\(_6\) can produce stable, catalytically active IrO\(_x\)·nH\(_2\)O nanoparticle suspensions, the yield is limited by an equilibrium between small molecule, anionic intermediates and the colloid at a given pH.\(^{128}\) The soluble, colorless Ir-containing anions formed in base can be converted to deep blue iridium oxide colloids by an acidic condensation reaction that can be monitored by UV-Vis spectroscopy. As the pH is lowered, the UV band at 313–318 nm decreases and the visible IrO\(_x\)·nH\(_2\)O band centered at 580 nm increases. In earlier papers, the colorless hydroxyiridate anion has been described as an Ir(IV) anion or as \([\text{Ir(OH)}_6]^{2-}\)\(^{127,129,164}\) although some reports have suggested that it is an Ir(III) complex.\(^{165,166}\)

A linear Beer’s law plot of these solutions at concentrations between 0.002 and 0.10 mM (Figure 2.1) establishes that the nuclearity of Ir complexes contributing to the 318 nm band does not change over this concentration range, and that the solution most likely contains monomeric complexes.
Electron paramagnetic resonance (EPR) experiments were performed on frozen solutions of the monomer to quantify the amount of paramagnetic Ir$^{IV}$. Figure 2.1B shows the EPR spectrum, which exhibits an almost axial signal characteristic of a low-spin ($S=1/2$) $d^5$ iridium(IV) hydroxy/aquo complex. The EPR signal exhibits complex features that may originate from the interaction of the unpaired electron with the iridium nucleus (Ir has two magnetic isotopes with $l=3/2$ in a 2:1 ratio) and/or nearby strongly coupled nuclei (e.g. $^1$H). Spin quantitation of the Ir$^{IV}$ complex yields 0.04 mM from a solution originally containing 0.13 mM K$_2$IrCl$_6$. This indicates that the majority (ca. 70%) of Ir in the solution exists in the EPR-silent ($d^6$, $S=0$) +3 oxidation state. We note that this is consistent with redox titrations of blue IrO$_x$·nH$_2$O colloids, which show an average oxidation state of 3.2.$^{127}$

Cyclic voltammetry (CV) of these solutions at 0.10 mM concentration, where the monomer is stable, helps to explain the mixture of oxidation states formed in the hydrolysis reaction. Figure 2.3 shows a CV at pH 13 on a glassy carbon electrode. There are two reversible one-electron redox processes that can be ascribed to Ir$^{III}$/Ir$^{IV}$ and Ir$^{IV}$/Ir$^{V}$ interconversions. The onset of high anodic current at potentials positive of +0.55 V vs. SCE is attributed to the oxygen evolution reaction (OER) ($\eta_{OER} = 330$ mV). In this solution the formal potential of the Ir$^{III}$/Ir$^{IV}$ couple is approximately coincident with the potential of the oxygen/water couple. This is consistent with the mixed oxidation state detected by EPR, and with earlier observations that the synthesis of IrO$_x$·nH$_2$O colloids from either Ir(IV) or Ir(III) involves an Ir(III) intermediate.$^{116,168,169}$
Figure 2.2. Cyclic voltammogram (red trace) of 0.10 mM iridium hydroxide in unstirred, air-saturated 0.1 M NaOH on a glassy carbon electrode at 10 mV/s. The gray trace is the clean glassy carbon electrode background current in 0.1 M NaOH. The dashed blue line indicates the formal potential of the oxygen/water couple at pH 13. The purple dots and lines indicate the potentials selected for the spectroelectrochemical experiments in Figure 2.4.

We attempted to measure the charge on the Ir(III) complex by the ion exchange method of Connick et al. \(^{170}\) Unfortunately, the monomeric anions are stable only at low concentration (less than 0.5 mM) in strong base (0.1 M NaOH), so these attempts were unsuccessful. Spectroelectrochemical experiments were then carried out to establish the contributions of Ir(III) and Ir(IV) anions to the spectral features shown in Figure 2.1A,B, and to identify the species present in each oxidation state.

Figure 2.3A–C shows the changes in the spectra as a function of time under controlled-potential conditions, at +350 mV vs. SCE for conversion of Ir\(^{\text{III}}\) to Ir\(^{\text{IV}}\), or at potentials at or negative of +100 mV vs. SCE for the conversion of Ir\(^{\text{IV}}\) to Ir\(^{\text{III}}\). When a +350 mV vs. SCE bias is applied (Ir\(^{\text{III}}\) → Ir\(^{\text{IV}}\)), the peak centered at 318 nm broadens and its absorbance decreases (Figure 2.4A). At the same time, the intensity of the peak centered at 220 nm increases dramatically. When the bias is shifted to +100 mV vs. SCE (Ir\(^{\text{IV}}\) → Ir\(^{\text{III}}\)), the 318 nm peak becomes narrower and similar in shape to the original spectrum within 30 min. (Figure 2.3A). A slight blue shift occurs and \(\lambda_{\text{max}}\) is then centered at 313 nm. At the same time, the peak centered at 220 nm decreases in intensity. As the electrolysis progresses at +100 mV and 0 mV vs. SCE, the peak centered at 313 nm continues to increase but does not recover to the absorbance value of the original spectrum. Under these conditions the absorbance at 220 nm increases, albeit at a slower rate than at +350 mV vs. SCE. This is most likely a consequence of light scattering, which is more pronounced at shorter wavelengths and longer timescales. Finally, the potential was returned to +350 mV vs. SCE (Ir\(^{\text{III}}\) → Ir\(^{\text{IV}}\), Figure 2.4A – second set of blue traces).
As observed before, the peak in the 313–318 nm range broadens and decreases in intensity, and the peak centered at 220 nm increases rapidly. Taken together the potential-dependent spectra indicate that the absorbance at 220 nm is predominantly from an Ir$^{IV}$ species, and that the 318 nm band is a combination of both Ir$^{III}$ and Ir$^{IV}$ species. The time-dependent absorbance values at 220 and 318 nm as a function of applied potential are summarized in Figure 2.3B,C.

TDDFT modeling was employed to correlate the spectro-electrochemical and EPR results with specific structures and Ir oxidation states. In order to validate the TDDFT method, calculations were first done for the complexes [IrCl$_6$]$^{3-}$ and [Ir(H$_2$O)$_6$]$^{3+}$. Table 2.1 summarizes the calculated energies of the $d$–$d$ transitions, where we find good agreement between the experimental and modeled spectra.\textsuperscript{166,171}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Modeled</th>
<th>Experimental</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IrCl$_6$]$^{3-}$</td>
<td>439 nm</td>
<td>415 nm</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>392 nm</td>
<td>356 nm</td>
<td></td>
</tr>
<tr>
<td>[Ir(H$_2$O)$_6$]$^{3+}$</td>
<td>338 nm</td>
<td>310 nm</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>303 nm</td>
<td>265 nm</td>
<td></td>
</tr>
</tbody>
</table>

The extinction coefficient of the monomeric ions at 318 nm was determined earlier to be ca. 3300 M$^{-1}$cm$^{-1}$,\textsuperscript{128} which suggests a ligand-to-metal charge transfer (LMCT) process. Simulated spectra of possible Ir$^{III}$ and Ir$^{IV}$ anions are shown in Figure 2.4. The calculated spectra validate the assignment of the 220 nm band to a Ir$^{IV}$ anion, namely Ir$^{IV}$(OH)$_6$$^{2-}$. However, the transition at 318 nm cannot be as clearly ascribed to a single anion. Both Ir$^{IV}$(OH)$_6$$^{2-}$ and Ir$^{III}$(OH)$_5$(H$_2$O)$_2$$^{2-}$ have calculated absorption bands in the 300-400 nm region, and the low symmetry of the
latter complex complicates the calculation of extinction coefficients. However, the more symmetric Ir\textsuperscript{III}(OH)\textsubscript{6}\textsuperscript{3-} anion has very little calculated absorbance at wavelengths longer than 300 nm. Taken together with the EPR results, this suggests that the predominant Ir(III) species in air-saturated solutions at pH 13 is the Ir\textsuperscript{III}(OH)\textsubscript{5}(H\textsubscript{2}O)\textsuperscript{2-} anion. Alkaline hydrolysis of IrCl\textsubscript{6}\textsuperscript{2-} thus produces a mixture of Ir(III) and Ir(IV) monomers as the dianions Ir\textsuperscript{III}(OH)\textsubscript{5}(H\textsubscript{2}O)\textsuperscript{2-} and Ir\textsuperscript{IV}(OH)\textsubscript{6}\textsuperscript{2-}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Simulated TDDFT spectra for various iridium(III/IV) complexes}
\end{figure}

2.3.2 As-synthesized and purified ligand-free IrO\textsubscript{x}·nH\textsubscript{2}O nanoparticles

The monomeric Ir(III/IV) anions could be separated from IrO\textsubscript{x}·nH\textsubscript{2}O nanoparticles by precipitating the colloids with isopropanol and then re-suspending them in polar solvents. This was confirmed by the disappearance of the absorption peak at 313 nm (Figure 2.5A). At the same time, the scattering background increases, suggesting that the flocculation of the colloids is not completely reversible. Analysis of TEM images shows that the diameter of the primary nanoparticles remains the same, 1.4 ± 3 and 1.2 ± 3 nm before and after purification, respectively (Figure 2.5B,C).
In order to determine the effect of the monomeric anions on the electrocatalytic activity of IrO$_x$·nH$_2$O nanoparticles, the colloidal solutions were studied as dispersed redox catalysts at a rotating disk electrode. Figure 2.6 shows voltammetry of these nanoparticle solutions at pH 13. The LF-IrO$_x$·nH$_2$O shows the highest electrocatalytic activity while the LT-IrO$_x$·nH$_2$O nanoparticles are moderately active. Upon purification of LT-IrO$_x$·nH$_2$O, i.e. removal of the monomeric anions, the apparent catalytic activity is substantially reduced. In this experiment, PCOOH–capped IrO$_x$·nH$_2$O nanoparticles exhibited the lowest electrocatalytic activity, possibly due to slow electron transfer to the electrode through the capping ligands.

The difference in electrocatalytic activities of the nanoparticle solutions is most likely related to the presence (or absence) of monomeric Ir(III/IV) anions. Since these anions are a precursor to the formation of IrO$_x$·nH$_2$O nanoparticles, under anodic bias, i.e. conditions where OER catalysis occurs, the local decrease in pH can cause the monomers to condense to catalytically active IrO$_x$·nH$_2$O nanoparticles on the electrode surface. The in-situ formation of IrO$_x$·nH$_2$O nanoparticles on the electrode can result in relatively high catalytic currents. The inset in Figure 2.6 shows the color of the various IrO$_x$·nH$_2$O colloidal solutions. The lack of blue color in solution 1 (LF-IrO$_x$·nH$_2$O), which shows the highest catalytic activity, indicates a low concentration of colloidal IrO$_x$·nH$_2$O relative to the colorless monomeric anions. Solution 2 (LT-IrO$_x$·nH$_2$O) has a deeper blue color, i.e. a predominance of
colloidal IrO₃·nH₂O relative to monomer. The increased concentration of colloidal IrO₃·nH₂O in this case is most likely due to the longer time allowed for the slow hydrolysis reaction.

Figure 2.6 Cyclic voltammograms of deaerated 1 mM (based on total Ir) nanoparticle solutions at pH 13: (1) LF-IrO₃·nH₂O, (2) as-synthesized LT-IrO₃·nH₂O, (3) purified LT-IrO₃·nH₂O, and (4) PCOOH-capped IrO₃·nH₂O. All CVs were taken at 20 mV/s using a glassy carbon rotating disk electrode (blank) with rotation speed at 600 rpm in a pH 13 NaOH solution. Significant differences in the electrocatalytic activity of the colloids as dissolved redox catalysts are observed. The inset picture shows the various IrO₃·nH₂O solutions.

2.3.3 IrO₃·nH₂O nanoparticle-modified photoelectrodes

TiO₂ electrodes soaked in PCOOH–capped IrO₃·nH₂O colloidal solutions show effective deposition of IrO₃·nH₂O nanoparticles. This same procedure was followed with the as-synthesized and purified LT-IrO₃·nH₂O colloids. Figure 2.7 compares a bare mesoporous TiO₂ slide (Slide 1) with post-deposition slides of purified LT-IrO₃·nH₂O, PCOOH–capped IrO₃·nH₂O, and as-synthesized LT-IrO₃·nH₂O (Slides 2–4, respectively). The lack of coloring on Slide 2 demonstrates little to no adsorption of LT-IrO₃·nH₂O particles when the purified colloid solution (free of monomeric Ir³⁺(OH)₅(H₂O)₂⁻ and Ir⁴⁺(OH)₆⁻) was used. However, slides immersed in PCOOH–capped and as-synthesized LT-IrO₃·nH₂O colloidal solutions show significant deposition of the nanoparticles (Slides 3 and 4, respectively). These results highlight the necessity of an anchoring group to attach colloidal particles to the TiO₂ surface. For ligand-capped IrO₃·nH₂O, PCOOH can act as the anchoring group. For as-synthesized LT-IrO₃·nH₂O, the adsorbed monomeric anions apparently anchor the colloids to the TiO₂ surface. Zeta-potential measurements indicate that as-synthesized and purified LT-IrO₃·nH₂O, as well PCOOH-capped IrO₃·nH₂O, have within experimental error the same zeta potential (at pH 12, ~25 ± 5 mV). This suggests that electrostatic factors do not differentiate purified LT-
IrO$_x$·nH$_2$O from the other colloids, and point to the capping/stabilizing behavior of the adsorbed monomeric anions.

