

# **The Promotion of Base Metal Catalysts for the Electrochemical Oxygen Evolution Reaction**

Submitted in partial fulfillment of the requirements for

the degree of

Doctor of Philosophy

in

Chemical Engineering

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April, 2013

## Acknowledgements

I would like to start by acknowledging those who have played an instrumental role in my achieving this level of academic success. This starts with my mom and dad; the two of them have always encouraged me to ask questions, be curious and helped to introduce concepts and ideas that have shaped me to this day.

I have had many wonderful teachers and I am thankful to all of them, but my undergraduate advisor, Carl Laird, inspired me to pursue a career in research. His sage advice helped me to learn a new passion for exploration in scientific research.

My thesis advisor, John Kitchin, has done everything a phenomenal advisor should. He has challenged me, helped me, and always been willing and excited to discuss anything with me. He has been a great mentor and serves as a great example of why you should never stop searching for a job that you love.

This thesis and the work done to produce it have been so much more fulfilling due to the people I have been fortunate to be surrounded by at CMU. The previous Kitchin group members; James, Spencer, Nilay, Robin and Rich, were fantastic sources of wisdom and kinship. My close friends, former housemates, and anyone who attended a Sunday night dinner have left an indelible imprint on me and made grad school the best years of my life. Of these people, I end with the most important influence, my fiancé Anita Lee. She has been there for me, an amazing person to always center me, helping me to strive to excel. I am extremely thankful and fortunate to have her in my life.

I would also like to acknowledge the sources of funding that have allowed this fundamental research to be conducted. The primary source of funding was through the Department of Energy's Early Career Award. I would also like to thank Phil and Marsha Dowd for graciously endowing a Fellowship through Carnegie Mellon and championing fundamental research.

## Abstract

As the energy needs of society continue to grow, and pressure to produce fewer emissions continues to mount, clean alternatives will be utilized to meet these demands. Conventional renewable technologies (wind and solar, etc.) have great potential, but cannot be used as base-load power, at least not in the traditional sense. Rather, these technologies would require the further adoption of energy storage technologies, such as water splitting, to convert the energy produced into chemical bonds for later use to match demand.

Water splitting currently suffers from large energetic barriers, on the oxygen side, that create a need for catalysts, and high costs associated with the best available catalysts, ruthenium and iridium. This work focuses on developing and understanding ways to promote the catalysis of the oxygen evolution reaction on earth-abundant base metal catalysts. We utilize a combination of electrochemical and in situ surface characterization techniques to correlate changes in the surface chemistry to changes in catalyst activity.

Three systems are examined for their potential effect on the OER. The first two focus on the promotion of NiO materials, examining the effect of changing the alkali cation present in the hydroxide electrolyte, and adding iron to the NiO materials. For the cations, the electrochemical activity is found to increase by a factor of two, switching from a LiOH solution to a CsOH solution of the same concentration. The use of in situ Raman spectroscopy suggests that different phases of the oxidized Ni oxyhydroxides are promoted in the presence of the different cations, with  $\gamma$ -NiOOH promoted in CsOH while  $\beta$ -NiOOH is observed



in LiOH. The addition of Fe results in large increases in OER activity up to a loading of 10 mol% Fe, where the further addition of Fe decreases activity. Raman spectra of the electrodes suggest at low Fe loadings, the Ni oxidation to  $\gamma$ -NiOOH is promoted, while further addition of Fe blocks access to active catalyst sites. Finally, we demonstrate the use of Fe-TAML molecular complex as an electrocatalyst for the OER. Fe-TAML is shown to be electrochemically active, and through immobilization, much higher catalyst utilization is achieved.

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## Introduction

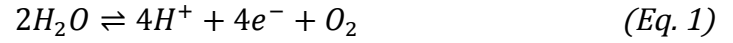
The global electricity usage in 2011 was 14k TWh, and this number is estimated to grow more than 70% in the next 25 years as energy consumption continues to grow and other parts of the world become more developed (1). As a society, we will need to choose to meet these increased energy demands with an increased reliance on renewable energy technologies if we are to avoid CO<sub>2</sub> related climate change. As we utilize more renewables, we will be forced to address some of the problems associated with them, mainly the uncertainty of supply. The current grid system requires having a near-constant baseline supply, which could be supplemented when the need occurs. In order to achieve reliable energy supplies from renewable sources, there is a need for better energy storage technologies to be developed.