Figure 2.7 Photograph of mesoporous TiO$_2$ slides: 1) bare TiO$_2$, 2) soaked in purified LT-IrO$_x$·nH$_2$O, 3) soaked in PCOOH–capped IrO$_x$·nH$_2$O, and 4) soaked in as-synthesized LT-IrO$_x$·nH$_2$O colloidal solution.

Figure 2.8 Adsorption isotherms of iridium-based solutions: (blue) monomer solution, (red) as-synthesized LT-IrO$_x$·nH$_2$O, (black) purified PCOOH-capped IrO$_x$·nH$_2$O. Fit lines represent Langmuir adsorption isotherms.

To quantify the coverage ($\Gamma$) of iridium oxide nanoparticles and monomeric anions on the photoanodes, adsorption isotherms were measured (Figure 2.8). 10 µm thick mesoporous TiO$_2$ electrodes (3 cm$^2$, roughness ca. 1000) were soaked overnight at different concentrations of the Ir-containing solutions. All systems studied could be modeled with Langmuirian adsorption behavior. The PCOOH–capped IrO$_x$·nH$_2$O shows the highest coverage ($3.4 \times 10^{-10}$ moles/cm$^2$) followed by
as-synthesized LT-IrOₓ·nH₂O and monomer solutions, which gave saturation coverages of 2.9 and 1.9 × 10⁻¹⁰ moles/cm², respectively. The values of the equilibrium constants were 72, 190, and 180 mM⁻¹, respectively, indicating especially strong binding of the monomer and the monomer-capped colloids to the TiO₂ surface. Since little adsorption of IrOₓ·nH₂O nanoparticles was observed when the colloids were purified to remove monomeric anions, it can be concluded that the anions play a key role in the deposition of IrOₓ·nH₂O onto mesoporous TiO₂ electrodes.

### 2.3.4 Photoelectrochemistry

Recently, Bard and coworkers tested the effects of various OER catalysts on tungsten-doped bismuth vanadate photoanodes using scanning electrochemical microscopy. They determined that despite having excellent electrocatalytic activity for OER, iridium oxide performed poorly as a co-catalyst in comparison to cobalt oxide and platinum for photoelectrochemical water oxidation. In contrast, a report by Grätzel and coworkers showed that electrodeposited iridium oxide on nanostructured hematite electrodes resulted in a significant performance enhancement for the photoelectrochemical OER. We can now consider these seemingly inconsistent results in light of the likely presence of adsorbed monomeric Ir(III) and Ir(IV) anions and their electrochemical reactions.

Slow linear sweep voltammetry (LSV) under intermittent AM1.5 illumination was used to characterize the photoresponse of metal oxide photoanodes in the absence and presence of monomeric Ir(III/IV) anions and IrOₓ·nH₂O catalyst particles. In Figure 2.10A, uncatalyzed mesoporous anatase photoelectrodes show the expected photoresponse at positive potentials, with photocurrents of ~0.17 mA/cm² corresponding to the UV light-driven OER. The photocurrent of these electrodes is dramatically reduced (by ca. 75%) when the electrode is exposed to a 10 µM solution of the Ir(III/IV) monomer for 10 seconds (Figure 2.10A, blue trace). The TiO₂ electrode can be modified with IrOₓ·nH₂O nanoparticles by immersion in a 1 mM Ir(III/IV) monomer solution followed by immersion in a 0.5 mM purified LT-IrOₓ·nH₂O solution (Figure 6A, red trace). In this case, the photocurrent is even further diminished, although there is an increase in the dark current at high overpotential due to electrocatalysis of the dark OER (Figure 2.10A, red trace). The presence of the monomeric Ir(III/IV) anions is detrimental to PECs that utilize IrOₓ·nH₂O as the OER catalyst, most likely because these electroactive anions can desorb and mediate charge recombination at the FTO back contact of the mesoporous TiO₂ film, as sketched in Figure 2.10B.
Figure 2.9 (A) Linear sweep voltammograms (LSV) at 10 mV/s in 0.1 M NaOH under AM1.5 irradiation of bare mesoporous TiO$_2$ electrode (black), mesoporous TiO$_2$ electrode soaked in 10 µM iridium hydroxide solution for 10 seconds (blue), and mesoporous TiO$_2$ electrode soaked in 1 mM iridium hydroxide, and then in 0.5 mM purified LT-IrO$_x$·nH$_2$O for 3 minutes (red); (B) Cartoon representation of the short-circuiting of a TiO$_2$ water splitting anode by adsorption/desorption of electroactive hydroxyiridate anions. The Ir$^{III}$ form of the complex, converting it to Ir$^{IV}$, scavenges photogenerated holes. The oxidized complex desorbs and is reduced back to Ir$^{III}$ at the bare FTO surface. Covering the FTO surface with a dense layer of TiO$_2$ eliminates this electron transfer pathway.

We previously reported that IrO$_x$·nH$_2$O nanoparticle films could be grown on electrode surfaces through anodization of the monomer solutions$^{129}$. The photoelectrochemistry of such films on rutile-TiO$_2$ nanorods was studied by depositing IrO$_x$·nH$_2$O from a 0.5 mM monomer solution for 30 seconds at +1.0 V vs. Ag/AgCl. Figure 2.11 shows voltammograms of bare and IrO$_x$·nH$_2$O–modified rutile-TiO$_2$ nanorod electrodes. The photocurrent is nearly doubled relative to the unmodified electrodes, suggesting effective catalysis of the OER by electrodeposited IrO$_x$·nH$_2$O. The hydrothermal growth of these nanorods results in a dense 200-400 nm thick TiO$_2$ underlayer that physically separates the solution (which may still contain monomeric Ir$^{III/IV}$) from the FTO back-contact. Grätzel and coworkers observe a similar dense layer in their hematite electrodes$^{145}$. These results suggest that Ir(III/IV) anions mediate electron transfer between the FTO surface and the illuminated photoanode surface, effectively short-circuiting the electrode. Therefore, the physical separation of the FTO back contact from the solution is crucial for good photoelectrochemical performance when Ir(III/IV) anions are present.
Figure 2.10 Linear sweep voltammograms (LSV) at 10 mV/s in 0.1 M NaOH under AM1.5 irradiation of bare rutile-TiO$_2$ nanorods (NR) (black), and IrO$_x$$\cdot$nH$_2$O–modified through electrodeposition of Ir(III/IV) on rutile-TiO$_2$ NR (red).

Figure 2.11 (A) Linear sweep voltammograms (LSV) at 10 mV/s in 0.2 M phosphate buffer (pH 6.8) under AM1.5 irradiation of W-BiVO$_4$ photoelectrodes: (red) bare W-BiVO$_4$, (black) W-BiVO$_4$ electrodes modified with purified PCOOH–capped IrO$_x$$\cdot$nH$_2$O, and (blue) the same electrode as in the black trace dipped in 1 mM Ir(III/IV) solution for 30 seconds. (B) Cyclic voltammograms at 10 mV/s in 0.2 M phosphate buffer (pH 6.8) of bare W-BiVO$_4$ (red), W-BiVO$_4$ modified with purified PCOOH–capped IrO$_x$$\cdot$nH$_2$O (black), and the same electrode as the black trace dipped in 1 mM Ir(III/IV) solution for 30 seconds (blue).

We also performed photoelectrochemical experiments on tungsten-doped bismuth vanadate (W-BiVO$_4$) electrodes modified with IrO$_x$$\cdot$nH$_2$O. Purified PCOOH–capped IrO$_x$$\cdot$nH$_2$O colloid solutions were used to deposit the nanoparticles onto the photoanodes. Under these conditions the photocurrent was enhanced relative to the unmodified W-BiVO$_4$ photoanode, especially at low overpotential (Figure 2.11). However, when this modified electrode was dipped into a 1 mM Ir(III/IV) monomer solution for 30 seconds the photocurrent was dramatically reduced. This is
consistent with the observation from the TiO$_2$ electrodes that the monomer can effectively short-circuit the system. In addition, dark cyclic voltammograms (Figure 2.11B, blue trace) show a significant increase in Ir(III/IV) redox peaks after exposure to the monomer solution. This is further proof that the monomer strongly adsorbs and also penetrates the porous electrode to the FTO back contact. This suggests that if a dense W-BiVO$_4$ layer is used, similar to that in the rutile-TiO$_2$ nanorod or nanostructured hematite electrodes, it is likely that the presence of monomers will not degrade the photoelectrochemical performance of the system.

2.4 Conclusion

In summary, monomeric Ir(III/IV) anions strongly adsorb to the surface of metal oxide photoelectrodes and promote the deposition of IrO$_x$·nH$_2$O nanoparticles. However, the monomer is detrimental to the photoanode performance in IrO$_x$·nH$_2$O-based water oxidation systems. Enhanced photoelectrochemical performance can be obtained by using ligand-capped IrO$_x$·nH$_2$O catalyst particles that are purified to remove monomeric anions, or by using a blocking layer that restricts access of the monomeric anions to the electrode back contact.
Chapter 3

Assessing the viability of commercial membranes for use in buffered photoelectrochemical water-splitting cells

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3.1 Introduction

Much of current solar fuels research is focused on photoelectrolysis as a means of storing the energy of sunlight as hydrogen. Catalysts are deposited on the surfaces of light-absorbing materials (typically semiconductors) in liquid-junction solar cells to lower the overpotential for water splitting. Most of these cells incorporate membranes that allow the passage of electrolyte ions between electrodes while physically separating the H$_2$ and O$_2$ gases that are produced. For these devices to meet cost-performance targets it is imperative that their catalysts and electrodes be made from inexpensive, Earth-abundant materials that are stable at the operating pH of the cell. The combination of electrode materials and membrane requirements creates serious system-level challenges for water-splitting solar cells.

Electrolytic cells require 1.23 V thermodynamically to drive the water splitting reaction. The overall cell potential ($E_{\text{cell}}$) also includes electrode overpotentials and other losses that are summarized in Equation 1,

$$E_{\text{cell}} = 1.23 \, \text{V} + \eta_{\text{anode}} + \eta_{\text{cathode}} + iR_{\text{sol}} + E_{\text{M}} + E_{\text{pH}}$$  \[3.1.1\]

where $\eta_{\text{anode}}$, $\eta_{\text{cathode}}$, $iR_{\text{sol}}$, $E_{\text{M}}$ and $E_{\text{pH}}$ are respectively the potential losses due to anode and cathode kinetics, the solution resistance, the membrane resistance and pH gradients that can develop across the membrane or near the electrode surfaces. Most research on photoelectrochemical water splitting has focused on $\eta_{\text{anode}}$ and $\eta_{\text{cathode}}$ of the electrode materials and, with notable exceptions, has not considered the system-level losses $iR_{\text{sol}}$, $E_{\text{M}}$ and $E_{\text{pH}}$. Indeed, in strongly acidic or basic electrolytes, the effects of $iR_{\text{sol}}$ and $E_{\text{pH}}$ are almost negligible. This is the case for commercial water electrolyzers, which typically operate at high current density in strongly acidic or basic electrolytes.

A recent study by Jaramillo and coworkers has benchmarked the activity and stability of water oxidation catalysts for such cells in both acidic and basic media. A good number of catalysts are available for use at high pH. However, there are none that are acid-stable, efficient, and derived from Earth-abundant elements. While there are also good catalysts for the hydrogen evolution reaction in both acidic and basic media, the best photocathode materials, such as p-type silicon, are not stable at high pH. A number of new catalysts and photoelectrode materials have recently been discovered. However, they have limited pH stability and therefore buffering electrolytes are needed in the water-splitting solar cell. In addition, the synthesis and catalytic cycle of some of these catalysts depend on buffering ions that are involved in proton transfer at the active site. Thus, the control of pH and the matching of materials with their acid- or base-stability are important (and unresolved) system-level problems for water-splitting solar cells. To provide more understanding of these system-level losses, the mass-transport induced losses in buffered electrolytic cells are explored.
3.1.1 Charge and mass transport in buffer-based electrolysers

During bulk electrolysis, the overall current is carried by the flux of ions across the electrolytic cell. The flux ($J$) of an ion ($j$) in solution is mathematically described in Equation 3.1.2

$$J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j v$$  \[3.1.2\]

where the first, second and third terms are the diffusion, migration and convection components of the flux, respectively. In Equation 3.1.2, $D_j$, $C_j$ and $z_j$ are the diffusion coefficient (in cm$^2$ s$^{-1}$), bulk concentration (in mol cm$^{-3}$) and charge of the $j^{th}$ ion in the electrolyte; $T$, $F$ and $R$ are the temperature of the cell (in K), Faraday’s (in C) and molar gas (in J mol$^{-1}$ K$^{-1}$) constants, respectively. In a cell where density gradients and convective flows ($v$) are not present or constant, as is the case in the electrolytic cells considered for this study, the last term is disregarded. Therefore, the mass-transport and overall current is governed by diffusion of ions due to concentration gradients close to the electrodes ($\nabla C_j$) and migration of ions due to electrical potential gradients across the electrolytic cell ($\nabla \phi$).

The independent contributions of diffusional and migration flux to mass-transport of ions, and therefore the overall current, in an electrolytic cell can be schematically studied in a balance-sheet analysis.24 Here, the total current ($i$) will be the sum of both diffusional and migration components. The diffusional current ($i_{\text{diff}}$) is limited to concentration gradients present near the active electrodes in the cell, whereas the migration current ($i_{\text{migr}}$) is carried by all charged species at the bulk of the electrolyte (away from the active electrodes) under an applied electric field. In a buffered electrolytic cell, unlike commercial alkaline or acidic electrolysers, protons and hydroxides are in such a low concentration that the charge carriers now are the buffering ions. Figure 3.1 shows the balance-sheet analysis for a phosphate buffer-based electrolyzer with an ideal anion-exchanger as a separator. In this analysis, the counterions (Na$^+$ and K$^+$) are not considered as charge-carriers because they cannot migrate across the cell. Furthermore, this analysis disregards any effects the membrane can have on the mass-transport of phosphate anions across the cell.

In order to maintain a steady-state current of $4e^-$ per unit time, 4 moles of HPO$_4^{2-}$ must reach the anode via a combination of diffusion and migration. The number of HPO$_4^{2-}$ moles that will reach the anode via migration is determined using its transference number ($t_j$)

$$t_j = \frac{|z_j| C_j \lambda_j}{\sum_k |z_k| C_k \lambda_k}$$  \[3.1.3\]
which is the ratio of the charge, concentration and equivalent ionic conductance (in cm²Ω⁻¹mol⁻¹) of the $j$th ion over the sum of all ions ($k$) in the electrolyte. Table 3.1 summarizes the transport numbers calculated for the balance-sheet analysis in Figure 3.1.

Table 3.1. Transport numbers for phosphate buffer anions used for balance-sheet analysis at 3.5 M total buffer concentration

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (M)</th>
<th>Charge</th>
<th>$\lambda_0 \times 10^{-4}$ m²Ω⁻¹mol⁻¹</th>
<th>$t$</th>
<th>Moles @ 4e⁻ per unit time</th>
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<tr>
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<td>114</td>
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<td>1.75</td>
<td>-1</td>
<td>36</td>
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Figure 3.1 Balance-sheet of mass-transport analysis for 3.5 M phosphate buffer electrolytic cell with an ideal anion-exchanger. The (+) and (−) symbols indicate the anode and cathode electrodes, respectively. The anion-exchanger is depicted with a vertical black dashed line, and the diffusion boundaries at the anode and cathode electrodes are shown in vertical grey dashed lines (not to scale). The orange and green arrows indicate the migration and diffusional contributions, respectively, of the phosphate anions as charge carriers.

Based on these transference numbers, over 80% of $i_{\text{migr}}$ is carried by HPO₄²⁻. However, only 1.73 moles of HPO₄²⁻ reach the anode compartment via migration. The remaining necessary moles are supplied via diffusion near the surface of the electrode (2.27 moles of HPO₄²⁻). Since all charge transport processes must be electroneutral, alongside the diffusion of HPO₄²⁻, 4.54 moles of H₂PO₄⁻ diffuse away from the electrode. A closer inspection of Figure 3.1 predicts that there will be a constant migration of buffer anions from the cathode to the anode compartment. Furthermore, as a result of this $i_{\text{migr}}$-induced buffer concentration polarization the buffering capacity on both compartments should change as electrolysis progresses. This polarization should have an impact in $E_{\text{pH}}$ and will be
quantified in this study for model electrolytic cells that utilize commercial membranes as separators and buffers as electrolytes.

### 3.2. Experimental Methods

NaH$_2$PO$_4$, K$_2$HPO$_4$, CH$_3$COONa and CH$_3$COOH were used as received to prepare 1:1 buffers. For example, for the ca. 3.5 M phosphate buffer solutions, 1.75 moles of each phosphate salt were measured and dissolved Millipore-Q (18.2 MΩ-cm) water. All buffer solutions were titrated to determine the final buffer concentration (see Table 3.2) 1.00 M sulfuric acid and sodium hydroxide solutions were prepared by dilution of as-received concentrated solvents. The commercial membranes studied were Neosepta CMX (cation exchanger), AMX (anion exchanger) purchased from Ameridia, and the Fumasep® FBM bipolar membrane (FuMA Tech GmbH). The membranes were purchased wet and stored in the recommended 0.5 M sodium chloride solution. Prior to each experiment, the membranes were equilibrated in the buffer solution for at least one hour. For the acid-base bipolar membrane experiments, the membranes were equilibrated in 1.0 M sodium sulfate solution prior to the experiment.

<table>
<thead>
<tr>
<th>Table 3.2. Buffer electrolyte concentrations</th>
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<td>Composition</td>
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<td>3.5 M phosphate</td>
</tr>
<tr>
<td>1.0 M phosphate</td>
</tr>
<tr>
<td>0.1 M phosphate</td>
</tr>
</tbody>
</table>

All reported current densities were normalized to the projected geometric area of the membrane (0.38 cm$^2$). A 4-electrode H-cell configuration was used to acquire the polarization data, which consisted of measuring the potential drop across two Ag/AgCl reference microelectrodes (Microelectrodes, Inc.) with a multimeter when a constant current was applied (PAR173 potentiostat/galvanostat) across two platinum mesh electrodes, with and without the membrane. The ionic conductivity of all the buffer electrolytes was determined from the polarization data collected without the membrane. The membrane potential ($E_M$) of the bipolar membrane was determined by subtracting the polarization data with the membrane, from the polarization curves without the membrane. To quantify the potential losses due to buffer concentration polarization ($E_{ph}$), Equation 3.2.1 was used and the pH of the anode and cathode compartments was monitored as a function of time. A FEI field-emission SEM NanoSEM 630 was used for obtaining cross-sectional scanning electron microscopy images of the bipolar membrane.

\[
E_{pH} = 56.16 \text{ mV} \times (pH_{\text{cathode}} - pH_{\text{anode}}) \tag{3.2.1}
\]

For the acid/base experiments, a NiFeO$_x$ anode electrode was prepared by electrodeposition$^{179}$ and the cell configuration is shown in Figure 3.2. A stability
study was conducted by running the electrolysis cell under high current density conditions (25 mA/cm²) for six days. Potential drops (V1-6) across all the components of the cell were measured independently and periodically with a multimeter (Figure 3.2).

**Figure 3.2.** Cell configuration for the pH–polarized bulk electrolysis with a bipolar membrane under reverse bias.

### 3.3. Results and Discussion

#### 3.3.1 $\eta_{\text{anode}}$, $\eta_{\text{cathode}}$, $iR_{\text{sol}}$ and $E_M$ potential losses

The potential losses related to anode overpotential ($\eta_{\text{anode}}$), cathode overpotential ($\eta_{\text{cathode}}$), solution resistivity ($iR_{\text{sol}}$) and membrane resistivity ($E_M$) depend on the materials, electrolyte and steady-state current density used in a photoelectrochemical cell (PEC).

In general, $\eta_{\text{anode}}$ decreases as the pH increases, as has been observed with IrO$_x$·nH$_2$O, as well as many other electrocatalysts. Similarly, $\eta_{\text{cathode}}$ decreases as the pH of the solution is lowered. Here, the increased moles of protons help reduce the mass-transport potential losses. Furthermore, increasing the total electrolyte concentration results in decreasing both $\eta_{\text{anode}}$ and $\eta_{\text{cathode}}$ due to reduced charge-transport losses across the cell. The cell dimensions as well as the solubility limit of the electrolytes account for $iR_{\text{sol}}$. Figure 3.3 shows the equivalent conductance and conductivity of phosphate buffer as a function of buffer concentration. As expected, phosphate buffer follows Kohlrausch’s law, where the equivalent conductivity of the electrolyte decreases linearly with the square root of the concentration. Equation 3.3.1 is used to determine the potential losses due to solution resistivity as a function of the cell dimensions.
Here, \( A_{elec} \) and \( A_{cell} \) are the electrode and cell areas (in cm\(^2\)), respectively, \( l \) is the distance between the electrodes i.e. pathlength (in cm), \( J \) is the operating current density (in A cm\(^{-2}\)) and \( \sigma_{sol} \) is the conductivity of the solution (in \( \Omega^{-1} \text{cm}^{-1} \)). For instance, a PEC (\( l = 0.1 \) cm, \( A_{elec} = A_{cell} = 1 \) cm\(^2\)) working at 10 mA cm\(^{-2}\) in a 1.0 M phosphate buffer solution, the corresponding \( iR_{sol} \) potential loss is 14 mV. Since \( iR_{sol} \) increases linearly with pathlength it is important to design cells with small anode–cathode distances, as well as efficient membranes or separators that maximize collection of gaseous products and minimize product crossover.

Membranes and separators act as a series resistor in a PEC since they exclude the transport of certain charged species across the cell. Therefore, in order to determine the potential loss due to the separator (\( E_M \)), the resistivity of the membrane is determined in the current range of interest. For commercial anion and cation exchange membranes (ca. 200 µm thick) the resistivity increases as a function of current density, and is in the range of 5 – 10 \( \Omega \text{ cm}^{-2} \) at 3.5 M phosphate buffer concentrations. Therefore, for a PEC operating at 10 mA/cm\(^2\) in this highly concentrated buffer \( E_M \) is about 100 mV. This value can be further decreased using thinner membranes and/or increasing the concentration of the electrolyte.

Table 3.3 provides a brief survey of typical experimentally determined values for the potential losses previously discussed. Considering the potential losses discussed so far, and choosing the materials that show the lowest potential losses at 10
mA/cm² in 1 M phosphate buffer (ηanode 260 mV, ηcathode 45 mV, iRsol 14 mV, EM 130 mV) we find that based on Equation 3.1.1: Ecell = 1.23 V + 0.45 + E_pH.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Conditions</th>
<th>Potential (mV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ηanode</td>
<td>NiFeO₅</td>
<td>1 M NaOH, 10 mA/cm²</td>
<td>380</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>NiCoO₅</td>
<td>1 M NaOH, 10 mA/cm²</td>
<td>360</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>NiO₅</td>
<td>1 M NaOH, 10 mA/cm²</td>
<td>410</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>IrO₅</td>
<td>1 M H₂SO₄, 10 mA/cm²</td>
<td>300</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M P, 25 mA/cm²; pH 8.2</td>
<td>260</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>NiB⁺₁</td>
<td>0.1 M B, 1 mA/cm², pH 9.2</td>
<td>425</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>CoP⁺₁</td>
<td>0.1 M P, 1 mA/cm², pH 7</td>
<td>280</td>
<td>139</td>
</tr>
<tr>
<td>ηcathode</td>
<td>Ni₂P</td>
<td>0.5 M H₂SO₄, 10 mA/cm²</td>
<td>110</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 M NaOH, 10 mA/cm²</td>
<td>200</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>0.5 M H₂SO₄, 10 mA/cm²</td>
<td>25</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>CoP</td>
<td>0.5 M H₂SO₄, 10 mA/cm²</td>
<td>80</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>NiMo(a)</td>
<td>1 M H₂SO₄, 10 mA/cm²</td>
<td>45</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>NiMoCo</td>
<td>1 M H₂SO₄, 10 mA/cm²</td>
<td>50</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>FeP</td>
<td>0.5 M H₂SO₄, 10 mA/cm²</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M P, 10 mA/cm²</td>
<td>102</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>MoS₂/RGO</td>
<td>0.5 M H₂SO₄, 10 mA/cm²</td>
<td>150</td>
<td>181</td>
</tr>
<tr>
<td>iRsol</td>
<td>3.5 M P,</td>
<td>l = 0.1 cm, A_idec = A_icell = 1 cm², 25 mA/cm²</td>
<td>16</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>1.0 M P,</td>
<td>l = 0.1 cm, A_idec = A_icell = 1 cm², 10 mA/cm²</td>
<td>14</td>
<td>103</td>
</tr>
<tr>
<td>EM</td>
<td>CMX</td>
<td>3.5 M P, 25 mA/cm²</td>
<td>51</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>AMX</td>
<td>3.5 M P, 25 mA/cm²</td>
<td>65</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 M P, 10 mA/cm²</td>
<td>130</td>
<td>103</td>
</tr>
</tbody>
</table>

PM: phosphate buffer; B⁻: borate buffer; RGO: reduced graphene oxide; CMX: commercial cation exchange membrane; AMX: commercial anion exchange membrane

Commercially available PEM and alkaline water electrolysers operate in the range of Ecell = 1.7 – 1.9 V (efficiency 65–72%). Therefore, any PEC operated with buffer solutions must perform in this range in order to be competitive with PV–electrolyzer systems. To attain this, the potential losses due to E_pH must be kept below 100 mV. The following sections quantitate and discuss the potential losses due to pH gradient formation across an electrolytic cell operating with buffered electrolysates and two types of commercial membranes: monopolar and bipolar.

### 3.3.2 E_pH with monopolar ion exchange membranes in buffered electrolysates


The pH polarization of the cell using two monopolar commercial membranes (CMX and AMX) were studied using constant current electrolysis of 3.5 M phosphate buffer electrolyte for 24 hours (Figure 3.4). The overall pH polarization of the cell is strongly influenced by the chemical nature of the membrane. The
cathode compartment polarizes essentially at the same rate when either a CMX or AMX membrane is used. However, the cell polarization is more symmetrical when the CMX membrane is implemented (note that now the pH lowers in the anode compartment). This is because only non-buffering ions (Na\(^+\) and K\(^+\)) are the charge carriers in this configuration and the buffering ions are continuously consumed during the electrolysis. Indeed, the pH polarization in the anode compartment is minimal when implementing the AMX membrane, because the compartment is saturated with buffering anions.