Though the role of renewables will increase, the preponderance of our energy will still come from traditional carbonaceous sources. As such, it will also be important to explore more efficient ways of utilizing these resources(2-5), with the imminence of carbon management legislation in mind.

Electrochemistry offers the potential to address both of these issues. Renewable power could be stored in the form of chemical bonds using a technology such as electrochemical water splitting (scheme 1), or the electrochemical separation of O<sub>2</sub> from air (scheme 2) could provide a much cheaper source of O<sub>2</sub> for the oxy-combustion of coal (3, 6, 7), compared to the current oxygen separation technology of choice, cryogenic distillation (8, 9).

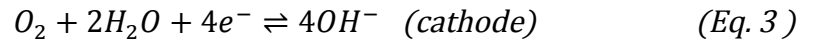
Oxycombustion is the burning of coal in an oxygen rich environment. This results in an elevated flame temperature relative to air, which increases the combustion efficiency and thus produces a much more sequestration-ready effluent stream. Another benefit of oxycombustion is that the furnace only contains O<sub>2</sub> and CO<sub>2</sub> gases, which eliminates the need for the difficult N<sub>2</sub>/CO<sub>2</sub> separation.

Scheme 1 proceeds via the following reaction pathway,

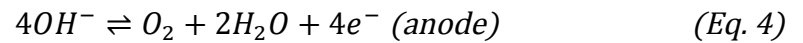


Eq. 1 is known as either the water oxidation (WO) reaction, or the oxygen evolution reaction (OER), while Eq. 2 is known as the hydrogen evolution reaction (HER).

Scheme 2 (shown in alkaline media) proceeds via the following sequential reactions,



transport



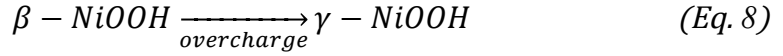
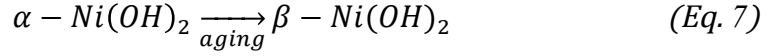
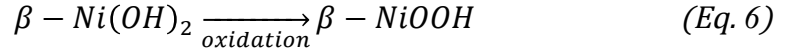
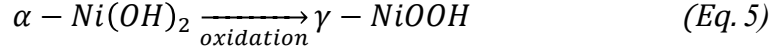
where Eq. 4 is known as the oxygen reduction reaction (ORR) and Eq. 5 is another way of depicting the OER in alkaline electrolyte.

However, a major limitation of both of these technologies is that much higher potentials than the thermodynamic limit are required to drive the reaction at practical rates. To address this limitation, catalysts have been developed to catalyze both half reactions. In the case of water splitting, the OER is considerably more difficult than the HER. Comparatively, the HER is a more facile reaction, involving the association of two protons with catalysts achieving significantly lower overpotentials ( $\sim 0.05$  V to achieve  $1 \text{ mA/cm}^2$ )(10). The OER is a 4-electron, multi-step process, which at present requires an additional 0.2V to achieve  $1 \text{ mA/cm}^2$  for the best performing catalysts (11, 12), which are made from materials (Ru and Ir) that are prohibitively expensive. For the current best-performing catalysts made from more earth-abundant materials, the overpotential becomes 0.35-0.4 V (12-16). For more practical current densities ( $\sim 250 \text{ mA/cm}^2$ ) common in commercial electrolyzers, much higher potentials are required, and account for much of the cost of electrolytic water splitting (17).

This work will focus on the catalysis of the oxygen evolution reaction, and specifically ways in which base metal materials (containing Ni and Fe) can be used to promote the OER. Significant challenges face the implementation of these electrochemical technologies, but can be summed up as primarily how one can increase activity while minimizing cost.