![Figure 3.4. Time-dependent pH gradient formation in electrolysis cells with AMX (blue) and CMX (red) membranes in 3.5 M phosphate buffer at 25 mA/cm\(^2\).](image)

A titration analysis of the cathode compartment after 24 hours of electrolysis with 3.5 M phosphate buffer confirms that phosphate is depleted on this side of the cell. When 8.5 meq of charge was passed in the cell, 7.6 mmol phosphate migrated through the AMX membrane. The number of equivalents that can migrate through the membrane can be calculated from the current and time using Coulomb’s law:

\[
meq_{\text{theoretical}} = \frac{it}{F} = \frac{9.5 \times 10^{-3} \text{ A} \times 8.64 \times 10^4 \text{ s}}{96,484 \text{ C/meq}} = 8.5 \text{ meq}
\]  

[3.3.2]

If the current were carried entirely by H\(_2\)PO\(_4^-\) anions, we would expect 8.5 mmol to migrate from the cathode to the anode compartment. In the case of the doubly charged HPO\(_4^{2-}\) anion, we would expect 4.25 mmol. The observed 7.6 mmol indicates that about 75% of the charge is carried by H\(_2\)PO\(_4^-\), and about 25% by HPO\(_4^{2-}\). This ion transport behavior is essentially opposite from that predicted by the balance-sheet analysis in Figure 3.1. The reason for this disparity is that the analysis does not take into account membrane effects in the mass-transport. For example, it is likely that the diffusivity of HPO\(_4^{2-}\) is decreased within the membrane because of its greater charge density in comparison to H\(_2\)PO\(_4^-\).
Equation 3.2.1 was used to determine the potential loss this pH polarization corresponds to. Table 3.4 summarizes $E_{\text{pH}}$ values corresponding to various buffer electrolyte–membrane combinations.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Membrane</th>
<th>Time (h)</th>
<th>pH$_{\text{anode}}$</th>
<th>pH$_{\text{cathode}}$</th>
<th>$E_{\text{pH}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M P$_i$, pH 6.73</td>
<td>AMX</td>
<td>6.5</td>
<td>5.55 ± 0.05</td>
<td>11.30 ± 0.03</td>
<td>340 ± 2</td>
</tr>
<tr>
<td>3.5 M P$_i$, pH 6.72</td>
<td>AMX</td>
<td>24</td>
<td>5.91 ± 0.06</td>
<td>11.33 ± 0.03</td>
<td>320 ± 2</td>
</tr>
<tr>
<td>3.5 M P$_i$, pH 6.72</td>
<td>CMX</td>
<td>24</td>
<td>2.22 ± 0.07</td>
<td>11.27 ± 0.03</td>
<td>535 ± 3</td>
</tr>
<tr>
<td>3.5 M acetate, pH 4.39</td>
<td>AMX</td>
<td>18</td>
<td>4.27 ± 0.06</td>
<td>12.53 ± 0.27</td>
<td>489 ± 11</td>
</tr>
<tr>
<td>3.5 M NaNO$_3$</td>
<td>CMX</td>
<td>0.2</td>
<td>1.33 ± 0.19</td>
<td>11.66 ± 0.21</td>
<td>611 ± 11</td>
</tr>
</tbody>
</table>

Based on these results, when a non-buffering salt is utilized a substantial pH gradient is formed within a few minutes. The incorporation of buffer ions in the electrolyte reduces the rate of pH gradient formation, and increasing the buffer concentration further (from 1.0 to 3.5 M using an AMX membrane) reduces the rate. This result is in accordance with the idea that increased buffer concentrations increases its buffering capacity near the pK$_a$ of the buffer. Furthermore, the pH gradient formation is not particular of phosphate buffer electrolytes. In the case of acetate buffer, the pH polarization rate is faster and greater than that of a phosphate buffer electrolyte. Since acetate is a negatively charged ion, its balance-sheet analysis is similar to Figure 3.1 except acetate is the only charge carrier for both the $i_{\text{migr}}$ and $i_{\text{diff}}$.

In the previously described experiments the electrolysis was run continuously for 18–24 hours, which is different from the operation of an actual photoelectrochemical cell. In order to simulate the diurnal cycle of an efficient PEC, electrolysis was cycled between 8 hours at 25 mA cm$^{-2}$ and 16 hours at zero current. The results of these experiments, comparing phosphate and acetate buffers with the AMX anion exchange membrane, are shown in Figure 3.5. Again, the largest pH excursion is on the cathode side of the cell because the buffer anions are driven by migration from the cathode to the anode, and in the case of phosphate a precipitate forms in the anode compartment. For both phosphate and acetate buffers, the “on” cycles increase the pH gradient while the “off” cycles lead to a recovery or depolarization. However, a marked difference can be seen in the third cycle. In the third “on” cycle the pH gradient increases for both buffers, but for the acetate buffer $E_{\text{pH}}$ is a factor of ca. 2 higher than for phosphate. However, after the “off” cycle a dramatic difference is observed in the recovery of the two systems. $E_{\text{pH}}$ is reduced by 118 mV for the phosphate buffer, while that of acetate is reduced by 421 mV.

The diffusion of neutral and charged ions through the membrane, which is responsible for membrane depolarization at zero current, is illustrated schematically in Figure 3.6. In the case of the phosphate buffer (Figure 3.6A), depolarization of the cell through the anion exchange membrane cannot occur by simple diffusion of acidic H$_2$PO$_4^-$ ions from the anode to the cathode because that process would be
electrogenic. Three other possible non-electrogenic processes are diffusion of neutral $H_3PO_4$, which is present in appreciable quantities below pH 4, diffusion of $Na^+H_2PO_4$ ion pairs, and simultaneous diffusion of $2H_2PO_4^-$ and $HPO_4^{2-}$ in opposite directions. In the case of acetate buffer (Figure 3.6B), the AMX is depolarized by diffusion of neutral acetic acid molecules from the anode to the cathode.

**Figure 3.5.** pH changes induced in 3 electrolysis cycles of 8 hours ON at 25 mA/cm$^2$ and 16 hours OFF at zero-current in 3.5 M phosphate–AMX and 3.5 M acetate–AMX

**Figure 3.6** Schematic of the flux of buffering ions and neutral acids via migration and diffusion across an AMX membrane of (A) phosphate buffer and (B) acetate buffer electrolytes.
3.3.3. $E_M$ and $E_{pH}$ with bipolar ion exchange membranes in buffer electrolytes


Bipolar membranes (BM) consist of a layered structure of an anion- and cation-exchange membrane layers in series. BM have been studied experimentally and theoretically for over 50 years for several applications, most notably desalination by electrodialysis. More recently, BM concepts have been implemented in the development of rectifying nanodiodes in nanofluidic devices and CO$_2$ capture.

The ionic polarization characteristics of BMs are dramatically different with fields applied in opposite directions (analogous to the electronic current in a semiconductor $p$-$n$ junction) and have been studied thoroughly.

![Figure 3.7 Bipolar membrane under (A) forward and (B) reverse bias conditions. The solid dark arrow indicates the direction of the applied voltage at the electrodes. The black dashed arrows indicate the direction of the migration of ions as a result of the applied voltage. Red dashed arrows indicate the attempted migration of ions that is impeded by the membrane under reverse bias.](image)

To illustrate the typical behavior of a BM, consider a two-electrode electrolytic cell containing a 1:1 electrolyte, $M^+X^-$ (e.g. NaCl) with a BM separating the anode and cathode compartments. Under forward bias conditions, a field is applied to drive cations through the cation exchange layer (CEL) and into the anion exchange layer (AEL), with anions migrating in the opposite direction as shown in Figure 3.7A. The accumulation of ions at the junction results in charge compensation of the layers, which allows passage of co-ions through the AEL (Na$^+$) and CEL (Cl$^-$). Under reverse bias conditions, the electric field drives out of the membrane the majority of mobile ions on both sides of the membrane and a depletion layer forms at the AEL/CEL junction (Figure 3.7B). The electric field in this region opposes the flow of ions until a threshold bias is reached that induces water dissociation to H$^+$ and OH$^-$ ions. The protons and hydroxide ions generated in the depletion region
become the charge carriers and migrate through the AEL and CEL, respectively (Figure 3.7B). Thus, under reverse bias conditions, acid and base flow into the cathode and anode compartments, respectively.

Recently, Kohl and coworkers implemented a BM in a hybrid fuel cell.\(^{197,198}\) In their experiments, the configuration of the membrane with respect to the electrodes was key to the performance of the fuel cell. Specifically, the long-term stability of the cell was enhanced under conditions in which water accumulated at the AEL/CEL junction. These results inspired the study of such membranes as potential separators for buffered electrolytic cells.

Figure 3.8 shows the membrane potential \(E_M\) of a BM as a function of applied current density and bias direction using a 3.6 M phosphate buffer electrolyte on both sides of a water electrolysis cell. Under forward bias, the BM behaves similarly to an anion-exchange membrane (AMX), although with roughly twofold higher series resistance. Referring to Figure 3.6a, under forward bias phosphate buffer anions (\(\text{HPO}_4^{2-}\) and \(\text{H}_2\text{PO}_4^-\)) are driven into the AEL from the cathode side of the cell and cross the membrane to the anode side. Simultaneously, \(\text{Na}^+\) and \(\text{K}^+\) ions migrate in the opposite direction. The effect of this is twofold. First, the buffer capacity decreases on the cathode side of the cell, and second, the cathode pH rises as a result of the water reduction reaction, which consumes protons. Secondly, the anode pH decreases because the anode reaction generates protons, although the effect on anode pH is less because the buffer concentration increases on that side.

![Figure 3.8](image_url)

**Figure 3.8** Membrane potential \(E_M\) of a BM as a function of current density under forward (black) and reverse bias (blue) conditions, with 3.6 M phosphate buffer in both the anode and cathode compartments of the cell. The potential of an AMX membrane is shown for comparison.
Using Equation 3.2.1, $E_{pH}$ values were calculated from the anolyte and catholyte pH values and are plotted in Figure 3.8. As expected, lower buffer concentrations lead to more rapid polarization and a higher value of $E_{pH}$ in the forward bias configuration. At high buffer concentration, the pH polarization under forward bias is smaller than that of a cell with an anion exchange membrane (AMX). However, the BM suffers significant blistering and buffer salt precipitation when used for extended periods of time under these conditions, especially at high buffer concentrations (Figure 3.10).

![Figure 3.9](image)

**Figure 3.9** $E_{pH}$ in various phosphate buffer concentration solutions (0.14 M, 1.00 M or 3.6 M) and membranes (BM or the anion exchange membrane, AMX) under forward or reverse bias at a constant current density of 25 mA/cm$^2$. For comparison purposes, prior results with AMX membranes are shown (marked with an asterisk).

![Figure 3.10](image)

**Figure 3.10.** Cross-sectional scanning electron microscopy of BM after 24 h bulk electrolysis in 3.6 M phosphate buffer under forward bias conditions. The accumulation of ions at the AEL/CEL junction induces the precipitation of the buffer electrolyte.
In contrast to the forward bias case, under reverse bias the membrane potential of the BM increases rapidly with current and reaches a plateau at current densities above 8 mA/cm$^2$ (Figure 3.8). As illustrated in Figure 3.7B, under these conditions the AEL and CEL are, respectively, charge-compensated by OH$^-$ and H$^+$ ions, which are generated by dissociation of water in the depletion layer. The large $E_M$ observed in the reverse bias case corresponds to the free energy needed to drive water dissociation. The internal pH in the CEL and AEL of the BM will be close to zero and 14, respectively (assuming a 1 M ion exchange capacity of each membrane layer and full dissociation of the fixed charged groups). Thus the pH difference is approximately 14 units and the potential difference is calculated to be 830 mV, in good agreement with the measured membrane potential (873 ± 20 mV) above 8 mA/cm$^2$. The H$^+$ and OH$^-$ ions generated by water dissociation are neutralized by the pH 6.5 phosphate buffer as they exit the membrane, corresponding to losses of ~385 mV and ~445 mV on the cathode and anode sides of the membrane, respectively.

The large value of $E_M$ measured in the reverse bias case implies transference numbers close to unity for H$^+$ and OH$^-$ in the CEL and AEL, respectively. Consistent with this, we observe minimal pH changes across the membrane after prolonged electrolysis. This observation suggests an alternate approach to water electrolysis with a BM cell, using acidic and basic solutions, respectively, in the cathode and anode compartments. In this case the transference numbers of H$^+$ and OH$^-$ should remain high, but the pH drops at the membrane–solution interfaces should be negligible. In previous BM literature, this configuration was used to assess the independent contributions of protons and hydroxide anions generated at the junction in the overall current density of an electrodialysis cell.$^{199,200}$

This idea is demonstrated using two good electrocatalysts (NiFeO$_x$ and Pt mesh) as anode and cathode electrodes in basic and acidic solutions, respectively (Figure 3.11). In this configuration, the cation exchange layer is facing the acidic electrolyte and Pt cathode, and the anion exchange layer faces the anode in basic solution. Since the BM is already polarized by the electrolytes ($E_{pH} = 828$ mV), water dissociation at the BM junction and overall water splitting commences at very low current densities. Under these conditions, the onset of water electrolysis occurs at 1.45 V, i.e., at an overpotential of 220 mV, which represents the sum of the overpotentials of the catalytic electrodes. At a current density of 10 mA/cm$^2$, which is typical of efficient photoelectrolytic cells, the total cell potential, corrected for solution resistance, is 1.64 V. Furthermore, the system is quite robust. During a long-term electrolysis experiment the uncorrected cell potential increased by 600 mV at 25 mA/cm$^2$ (Figure 3.12), but most of the increase could be attributed to an increase in overpotential at the Pt cathode. The $E_M$ and $\eta_{anode}$ remain essentially constant over the 140 hours experiment.
Figure 3.1. Cell voltage as a function of applied current density (black) and solution resistance-corrected cell voltage (blue). The dashed lines indicate the cell voltage at 10 mA/cm$^2$.

Figure 3.12. Long-term stability of the pH-polarized/reverse-bias BM water splitting cell. A stability study was conducted by running the electrolysis cell under high current density conditions (25 mA/cm$^2$) for six days. The cell configuration presented in Figure 3.2 was used and the potential drops across the cell components were measured periodically using a multimeter.
With solar absorbers of near-optimum bandgaps, the electrolysis cell potential at 10 mA/cm$^2$ current density corresponds to a maximum solar-to-fuel conversion efficiency in the range of 28-29%. Importantly, this configuration is compatible with acid-stable photocathode materials, such as p-Si, and Earth-abundant anode catalysts, such as NiFeO$_x$, addressing a significant problem in the design of water-splitting photoelectrochemical cells.

### 3.4. Conclusions

The viability of solar fuel production in PECs is dependent on the efficiency of the electrolysis reaction, which in turn depends on series losses in the cell. When gaseous products such as hydrogen and oxygen are made, or when organic compounds are synthesized at the cathode, a membrane or separator is likely to be needed in the PEC to prevent crossover and product loss. Spurgeon and Lewis have recently demonstrated that water electrolysis can be sustained with low resistive loss in vapor-phase electrolysis cells that resemble PEM fuel cells. However in those cells acidic membranes were used, and such membranes may not be compatible with catalysts such as CoP$_x$ and NiB$_x$, or with semiconductors that are unstable in an acidic environment.

The most problematic source of loss in buffer-based electrolysis cells is the development of a pH gradient across the membrane. At steady-state, large pH gradients ($E_{\text{pH}} = 300$ mV) develop across either anion- or cation-exchange membranes, even in concentrated buffer solutions (e.g., 3.5 M phosphate). The problem is exacerbated by migration of buffer anions across the AMX anion exchange membrane. This polarization is only partially mitigated by back-diffusion of neutral acids and bases, and thus it appears that neither kind of membrane is effective for a photoelectro-chemical cell that operates near neutral pH.

In summary, we have studied the performance and operation of BMs within the range of current densities anticipated for efficient water-splitting photoelectrochemical cells. Under reverse bias, the BM minimizes the formation of a pH gradient across the cell. However, it does so at the expense of a membrane potential, which corresponds to water dissociation to strong acid and base. Thus, the BM does not present a viable solution for buffer-based water-splitting solar cells. However, the overall losses in a BM-based cell can be minimized when strongly acidic and basic electrolytes are used on the cathode and anode sides of the cell, respectively. This finding allows for the individual optimization of anode and cathode materials and opens the door to efficient water electrolysis cells derived from known Earth-abundant materials.
Chapter 4

Temperature–, pH– and isotope–dependent effects on the kinetics of the oxygen evolution reaction catalyzed by colloidal iridium oxide films

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4.1 Introduction

The electrochemical oxygen evolution reaction (OER) has been studied mechanistically since the 1960’s.\textsuperscript{4,45,46,203} As a complex 4-proton, 4-electron oxidation process that occurs at very positive potentials where all metals are thermodynamically unstable, the OER is mechanistically complex. Over the past 20 years, our fundamental understanding of the mechanism for the oxygen evolution reaction (OER) in heterogeneous systems has increased. This has been in part due to innovations in synchrotron- and X-ray-based techniques that allow \textit{in-situ} probing of electrochemical systems. For instance, kinetically-relevant oxidation states have now been unambiguously determined for Co, Ir and Mn-based catalysts.\textsuperscript{79,142,204-208} Despite its low terrestrial abundance, iridium oxide is of particular interest because it exhibits high stability and low overpotentials for OER (less than 300 mV) across a broad range of pH. On this study, we focus on providing a more in-depth understanding of proton transfer in the catalytic mechanism of the OER on iridium oxide nanoparticle films. A survey of previous spectroelectrochemical work and hydrogen/deuterium kinetic studies on iridium oxide catalysts is presented prior to discussing the preliminary results derived from this solely electrochemical study.

Kötz \textit{et al.} performed an \textit{ex-situ} x-ray photoelectron spectroscopy (XPS) study on iridium oxide films for OER in acidic media.\textsuperscript{207} Based on their results, a model for the corrosion and OER mechanism was proposed to incorporate various deprotonation steps and changes in the iridium oxidation state from +III to +VI (Figure 4.1). Potential-dependent XPS spectra show a shift in the O1s peak upon increasing the potential to more anodic values, which suggests a transition from oxygen being bound as a hydroxide to an oxide.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure41.png}
\caption{Proposed catalytic cycle for oxygen evolution on iridium oxide thin films. Adapted from reference 207.}
\end{figure}

Using conventional redox titrations, Harriman and coworkers determined that colloidal hydrated iridium oxide colloids (IrO\textsubscript{x}-nH\textsubscript{2}O) have, as prepared, an iridium
formal oxidation state of Ir$^{3.2+}$. Moreover, their UV-Vis spectroelectrochemical experiments show that full oxidation of the iridium oxide colloid (not just its surface) to Ir$^{4+}$ is necessary prior to any oxygen evolution. These results are consistent with the ex-situ XPS study and suggest that Ir$^{4+}$ is the starting point of the catalytic cycle.

Lengeler and Hüppauff did an in-situ extended x-ray absorption spectroelectrochemical study on anodically formed iridium oxide films to assess valence changes of iridium as a function of applied potential in acidic media. Under these conditions, the oxidation state of iridium progressively changes from Ir$^{3+}$, prior to the onset of OER, up to Ir$^{4.8+}$ at overpotentials greater than 220 mV. The fractional oxidation state of iridium under oxygen evolution conditions suggests the coexistence of Ir$^{3+}$, Ir$^{4+}$ and Ir$^{5+}$ species at the surface of the iridium oxide films and supports the proposed mechanism in Figure 4.1. Nilsson and coworkers have recently expanded on this work using in-situ ambient pressure synchrotron-XPS measurements on iridium oxide nanoparticle films. Spectral changes of the Ir 4f$_{5/2}$ and Ir 4f$_{7/2}$ peaks from the open-circuit voltage to a potential in which oxygen evolution occurs were used to assess changes in the oxidation state of iridium and correlate them to the mechanism of the OER. Their results show that, under oxygen evolving conditions, there is a simultaneous increase of Ir$^{5+}$ at the surface of the catalyst and a decrease in the concentration of surface hydroxides. Moreover, their study suggests that the OER occurs on single Ir sites that favor the formation of OOH intermediates. These results are also consistent with recent work in-situ infrared spectroscopy of photochemically oxidized iridium oxide nanoparticles by Frei and coworkers, in which they demonstrate the formation of a stable Ir$^{2+}$–OOH moiety under photochemical oxygen evolution at conditions near neutral pH. Similarly, Minguzzi et al. show the presence of both Ir$^{5+}$ and Ir$^{3+}$ at potentials where oxygen evolution occurs using in-situ spectroelectrochemical X-ray absorption near edge structure of iridium oxide films in acidic media. This suggests an OER mechanism of a fast 2$e^-$ transfer step between Ir$^{5+}$ and Ir$^{3+}$ that catalyzes oxygen evolution.

Taking all these studies together, we can conclude, somewhat unsurprisingly, that a combination of Ir$^{3+}$, Ir$^{4+}$ and Ir$^{5+}$ sites are involved in the catalysis of the OER. Furthermore, under near neutral conditions, iridium catalysts seem to favor the formation of a hydroperoxo intermediate. These studies, however, provide little conclusive information about proton transfer during the various steps of the OER catalytic cycle. In this regard, measuring changes in the rate of the OER as a function of hydrogen/deuterium isotopes can be a more useful approach.

4.2 Experimental Methods

All chemical used were used as received from commercial sources without further purification or treatment: K$_2$IrCl$_6$ (Aldrich, technical grade), NaOH solution (Fluka, 1 M), H$_2$SO$_4$ (EMD, ACS grade, 95.0–98.0%), Na$_2$SO$_4$ (Sigma-Aldrich, ACS
reagent, 99+%), D$_2$SO$_4$ (Aldrich, 96–98 wt% in D$_2$O, 99.5 atom% D), D$_2$O (Aldrich, 99.9 atom % D). All the aqueous solutions were prepared in Millipure water (18.2 MΩ-cm). The deuterated sulfuric acid solutions were prepared immediately prior to the execution of the experiment by taking the appropriate aliquot of D$_2$SO$_4$ and dissolving in D$_2$O with the appropriate amount of Na$_2$SO$_4$ as supporting electrolyte. For the sake of simplicity, the electrolyte solutions will be described throughout the text using their measured pH rather than chemical composition. Table 4.1 presents the composition of the various electrolytes as a function of pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.7</td>
<td>1.0 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1 M H$_2$SO$_4$ + 0.9 M Na$_2$SO$_4$</td>
</tr>
<tr>
<td>2.0</td>
<td>0.01 M H$_2$SO$_4$ + 0.99 M Na$_2$SO$_4$</td>
</tr>
<tr>
<td>3.2</td>
<td>0.001 M H$_2$SO$_4$ + 0.999 M Na$_2$SO$_4$</td>
</tr>
</tbody>
</table>

Iridium hydroxide solutions were prepared as described before and used to anodically deposit colloidal iridium oxide films on rotating disk electrodes (RDE). Briefly, 0.05 mmoles of K$_2$IrCl$_6$ were dissolved in 50 mL of 6 mM sodium hydroxide solution (prepared by dilution from 1 M NaOH solution), and quickly heated to 70 °C followed by immediate cooling in an ice bath. The colorless solution was stored at 2 °C until used for depositions. All electrolyte sulfuric acid solutions were prepared by dilution of concentrated sulfuric acid and sodium sulfate was added as a supporting electrolyte to maintain the ionic strength of the electrolyte constant.

Thin films of IrO$_x$·nH$_2$O colloids were anodically deposited on gold rotating disk electrodes (Au RDE, 0.126 cm$^2$ geometric area). Prior to each deposition the Au RDE was mechanically polished using 1.0, 0.3 and 0.05 micron alumina slurries (Buehler) in a Microcloth polishing pad (Buehler) for 1 minute with each slurry sequentially, then sonicated in 6 M HCl for 10 min, nanopure water 10 min, isopropanol 10 min, acetone 10 min, and again in nanopure water for 10 min. The as-prepared 1 mM Ir monomer solution was used to deposit the iridium oxide films at a potential of +1.0 V vs. Ag/AgCl for 15 min at a rotation rate of 800 rpm. The coverage of these films was, on average, 12 ± 2 mC/cm$^2$.

A circulating, constant-temperature bath (VWR 1160 recirculating chiller) connected to a jacketed bulk electrolysis cell (BAS, Inc. MR–1194), maintained the temperature of the electrolyte solution within ±1 °C. Temperature-dependent measurements were conducted isothermally, i.e. the Ag/AgCl reference electrode was in the same cell and kept at the same temperature as the working electrode. All potentials are converted to overpotential (η) and corrected by accounting for the change in the standard reduction potential of the H$_2$O/O$_2$ and Ag/AgCl redox couples as a function of temperature. For instance, at 25 °C and pH 0, $E (H_2O/O_2) =$
1.229 V vs. NHE and \( E^\circ (Ag/AgCl) = 0.222 \text{ V vs. NHE} \); therefore an applied potential of +1.0 V vs. Ag/AgCl corresponds to

\[
\eta = (+1.0 \text{ V vs. Ag/AgCl} + 0.222 \text{ V vs. Ag/AgCl}) - 1.229 \text{ V vs. NHE} = -0.007 \text{ V} \tag{4.2.1}
\]

However, at 15 °C and pH 0, \( E^\circ (H_2O/O_2) = 1.242 \text{ V vs. NHE} \) and \( E^\circ (Ag/AgCl) = 0.229 \text{ V vs. NHE} \); and now, an applied potential of +1.0 V vs. Ag/AgCl corresponds to \( \eta = -0.013 \text{ V} \). The temperature dependence of the standard potential of \( H_2O/O_2 \) and Ag/AgCl redox couples is determined by their temperature coefficients. The temperature coefficients for the \( H_2O/O_2 \) and Ag/AgCl redox couples are –0.8456 mV/°C and –0.685 mV/°C, respectively.²¹¹

Recently, McCrory et al. suggested that LSV data collected at 10 mV/s scan rate and 1600 rpm rotation rate of the RDE are in good agreement with 30 s duration, steady-state potential- and current-step experiments under the same rotation conditions.⁹⁰ Therefore, the Tafel plots in this study were generated using data of slow linear sweep voltammograms (LSV) at a scan rate of 5 mV/s and 1600 rpm in different electrolytes and temperatures. All Tafel plots were corrected for the uncompensated resistance between the reference and working electrode (7 ± 3 Ω for all electrolytes in this study). Prior to each LSV measurement, the cell was allowed to equilibrate at the desired temperature while saturating the solution with \( O_2 \) for 30 min. The reported current densities in this chapter are normalized to the geometric area of the Au RDE. All electrochemical measurements and colloid depositions were performed on a Pine Instruments Bipotentiostat AFCBP 1.