The choice of nickel oxide as a material of study is for two main reasons, its industrial relevance (18) and its relative abundance. NiO has been used as the

anode material of choice in industrial electrolyzers as it exhibits moderate activity, good stability under highly oxidizing conditions and low cost. Because of this focus, research has been aimed at ways to better understand the oxidation mechanism(15, 19-22) and increase the activity of Ni anodes for the OER catalysis(23-26). Despite the number of studies on Ni materials, there has still been disagreement on the exact mechanism (27, 28) and the nature of the active site (25, 29). Bode (30) first hypothesized the electrochemical oxidation/reduction behavior of nickel oxide as follows in Eq. 9-12. The  $\alpha$  and  $\gamma$  phases are characterized by larger inter-layer spacing and incorporation of water into the structure. The  $\beta$  phases are more well-ordered and do not contain water in the structure. Another key distinction is that the oxidation state of  $\beta$ -NiOOH is  $\sim 3$  while the oxidation state of  $\gamma$ -NiOOH is  $\sim 3.7$ . The disagreement mainly comes in discussing which of the phases is responsible for oxygen evolution. The literature has tended identify  $\beta$ -NiOOH as the more active phase (27, 31), even suggesting that further oxidation of  $\beta$ -NiOOH is a deactivation mechanism. More recently however, Yeo and Bediako (25, 29) have noted that higher oxidation state metal centers are likely to explain the increase in OER activity, as evidenced by in situ X-ray absorption and Raman spectroscopies.



With these uncertainties and the advances of spectroscopic techniques in mind, we look to clarify the promotion mechanisms of NiO anode materials through i) the addition of small loadings of iron, first described by Corrigan (23), and ii) the choice of alkali cation in the hydroxide electrolyte solutions.

With the knowledge of increased electrochemical OER activity with the addition of Fe to NiO films, coupled with the role Fe plays in oxygen activity and many biological oxidations, we look to extend our study to a new class of Fe-based molecular catalysts to facilitate the OER. Specifically we look to demonstrate the use of an immobilized  $Fe^{III}$ - tetra amido macrocyclic ligand (TAML) for the prolonged evolution of  $O_2$  via water oxidation. Molecular catalysts are thought to be promising materials for further research due to the ability to easily functionalize the ligands for desired chemistries.

## 1.1 Review of Ni-Fe literature

Corrigan was originally studying nickel metal hydride batteries and was interested in ways to limit the reactivity toward the parasitic side reaction, the evolution of gaseous oxygen (23). Noting the presence of Fe impurities in KOH, it was first demonstrated that pre-electrolysis to plate out some of the iron resulted in a

decrease in the OER activity on the Ni anode material. It was then demonstrated that adding 10 ppm Fe to the pre-treated KOH solution greatly increased the OER activity, and an even more pronounced effect was noted when 10% Fe was coprecipitated on the electrode surface along with Ni.

Much of the subsequent work on this system has focused on the mechanism of Fe incorporation into the  $\text{Ni(OH)}_2$  material. Kamnev et al. (32-34) used a combination of transmission Mossbauer, Auger electron (AES), and Fourier transform infra-red absorption (FTIR) spectroscopies to examine a number of compositions of Ni(II)-Fe(III) binary hydroxide films made via electrodeposition. These works resulted in several observations, i) that there was no change in Fe valency detected via Mossbauer spectroscopy, ii) the composition of the near-surface contained higher Fe loadings compared to the bulk ratios contained in the precursor salt solutions, and that Fe composition increases in the first few subsurface layers, iii) the FTIR data give evidence to the formation of a  $\text{NiFe}_2\text{O}_4$  ferrite phase at as low as 10% Fe composition, and the intensity of the ferrite peaks continues to increase with increased loading up to 60% (the highest value in the study). There were some limitations to their work in the sense that there were no experiments done to test the bulk composition of their as-deposited films, and they were unable to detect the nature of active phase (i.e. the Mossbauer data suggest the valency of the Fe to be +3, and the ex situ FTIR data suggest the formation of a ferrite phase, but there was no way of concluding that the ferrite phase is responsible for the increase in OER activity).