4.3. Results and Discussion

The pH- and temperature-dependent electrochemistry of colloidal iridium oxide films is shown in Figure 4.2. All LSV traces show the catalytic behavior of the films in the exponential increase of the current density as a function of overpotential. At current densities greater than 75 mA/cm², the current response becomes more linear suggesting high ohmic losses due to solution resistivity. Moreover, Figure 4.2 shows that, in general, the overpotential for the OER decreases as a function of temperature. This is not unexpected because an increase in temperature usually produces greater reaction rates (measured here as current densities). In the particular case of films at pH 0.8, this trend was not observed because of the poor stability of the films. Experiments are underway to correct this problem. This issue notwithstanding, valuable information about the kinetics of the OER and various figures of merit for the iridium oxide films can be obtained from these experiments.
Figure 4.2 Linear sweep voltammograms (5 mV/s) of colloidal iridium oxide films at various temperatures and electrolytes (A) pH –0.7, (B) pH 0.8, (C) pH 2.0, and (D) pH 3.2. The gray outline of the traces shows the standard deviation of three independent LSV experiments at each temperature.

A current density of 10 mA/cm² has been posed as an appropriate figure of merit for electrocatalysts because it represents the approximate current density expected of a 10% efficient solar-to-fuel device at 1 sun illumination. Table 4.2 summarizes the temperature and pH-dependent overpotentials for OER at a current density of 10 mA/cm² for the colloidal iridium oxide films. It is important to point out that these are short-term overpotentials and further experiments are needed to determine the stability of these films at this current density. However, the LSV traces presented in Figure 4.2 are the average of the three voltammograms of the same deposited film and their consistency points to the robustness of the films even after being slowly ramped to very high current densities.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>pH –0.7</th>
<th>pH 0.8</th>
<th>pH 2.0</th>
<th>pH 3.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>268</td>
<td>226</td>
<td>221</td>
<td>242</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>260</td>
<td>207</td>
<td>220</td>
</tr>
<tr>
<td>40</td>
<td>250</td>
<td>-</td>
<td>187</td>
<td>207</td>
</tr>
<tr>
<td>60</td>
<td>205</td>
<td>161</td>
<td>-</td>
<td>182</td>
</tr>
</tbody>
</table>
Potential-dependent activation energies not only indicate the kinetic energy barrier for the OER, but also allow the determination of the transmission coefficient \((a_a)\), an important kinetic parameter in Tafel analysis (see section 4.3.1). These activation energies \((E_a)\) were determined from the slopes of Arrhenius plots at different overpotentials. Figure 4.3A shows representative plots from which the data were extracted and Appendix B provides all the plots for reference. The pH-dependence of the \(E_a\) is presented in Figure 4.3B. The general trend is that the energy barrier decreases with increasing pH. Furthermore, \(E_a\) always reaches a maximum between 200–300 mV overpotential. These values are quite small but within the same range of previously reported values for \(\text{Pt}_{4.5}\text{Ru}_{4}\text{Ir}_{0.5}\) and \(\text{PtIr}\) under similar conditions (Figure 4.3B).\(^{48}\) A possible explanation for the low \(E_a\) could be to uncorrected overpotential values for series solution resistance \(iR\) losses. Figure 4.4 shows a comparison of Arrhenius plots and the corresponding extracted \(E_a\) values. There are slight changes in the slopes, but not enough to affect \(E_a\) significantly.

Although the overpotential range available for data collection is decreased, the effect of \(iR\) correction is not evident on the \(E_a\). The values of \(a_a\) in Table 4.3 were determined by taking the negative of the slope from a linear regression analysis of the plots in Figure 4.3B at overpotentials greater than 300 mV (those relevant for Tafel analysis) and dividing by Faraday’s constant.

**Figure 4.3** (A) Representative potential-dependent Arrhenius plots at pH 2.0 and (B) Potential-dependent activation energies of colloidal iridium oxide films at various pH and, \(\text{Pt}_{4.5}\text{Ru}_{4}\text{Ir}_{0.5}\) and \(\text{PtIr}\) in 0.5 M H\textsubscript{2}SO\textsubscript{4}.\(^{48}\)

**Table 4.3** Transfer coefficients determined from potential-dependent activation energies

<table>
<thead>
<tr>
<th>pH</th>
<th>Slope (kcal/mol mV)</th>
<th>Slope (kJ/mol V)</th>
<th>(a_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−0.7</td>
<td>−0.0168</td>
<td>−69.9</td>
<td>0.73</td>
</tr>
<tr>
<td>2.0</td>
<td>−0.00296</td>
<td>−12.3</td>
<td>0.13</td>
</tr>
<tr>
<td>3.2</td>
<td>−0.00362</td>
<td>−15.1</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Figure 4.4 (A) Representative potential-dependent Arrhenius plots at pH 2.0 with and without \(iR\) correction to the overpotential and (B) Potential-dependent activation energies of colloidal iridium oxide films at pH 2.0 with and without \(iR\) correction to the overpotential.

The reaction order \((\rho)\) with respect to the proton concentration is defined and estimated by Equation 4.3.1. Figure 4.5 shows the plots used to extract the slopes and the reaction order with respect to the proton concentration summarized in Table 4.4.

\[
\rho = -\left(\frac{\partial \log j}{\partial a_{H^+}}\right)_{E,T} = -\frac{1}{2.303} \left(\frac{\partial \ln j}{\partial a_{H^+}}\right)_{E,T} \tag{4.3.1}
\]

Figure 4.5 pH-dependence of the current density at different overpotentials and temperatures (A) 15°C, (B) 40°C and (C) 60°C.

Although these reaction orders are very small, fractional reaction orders with respect to protons have been reported for hematite films used for OER under alkaline conditions. Note that even when \(iR\)-corrections to the overpotential are taken into account, the reaction order remains small and within the standard deviation of the uncorrected values (Table 4.4). Such small reaction orders suggest that the reaction rate for the OER on these iridium oxide films is not influenced by
changes in pH. Therefore, the rate of OER in these colloidal iridium oxide films can be estimated by Equation 4.3.248

\[ i_k = nFAl[H^+]^{0.1} \exp \left( \frac{\alpha_{\ell}F\eta}{RT} \right) \approx nFAl \exp \left( \frac{\alpha_{\ell}F\eta}{RT} \right) \]  

[4.3.2]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>200 mV</th>
<th>250 mV</th>
<th>300 mV</th>
<th>350 mV</th>
<th>400 mV</th>
<th>Average ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 slope ρ</td>
<td>0.3262</td>
<td>0.4165</td>
<td>-0.1893</td>
<td>-0.1675</td>
<td>-0.1261</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>40 slope ρ</td>
<td>0.3347</td>
<td>0.2006</td>
<td>-0.097</td>
<td>-0.2163</td>
<td>-0.2469</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>60 slope ρ</td>
<td>0.1234</td>
<td>-0.0864</td>
<td>-0.2064</td>
<td>-0.2482</td>
<td>-0.2453</td>
<td>0.09 ± 0.03</td>
</tr>
<tr>
<td>15* slope ρ</td>
<td>0.3942</td>
<td>-0.182</td>
<td>-0.1913</td>
<td>-0.3505</td>
<td>-0.3285</td>
<td>0.11 ± 0.04*</td>
</tr>
</tbody>
</table>

Notes: *values extracted from iR-corrected overpotentials

4.3.1 Tafel analysis

The LSV data were transformed to obtain potential-dependent Tafel slopes (Figures 4.6, 4.7 and 4.8). In this representation (the first-derivative of the Tafel plot), the lack of a constant Tafel slope at any potential range is evident.

Figure 4.6 Average potential-dependent Tafel slope of iridium oxide films at 15 °C in various pH electrolytes. All plots are corrected for solution series resistance (iR). The gray error bars represent the standard deviation of three independent measurements of the slope at each potential.
Figure 4.7 Average potential-dependent Tafel slope of iridium oxide films at 40 °C in various pH electrolytes. All plots are corrected for solution series resistance ($iR$). The gray error bars represent the standard deviation of three independent measurements of the slope at each potential.

Figure 4.8 Average potential-dependent Tafel slope of iridium oxide films at 60 °C in various pH electrolytes. All plots are corrected for solution series resistance ($iR$). The gray error bars represent the standard deviation of of three independent measurements of the slope at each potential.

The transfer coefficient ($\alpha_a$) was determined using Equation 4.3.3 using the local minimum Tafel slopes identified from each plot. Table 4.5 provides a summary of these results.
Table 4.5 Temperature- and pH-dependent transfer coefficient as determined from local minima of the potential-dependent Tafel slope plots of iridium oxide films under oxygen evolution conditions

<table>
<thead>
<tr>
<th>pH</th>
<th>Tafel slope (mV/dec)</th>
<th>αₐ</th>
<th>Tafel slope (mV/dec)</th>
<th>αₐ</th>
<th>Tafel slope (mV/dec)</th>
<th>αₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>–0.7</td>
<td>78 ± 2</td>
<td>0.73 ± 0.02</td>
<td>47 ± 2</td>
<td>1.32 ± 0.06</td>
<td>43 ± 7</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>0.8</td>
<td>103 ± 5</td>
<td>0.56 ± 0.03</td>
<td>105 ± 30</td>
<td>0.6 ± 0.2</td>
<td>91 ± 17</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>2.0</td>
<td>116 ± 2</td>
<td>0.493 ± 0.008</td>
<td>90 ± 1</td>
<td>0.690 ± 0.008</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.2</td>
<td>144 ± 2</td>
<td>0.397 ± 0.006</td>
<td>99 ± 4</td>
<td>0.63 ± 0.03</td>
<td>80 ± 3</td>
<td>0.78 ± 0.03</td>
</tr>
</tbody>
</table>

Although the Tafel slopes obtained in this study cannot be used to obtain precise information about the *rds* of the OER in these films, it presents the fact that, under these conditions, αₐ is also potential dependent. Figure 4.9 shows the change in αₐ as a function of overpotential and temperature. Similarly to the results in Table 4.5, αₐ increases as the pH is lowered. Moreover, αₐ reaches a maximum, if at all, at the same point in which the Tafel slope is at a minimum. It is important to recall that αₐ is related to symmetry factor β, which is associated to the position of the transition state of an electron-transfer reaction as well as the shape of the potential energy profiles at this transition state, through Equation 4.3.4:

$$\alpha_a = \frac{2.303RT}{F} \left( \frac{\partial \log j}{\partial E} \right)_{pH}$$

[4.3.3]

$$\alpha_a = \frac{n_p}{\nu} + n_q \beta$$

[4.3.4]

where $n_p$ is the number of electrons transferred prior to the *rds*, $\nu$ is the stoichiometric number and indicates how many times the *rds* must occur in order to complete a full cycle, $n_q$ is the number of electrons transferred in the *rds*, and $\beta$ the well-known symmetry factor. Although, the value of $\beta$ is experimentally determined to usually be $\frac{1}{2}$ and potential-independent, there have been instances in which this is not the case. In 1-electron, homogeneous systems, the potential-dependence of the Tafel slope and $\beta$ suggest a high reorganization energy ($\lambda$) per mole of the reactant specie.

Based on previous theoretical work by Savéant and Hammes-Schiffer, Dawlaty and Haghighat propose that the potential-dependence of $\beta$ in heterogeneous coupled electron- and proton-transfer steps is related to the chemical nature of the transition state, *i.e.* how much contribution of protonic and electronic states is evident in the transition state. For example, a higher potential-dependence of $\beta$ is expected for a transition state that has more electronic than protonic character. This potential-dependence will, in turn, be reflected in αₐ for multi-step heterogeneous electron-transfer reactions.
Figure 4.9 Average potential-dependent transfer coefficients of iridium oxide films at various temperatures and pH. All plots are corrected for solution series resistance ($iR$). The gray error bars represent the standard deviation of the slope at each potential. The general trends are 1) $\alpha_a$ reaches a maximum and decreases as the potential is increased, and 2) at lower pH values, $\alpha_a$ is greater.

The iridium oxide films in this study show no pH-dependence on the reaction rate, as well as a strong potential-dependence of $\alpha_a$. Taken together, these results suggest that even though protons are involved in the OER, an electron-transfer step is rate limiting for the OER in these films.

4.3.2 Hydrogen/deuterium kinetic isotope effect

Preliminary hydrogen/deuterium kinetic isotope effect (KIE) experiments were done on similarly prepared iridium oxide nanoparticle films. Briefly, iridium oxide nanoparticles are synthesized by an acidic condensation method and electroflocculated (deposited as films) onto a Au RDE at an anodic potential of +1.3 V vs. Ag/AgCl. These films are less active than those previously discussed with an average overpotential for the OER of (0.36 ± 0.02) V at 10 mA/cm$^2$ at all temperatures tested in 1 M H$_2$SO$_4$, as determined from the linear sweep voltammograms (LSVs) in Figure 4.10.

Figure 4.10 Linear sweep voltammograms (5 mV/s) of colloidal iridium oxide films, prepared by an acidic condensation method and electroflocculation at 1.3 V vs. Ag/AgCl, at various temperatures.
The potential- and temperature-dependence of the KIE on these iridium oxide films was determined by taking the ratio of the measured current in 1 M H₂SO₄/H₂O and 1 M D₂SO₄/D₂O electrolytes (Figure 4.11). The general trend is that the KIE is constant at low overpotentials (prior to the onset of the OER), increases up to a maximum (different at different temperatures), and decreases until it reaches a plateau.

![Figure 4.11](image)

**Figure 4.11** Temperature-dependent kinetic isotope effect on the oxygen evolution reaction current measured for iridium oxide films.

To date, only three reports are available on the H/D KIE of heterogeneous iridium oxide catalysts for the OER. Norris *et al.* reported a KIE of 1.0 on photochemically oxidized iridium oxide colloids in silica buffer.²¹⁹ These results suggest (similarly to the results on this study) that proton transfer does not limit the rate of the OER on the iridium oxide colloid. Blakemore *et al.* reports on the KIE of iridium oxide films prepared from electrochemical decomposition of various organic and inorganic precursors as 2.8 ± 0.1 in unbuffered 0.1 M KNO₃.¹¹⁶ In this report,¹¹⁶ it is suggested that a KIE of 2.8 is consistent with the formation of a hydroperoxo species as rate-limiting as reported by Frei and coworkers.⁸⁴ In this study, except for at 25 °C, all KIE traces reach a maximum around 2.7. The temperature-dependence of the KIE can be diagnostic for a proton tunneling mechanism.²²⁰ Furthermore, Hammes-Schiffer and coworkers have theoretically studied the temperature-dependence of electrochemical KIE in proton-coupled electron-transfer systems (PCET).²²¹ The temperature-dependence of the KIE differs from systems that are in the normal (KIE decreases with increasing T) and inverted (KIE increases with increasing T) Marcus region. Based on the data presented in Figure 4.11, no temperature-dependence is obvious or can be speculated. It is possible that utilizing the ratio of exchange current densities (i₀) extracted from temperature-dependent Tafel slopes a clearer trend in the KIE is observed. Finally, the consistent changes of the measured KIE as a function of overpotential suggests that the mechanism and kinetically relevant intermediates of the OER change as a function of reaction rate on the colloidal iridium oxide films.
4.4 Summary and Future works

This chapter presents an electrochemical study of temperature, pH and hydrogen/deuterium isotope effects on the rate of the OER on colloidal iridium oxide films. Altogether, the results suggest that an electron-transfer step is rate-limiting for the OER in these films. The lack of pH-dependence of the rate for OER on the iridium oxide films is surprising, especially since a KIE is observed. It is likely that the discrepancy is due to the fact that all the data were extracted from slow LSVs, instead of steady-state controlled-current and controlled-potential measurements. The lack of a constant Tafel slope at any potential range is contradictory to previously reported\textsuperscript{129} Tafel slopes (from steady-state controlled potential measurements) for these colloidal iridium oxide films. Although extremely time-consuming, steady-state measurements could provide more precise measurements, especially in these highly active iridium oxide films. Indeed, the series losses due to the high current densities achieved in these films limit the overpotential range available for the study (Figure 4.12).

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure412.png}
\caption{Linear sweep voltammogram (5 mV/s) of a colloidal iridium oxide film at 60 °C and pH 0.7 under OER conditions with and without iR corrections to the overpotential.}
\end{figure}

There are various ways in which this study can be improved so that the extracted figures of merit are more valuable and truly provide useful insights into the mechanism of the OER in these iridium oxide films:

1) As suggested earlier, the combined use of steady-state controlled-current and controlled-potential measurements could prove more useful to extract kinetic parameters.

2) In general, the standard deviation in the data is less at lower temperatures. It is possible that at higher temperatures there is additional influence from temperature-induced convection and increases the variability in the
measured currents. The incorporation of sealed jacketed thermo-regulated cells might help mitigate this issue. Also, performing the electrochemical measurements non-isothermally, between the reference and working electrode, may help reduce errors in this regard.

3) Since the films are so catalytically active, a thickness-dependent study on the activity of the iridium oxide films could allow the determination of the optimal thickness for a kinetic study, in which there is a balance of high activity with minimized series $iR$ losses. A recent report by Savéant and coworkers explored the kinetics of proton and electron transfer within electrocatalytic films for the OER on rotating disk electrodes. This study incorporates Tafel analysis as well as modeling of kinetic currents in order to extract information about the rate of diffusion of the electron and protons during the OER across the catalytic film. The colloidal iridium oxide films in this study are amorphous, hydrated and electrically conducting. If such proton and electron transfer processes are occurring, (it is very likely that they are) it further complicates the kinetic analysis of the OER in these iridium oxide films. It will be valuable to apply a similar approach (using steady-state measurements) to understand the rates of proton and electron transfer on iridium oxide films. Since a KIE $\neq 1.0$ was measured for the iridium oxide films but no pH-dependence to the rate of the reaction, it could suggest that proton transfer within the film is occurring.

4) The reproducibility of the temperature-dependence of the hydrogen/deuterium KIE must be verified after the experimental method, i.e. the thickness of the electrocatalytic film, is optimized for regular aqueous electrolytes.
Chapter 5

Conclusions and Future Works
As a whole, this dissertation has focused on various model systems that have allowed a deeper understanding of the challenges on executing the water-splitting reaction efficiently.

On Chapter 2, we were able to characterize and assess the detrimental effect of monomeric iridium(III/IV) species on the efficiency of iridium oxide-based water-splitting photoelectrochemical cells. However, these monomeric species are necessary for linking the iridium oxide nanoparticles to metal oxide semiconductors. Current research is directed towards understanding the interfacial interaction of these monomeric iridium(III/IV) species onto metal oxide supports. A combination of calorimetric and in-situ environmental electron microscopy techniques, and density function theory (DFT) calculations suggest that reduced sintering of metal/metal oxide nanoparticles on metal oxide supports at high temperatures depends on how exothermic the heat of interfacial interaction between the nanoparticle precursor and the metal oxide support. Moreover, extending from these studies, current research is focused in utilizing these monomeric(III/IV) iridium species as single-site co-catalysts in water-splitting dye-sensitized solar cells. Preliminary results suggest that such cells outperform previously reported water-splitting dye-sensitized photoelectrochemical cells. Ongoing work is focused at elucidating the structure of the iridium catalyst after attachment to the titania support, as well as understanding the kinetics of charge-transfer on these photoanodes.

In a more device-development driven approach, Chapter 3 presents the first systematic study of series losses in model buffer electrolyte–membrane electrolytic cells. Here, the potential losses due to pH gradients were found to be the most detrimental, with losses greater than 300 mV using monopolar commercial ion exchange membranes. The pH gradients can be partially mitigated by back-diffusion of neutral buffer species and non-electrogenic ion transport processes. In the case of commercial reverse-bias bipolar membranes, an induced pH gradient using highly acidic and highly basic aqueous solutions (in the cathode and anode compartment, respectively) lowers the overall cell potential for water-splitting. This configuration allows the de-coupled optimization of anode and cathode materials. This flexibility is particularly useful for the optimization of cathode materials that are used for the electroreduction of carbon dioxide. Current work is focused on developing gas-diffusion electrolytic cells that incorporate bipolar membrane–electrode assemblies (BMEAs) that use CO₂ and humidified air as feedstock.

In Chapter 4, a thorough electrochemical study was performed to characterize the effect of multiple variables (pH, temperature and hydrogen/deuterium isotope) on the kinetics of the oxygen evolution reaction on colloidal iridium oxide films. Although inconclusive, the study provides a good platform to build from for characterizing thinner films of iridium oxide, as well as other oxygen evolution reaction electrocatalysts.
Appendix A

Rotating ring-disk electrochemistry: A case study of N(5)-ethylflavinium ion as an electrocatalyst for water oxidation

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A.1. Summary

This Appendix is focused in presenting a brief overview of the theory behind rotating disk electrochemistry (RDE), and from this, expand to rotating ring-disk electrodes (RRDE). For a very rigorous mathematical treatment of these techniques, the reader is referred to Chapter 9 of Bard and Faulkner, *Electrochemical Methods*.24 As a case study, the characterization of N(5)-ethylflavinium ion as a water oxidation electrocatalyst using RRDE is presented.

A.2 Flux of electroactive species in a rotating electrode experiment

The flux of species \( J_j \) in an electrochemical cell is described mathematically by (also Equation 3.1.2):

\[
J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j v \tag{A.2.1}
\]

where the first, second and third terms are the diffusion, migration and convection components of the flux, respectively. In a rotating electrode experiment, the convection component of the flux is controlled by the rotation rate of the electrode. Furthermore, the effect of electrical potential gradients \( \nabla \phi \) to the flux of electroactive species is estimated to be negligible by employing supporting electrolytes at concentrations greater than 0.1 M. Under these conditions, the flux equation is simplified to

\[
J_j = -D_j \nabla C_j + C_j v \tag{A.2.2}
\]

where \( v \) is the velocity vector and represents the motion of the solution. Von Karman and Cochran described the profile of the velocity of a fluid near a rotating disk by solving the hydrodynamic equations under steady-state conditions and laminar flow.22 Concisely, the rotating electrode drags the fluid towards its surface, and due to centrifugal force, the fluid moves radially outward from the center of the electrode (Figure A.1B).

The simplest mathematical treatment of Equation A.1.2 is based on the diffusion layer approach. Here, it is assumed that convection maintains the concentrations of all species uniform and equal to the bulk \( (C_b) \) beyond a certain distance \( (\delta) \) from the surface of the electrode. The thickness of \( \delta \) is determined by the rotation rate of the electrode \( (\omega, \text{rad/s}) \) and the kinematic viscosity of the solvent \( (\nu) \), and within it, mass-transport occurs mainly by diffusion (Equation A.1.3, Figures A.1C).

\[
\delta = 1.61 D_j^{1/3} \nu^{1/6} \omega^{1/2} \tag{A.2.3}
\]
Figure A.1 (A) Rotating disk electrode (RDE) construction; (B) Schematic of the resulting flow of solvent to and at the surface (blue and white arrows, respectively) of the RDE upon rotation at a constant $\omega$. (C) Schematic depiction of the convection- and diffusion-controlled ($\delta$) regions close to the surface of the RDE. The concentration of electroactive species is constant and equal to the bulk solution in the convection-controlled region. Within $\delta$, a gradient describes the unequal distribution of electroactive species close to the surface of the RDE.

### A.3 Rotating disk electrochemistry

In 1962, Benjamin Levich developed the theory of the rotating disk electrode and provided the first mathematical treatment of convection and diffusion towards a rotating electrode. The Levich equation describes the relationship between the mass-transport limited current of an electrochemical half-reaction ($i_l$) to the properties of the electroactive species and the rotation rate of the electrode (Equation A.3.1, for a cathodic reaction)

$$i_{lc} = 0.620 nFAD_O^{2/3}v^{-1/6}C_O\omega^{1/2} \quad [A.3.1]$$

where $n$, $F$, $A$, $D_O$ and $C_O$ are the number of electrons transferred, Faraday’s constant, the area of the RDE, the diffusion coefficient of the oxidized species, the bulk concentration of the oxidized species and the rotation rate of the RDE in rad/s, respectively. Since $i_{lc}$ is a linear function of the concentration of electroactive species, it is a robust approach for experimentally determining the diffusion coefficient of electroactive species in solution.
For a more detailed overview of the applications of RDE and its rigorous derivations the reader is referred to Bard’s book, Chapter 9.

**A.4. Rotating ring-disk electrochemistry**

An immediate drawback of the RDE is that reversal techniques (e.g. cyclic voltammetry, CV) are not as information-rich as in a traditional CV in a quiescent solution. This is due to the fact that the products generated at the RDE are constantly being pushed away from the surface of the electrode. In order to circumvent this, an additional electrode can be added in close proximity to the disk. A rotating ring-disk electrode (RRDE) is a double working electrode system in which the outer ring electrode can be used to monitor what is being generated at the disk (Figure A.2).

There are two common types of RRDE experiments, which are *collection* and *shielding* experiments. In a collection experiment, the products generated at the inner disk are monitored, and sometimes even quantified, at the outer ring electrode (Figure A.2B). During a shielding experiment, the flow of electroactive species to the outer ring electrode is perturbed by the reaction at the inner disk electrode. For either experiment, it is important to establish and understand how the currents generated at the inner disk ($i_D$) affect and/or control the measured current at the ring ($i_R$). The steady-state convective-diffusion equations for the RRDE are solved using Laplace transforms and their results are given in terms of Airy functions. The
rigorous mathematical solutions correlate $i_D$ and $i_R$ to a quantity $N$, namely the collection efficiency (Equation A.4.1)

$$N = \frac{i_R}{i_D}$$  \hspace{1cm} [A.4.1]

which depends solely on the geometry of the RRDE ($r_1$, $r_2$ and $r_3$, see Figure A.2B). It is a more common approach to determine the collection efficiency of the RRDE experimentally.