Guerlou-Demourgues et al. (35, 36) used a combination of electrochemical tests along with Fe<sup>57</sup> Mossbauer spectroscopy to describe the nature of the incorporated Fe along with the redox cycling behavior of the Ni(OH)<sub>2</sub> material. From these results, they concluded there were three distinct redox behaviors at different levels of Fe loading. For the case of no Fe present, the more well-structured β-NiOOH phase, was observed (characterized by 1 electron transfer per oxidation/reduction). For high loadings (≥ 20%) of Fe, the α-Ni(OH)<sub>2</sub> → γ-NiOOH redox pathway is observed (characterized by a ~1.7 electron transfer per oxidation/reduction). For low loadings (≤ 10%) of Fe, an intermediate electrochemical charge/discharge behavior was observed and was assigned to the presence of an “interstratified” phase, having a mix of both α and β phases of Ni(OH)<sub>2</sub> present in the reduced state of the film. The authors concluded from the results of their Mossbauer spectroscopic experiments that much of the Fe present was in the tetravalent (+4 oxidation) state. This conclusion differs from that of Corrigan et al. (37) and the in situ X-ray absorption results from Kim et al. (38) discussed below.

Kim et al. collected in situ X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) data from films of 9:1 Ni:Fe composition deposited onto pyrolytic carbon electrodes. The Ni and Fe K edge spectra indicate that at elevated potentials where the OER occurs, the oxidation states for Ni and Fe are 2 and 3, respectively. From the EXAFS data, it is seen that the Ni-Fe metal spacing is equivalent to that of the Ni-Ni spacing found for unsubstituted Ni(OH)<sub>2</sub> electrodes. These data suggest Fe is incorporated

into the Ni lattice and under oxidizing conditions exists in a phase most like FeOOH (38). However, one of the limitations of X-ray absorption techniques is that they are bulk techniques. The deposited films in this study were of order thousands of atomic layers thick, and this could account for the lack of oxidation state changes in the Ni and Fe XANES data.

Lastly, Krejci et al. (39, 40) determined that the method of Fe incorporation is important. While Corrigan (23) had demonstrated co-deposited films of Ni and Fe achieved long-term stability, Krejci's work found that polarizing a Ni(OH)<sub>2</sub> electrode to oxidizing potentials in the presence of Fe(NO<sub>3</sub>)<sub>3</sub> solution resulted in the decreased OER overpotentials while the electrode was in this solution; however, this effect could be reversed upon long-term oxidation in a Fe-free electrolyte or by placing the electrode into a fresh electrolyte solution with ~1 M LiOH additive.

The high activities for the OER on a binary metal oxide material comprised of two earth-abundant materials make this an interesting system for further study, with focus aimed at understanding the nature of these increases in activity. A better understanding of the promotion mechanism could lead to other mixed metal oxides with superior OER activity. Electroless techniques for synthesizing the catalyst materials offer more control of the resulting material compositions and facile characterization by ex situ techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed reaction spectroscopy (TPRS). For a better understanding of nature of the active site, we also utilize electrodeposition to produce thin-film electrodes, of order 1-10 atomic



layers based on the charge transferred during the deposition process. These materials are examined using electrochemical tests in combination with in situ Raman spectroscopy. The combination of these techniques allows us to correlate changes in catalyst surface chemistry to the changes in OER activity. Raman spectroscopy is a good choice for our system due to the lack of interference from water. While Raman can sometimes be plagued by low signal, advances in optics technology (specifically notch filters) and the utilization of surface enhanced Raman techniques (41-43) allow for much greater signal intensity, and in some cases molecular resolution.

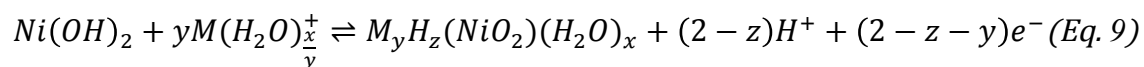
With this in mind, we look to observe the trend in electrochemical catalyst activity (i.e. mixed Ni-Fe hydroxide electrodes produce much higher OER activity relative to either single material) and elucidate the nature of the active phase responsible for this enhancement through the use of advanced spectroscopic techniques.