### A.4.1 Calibration of RRDE and collection efficiency determination

The collection efficiency, $N$, of an RRDE is established using a well-behaved electroactive specie (e.g. Fe(CN)$_6^{4-}$, Ru(NH$_3$)$_6^{2+}$) in a high concentration supporting electrolyte. Then, the disk potential is scanned in the direction that will drive its reduction or oxidation (it depends on the starting oxidation state of the electroactive species) and holding the ring potential at a potential in which all of what is generated at the disk is reverted to the original state of the electroactive specie. This is done at several rotation rates, and plotted up (see example in Figure A.3).

![Figure A.3](image-url) Disk voltammograms of 10 mM K$_3$Fe(CN)$_6$ in 1 M NaNO$_3$ aqueous solution at different rotation rates. The ring potential is constant at +0.36 V vs. Ag/AgCl. This experimental configuration is used for calibrating the collection efficiency of the RRDE.
The results from this calibration experiments are summarized in Table A.1 and the average collection efficiency is utilized as a parameter to analyze the results from the N(5)-ethylflavinium ion RRDE characterization.

<table>
<thead>
<tr>
<th>Rotation rate (rpm)</th>
<th>$i_D$</th>
<th>$i_R$</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-378.5</td>
<td>148.9</td>
<td>0.3934</td>
</tr>
<tr>
<td>500</td>
<td>-817.1</td>
<td>316.0</td>
<td>0.3867</td>
</tr>
<tr>
<td>900</td>
<td>-1075.0</td>
<td>413.0</td>
<td>0.3841</td>
</tr>
<tr>
<td>1300</td>
<td>-1297.3</td>
<td>478.7</td>
<td>0.3690</td>
</tr>
<tr>
<td>1700</td>
<td>-1477.3</td>
<td>547.0</td>
<td>0.3702</td>
</tr>
<tr>
<td>2000</td>
<td>-1605.9</td>
<td>582.4</td>
<td>0.3627</td>
</tr>
<tr>
<td>3000</td>
<td>-1944.1</td>
<td>674.6</td>
<td>0.3470</td>
</tr>
</tbody>
</table>

Average $N = 0.37 \pm 0.02$

A.5 (N)5-ethyl-flaviunium ion

The model compound presented in this work is the N(5)-ethylflavinium ion (Et-Fl$^+$), which reacts reversibly with water to form the corresponding pseudobase derivative Et-FIOH (Figure A.4).²²³

![Figure A.4](image)

Figure A.4 N(5)-ethylflavinium ion reacting reversibly with water via a 2-electron redox process. From Reference 223.

An initial electrochemical study investigated the possibility that a two-electron oxidation of Et-FIOH would lead to catalytic water oxidation, but this was found not to be the case.²²³ In the electrochemical study presented here it was demonstrated that at high oxidative potentials (greater than +1.9 V vs. NHE), the oxidation of Et-Fl$^+$ itself leads to catalytic water oxidation to form molecular oxygen. To our knowledge, this is the first report of catalytic water oxidation by an exclusively organic scaffold.
A.5.1 Cyclic Voltammetry of Et-Fl$^+$

Figure A.11 shows cyclic voltammogram of Et-Fl$^+$ in 0.5 M water/0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile. In analogy to the redox behavior of natural flavins, the reversible redox peaks are assigned to the conversion of Et-Fl$^+$ to the semiquinone Et-Fl$^-$ (+0.2 V vs. NHE) and the reduction of Et-Fl$^+$ to a fully reduced hydroquinone Et-Fl$^-$ (+0.5 V vs. NHE). At positive potentials (red trace, Figure A.5), Et-Fl$^-$ undergoes chemically irreversible oxidation at about +1.9 V and the current produced during the anodic oxidation of Et-Fl$^+$ is much stronger than the background current obtained in the absence of Et-Fl$^+$ (black trace, Figure A.5).

![Figure A.5 Cyclic voltammogram of 3 mM Et-Fl$^+$ in 2 M water/0.1 M TBAP in acetonitrile (red trace). Clean glassy carbon working electrode, background current (black trace) Scan rate: 100 mV/s. The dashed black line indicates the onset of the irreversible, catalytic current at +1.9 V vs. NHE.](image)

These large current values at potentials greater than +1.9 V vs. NHE can be interpreted in two possible ways: (1) electrocatalytic oxidation of the solvent by oxidized Et-Fl$^-$, which repeatedly regenerates Et-Fl$^+$ and leads to the increased current readings, or (2) electrochemical multi-electron decomposition of Et-Fl$^+$. The major difference between the two possible mechanisms is that mechanism (2) is expected to destroy Et-Fl$^+$ irreversibly, but mechanism (1) recovers Et-Fl$^+$ during the catalytic cycle.

To investigate whether the catalytic peak at +1.9 V involves the oxidation of water, cyclic voltammograms of Et-Fl$^+$ in the presence of varying concentrations of water in acetonitrile were obtained (Figure A.6). The current of the Et-Fl$^+$ catalytic peak at +1.9 V vs. NHE increased significantly as the water concentration increased, which suggests that water is, indeed, involved in the catalysis by Et-Fl$^+$. Furthermore, return cathodic scans show that the intensities of the Et-Fl$^+$ reduction peaks at +0.2 and –0.5 V vs. NHE remain unchanged after oxidation, which
confirms that Et-Fl\textsuperscript{+} does not decompose during the oxidation process at +1.9 V vs. NHE. It is important that the background current obtained in the absence of Et-Fl\textsuperscript{+} also increased with the increased water concentration (not shown). This increase is attributed to water oxidation by the glassy carbon electrode at potentials above +1.7 V vs. NHE. However, the increase in current as a result of the presence of Et-Fl\textsuperscript{+} is significantly higher than the increase of the background current in the absence of Et-Fl\textsuperscript{+}, which confirms that Et-Fl\textsuperscript{+} contributes significantly to the catalytic water oxidation at potentials above +1.9 V vs. NHE.

![Figure A.6](image)

**Figure A.6** Cyclic voltammograms of 3 mM Et-Fl\textsuperscript{+} in 0.1 M TBAP in acetonitrile in the presence of varying concentrations of pH 2 water: 0, 30, 60, 120, 240, 360 and 480 mM. Scan rate: 100 mV/s.

**A.5.2 Rotating ring-disk electrochemistry of Et-Fl\textsuperscript{+}**

As the catalytic water oxidation by Et-Fl\textsuperscript{+} occurs at a high overpotential of +1.9 V vs. NHE, it is not obvious whether Et-Fl\textsuperscript{+} catalyzes a four-electron water oxidation to form O\textsubscript{2} (\(E^\circ = 1.23\) V vs. NHE\textsuperscript{225}) or a two-electron water oxidation to form H\textsubscript{2}O\textsubscript{2} (\(E^\circ = 1.78\) V vs. NHE\textsuperscript{225}). In both cases, oxygen evolution would be observed, as the carbon electrode can oxidize H\textsubscript{2}O\textsubscript{2} to release O\textsubscript{2} (\(E^\circ = +0.68\) V vs. NHE\textsuperscript{225}).

Figure A.13 shows a shielding RRDE experiment in which the inner disk electrode was held at two different potentials (\(E_{\text{disk}} = +0.5\) and +2.5 vs. NHE), and the ring potential was scanned cathodically (from +0.5 V to −2 V vs. NHE). At a \(E_{\text{disk}} = +0.5\) V vs. NHE (Figure A.7, black trace), the ring electrode initially reduces only the species that are already present in the solution (two reduction plateaus at −0.1 V (a) and −0.5 V (b) from two one-electron reductions of Et-Fl\textsuperscript{+}). A third current plateau is observed at −1.2 V vs. NHE and corresponds to the reduction of protons present in solution. When \(E_{\text{disk}} = +2.5\) V vs. NHE, the ring voltammogram
(Figure A.7, red trace) the same initial behavior is observed, plateaus (a) and (b) due to the Et-Fl$. However, a significant increase in the current is observed at potentials more negative of $-0.5$ V vs. NHE because of simultaneous reduction of protons, and possibly oxygen, which migrate from the inner disk electrode.

![Figure A.7](image)

**Figure A.7** RRDE shielding experiments in which the disk potential ($E_{\text{disk}}$) kept at +0.5 V or +2.5 V vs. NHE (black and red traces, respectively). Conditions: 3.5 mM Et-Fl$^+$ in argon-purged 2 M water/0.1 M TBAP in acetonitrile, electrode rotation rate: 1000 rpm, scan rate: 100 mV/s. Inset shows the cyclic voltammogram of Et-Fl$^+$ for reference of what is happening at the chosen $E_{\text{disk}}$.

To test whether catalytic water oxidation by Et-Fl$^+$ occurs via the intermediate formation of $\text{H}_2\text{O}_2$, the formation of products at potentials where catalytic behavior is observed was monitored using RRDE collection experiments. Specifically, $\text{O}_2$ formation during Et-Fl$^+$ oxidation at the carbon disk electrode was monitored at the Pt ring electrode using the one-electron reduction of oxygen at $-1.0$ V vs. NHE ($\text{O}_2 + e^- \rightarrow \text{O}_2^-, E^\circ = -0.87$ V vs. SCE) and $\text{H}_2\text{O}_2$ formation was monitored using its oxidation at $+1.3$ V vs. NHE ($\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^-, E^\circ = +0.68$ V vs. NHE).

The disk voltammogram in Figure A.8 (black trace) shows that the current at the disk electrode increases at potentials above $+2.0$ V vs. NHE as a result of possible catalytic water oxidation by Et-Fl$. However, no current at the ring electrode was detected when the ring potential was kept at $+1.3$ V vs. NHE (Figure A.8, blue trace). It is important to mention that even though $\text{H}_2\text{O}_2$ is not detected within the time-scale of this experiment, its formation cannot be excluded. Because the working electrode is at such high anodic potentials it is possible that upon formation, the carbon electrode rapidly oxidizes $\text{H}_2\text{O}_2$ to molecular oxygen.
For comparison purposes, Figure A.8 also presents the measured ring current at –1.0 V vs. NHE to monitor oxygen formation. Alongside the current increase in at the disk, the ring current increases. At this cathodic potential, the reduction of both protons and oxygen is possible, however, a significant increase in $i_R$ is only observed when the disk is generating what we now can ascribe to $O_2$.

![Figure A.8 Rotating ring-disk electrode collection experiment to monitor and quantify the formation of oxygen catalyzed by Et-Fl'. Conditions: 3.5 mM Et-Fl', Ar-purged 2 M water/0.1 M TBAP in acetonitrile, electrode rotation rate: 1000 rpm, scan rate: 100 mV/s.]

Based on the results from Figure A.8 we can estimate the conversion efficiency of water to oxygen to be 93%.

The disk voltammogram in Figure A.8 reaches a maximum current of 9.96 mA, and the $i_{R,max}$ is 4.31 mA. At the disk electrode the number of electrons transferred for the conversion of water to oxygen is 4 ($n_D = 4$), whereas in the ring electrode the total number of electrons is $n_R = 5$, due to oxygen and proton reduction via Equations A.5.1 and A.5.2.

$$2H^+ + 2e^- \rightarrow H_2 \quad E^\circ = 0.00 \text{ V vs. NHE} \quad [A.5.1]$$

$$O_2 + e^- \rightarrow O_2^- \quad E^\circ = -0.83 \text{ V vs. Ag/AgCl} \quad [A.5.2]$$

Since the collection efficiency of the ring electrode is 0.374 (see section A.4.1) the maximum current that the ring electrode can achieve is
\[ i_{R,100\%} = \left( \frac{n_R}{n_D} \right) N_i D = \frac{5}{4} \times 0.371 \times 9.96 \text{ mA} = 4.61 \text{ mA} \]  \[\text{[A.5.3]}\]

Experimentally, \( i_{R,\text{max}} = 4.31 \text{ mA} \), and therefore, the yield of the OER (\( \eta_{\text{OER}} \)) is 93\% under these conditions. Using this yield we can estimate the turnover number (TON), namely the number of moles of substrate (water in this case) that a mole of catalyst (Et-Fl\(^+\)) can convert before being deactivated (Equation A.5.4).

\[ \text{TON} = \left( \frac{1}{1 - \eta_{\text{OER}}} \right) - 1 \]  \[\text{[A.5.4]}\]

The TON for Et-Fl\(^+\) under these conditions is 13. This value is very small, especially in comparison to photosystem II, in which the TON is estimated to be greater than 600,000.\(^{67}\) However, previous studies of Ru-based homogeneous OER catalysts by Meyer and co-workers showed that improvements in TON values can be achieved. The initially discovered Ru-based blue dimer shows a TON of 13.6,\(^{226}\) whereas the more recently developed Ru-based catalysts have TON values as high as 28,000.\(^{227}\)
Appendix B

Supporting Information for Chapter 4
B.1 Arrhenius plots for determining the potential-dependent activation energies as a function of pH

In this section, all the plots are presented, with and without $iR$-corrections to the overpotentials.

![Image of Arrhenius plots](image)

**Figure B.1** Arrhenius plots for pH 2.0 solutions with $iR$-corrected overpotential
Figure B.2 Arrhenius plots for pH 2.0 solution without $iR$-corrected overpotentials
Figure B.3 Arrhenius plots for pH – 0.7 solution with iR-corrected overpotentials

Figure B.4 Arrhenius plots for pH – 0.7 solution without iR-corrected overpotentials
Figure B.5 Arrhenius plots for pH 3.2 solution with \( iR \)-corrections to the overpotential
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