## **1.2 Cation Effects Introduction**

While much work has focused on understanding the oxidation-reduction behavior, and ways to increase the activity of NiO anode materials, little work has looked into the non-covalent interactions between the electrode surface and the electrolyte cation choice. Recent work has shown that the alkali hydroxides (Li, Na, K, and Cs) have significant effects on the electrochemical hydrogen oxidation, methanol oxidation and oxygen reduction reactions at the Pt(111) single crystal surface(44). For each reaction, the activity

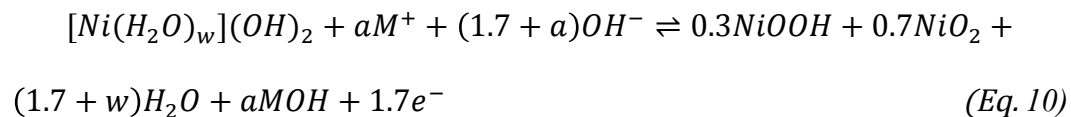
increases as one moves down the periodic table of alkali cations, i.e. as the cations get larger and softer. That work concludes that the decrease in hydration energy of the cations explains the majority of the corresponding increase in activity. It is notable that these reactions occur at potentials where it is likely that the electrocatalyst is in a metallic state, or at most has a high coverage of hydroxyl/oxo adsorbates. It has not been shown to our knowledge whether similar promotion effects would be observed at more oxidizing potentials where most metals become metal oxides. These conditions are highly relevant under oxygen evolution conditions, for example.

The works of Bernard (20) and Cheek(21) both employed the use of quartz crystal microbalance techniques in conjunction with electrochemical characterization to better understand the redox cycling behavior of  $\alpha$ -Ni(OH)<sub>2</sub> film materials in a series of alkali hydroxide electrolytes (Li, Na, K, Rb, and Cs). In the case of Bernard (20), the results indicate that the alkali metal cations are incorporated into the film material upon electrochemical oxidation of the Ni(OH)<sub>2</sub> film material. Water molecules were found to also be incorporated into the extended film structure, with 3 mol H<sub>2</sub>O per Li<sup>+</sup> ion, 2 per Na<sup>+</sup>, and 1 each for K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. The proposed mechanism is as follows.



Cheek (21) found; however, that the mechanism for  $\alpha$ -Ni(OH)<sub>2</sub> was consistent for each alkali cation present, with the only difference in QCM

mass being due to the different molecular weights of the cations. Also, rather than having water be incorporated into the surface during oxidation, the authors report that water is liberated upon oxidation, as follows.



From this equation, it can be seen that the cations are incorporated in order to maintain charge neutrality in the mixed (III/IV) oxidation state resultant material. While these QCM measurements were able to make suggestions on the oxidation mechanism, the results from the two studies were somewhat contradictory, which Cheek (21) ascribed to the differences in the conditions of film deposition. These studies also did not discuss differences in the electrochemical behavior of the films in the different electrolyte solutions. The results from Bernard (20) could suggest a possible correlation between water incorporation and electrochemical activity, but these same results were not reproduced by Cheek (21).

Our approach looks to determine what role the cation choice can have on the electrochemical OER activity through the use of cyclic voltammetry and chronoamperometry electrochemical characterization experiments on thin electrode films. The use of thin films allows for the direct observation of the active surface through the use of in situ Raman spectroscopy without interference from bulk contributions. The combination of these techniques allows us to correlate changes in surface chemistry to changes in electrochemical OER activity, and thus, describe the role of electrolyte cation in the promotion of the reaction.

### **1.3 Introduction to oxygen-evolving molecular catalysts containing first-row transition metals**

Photosynthesis, the solar-driven conversion of  $\text{H}_2\text{O}$  to  $\text{H}_2$  and  $\text{O}_2$  in plants, is one of the most important chemical reactions on earth. Two complementary protein complexes, Photosystems I and II, facilitate each of the coupled reactions, HER and OER. Study of the oxygen-evolving complex (OEC) within Photosystem II have resulted in a knowledge of its chemistry,  $\text{CaMn}_4\text{O}_5$ , and a proposed cubane structure (45). With this knowledge in mind, synthetic chemists have been interested in mimicking nature by creating transition metal molecular catalysts that can also facilitate the OER. At present, there have been many Mn clusters synthesized, but relatively few that can homogeneously evolve  $\text{O}_2$ . The most promising of these materials has been demonstrated as a homogeneous WO catalyst as well as a heterogeneous catalyst for both electrochemical and photoelectrochemical WO (16, 46).

Homogeneous WO over other first-row transition metal (Ni, Co, and Fe) complexes has been similarly limited, with no (to our knowledge) known Ni or Co-centered WO catalyst complexes (13). Fe poses an interesting case, due to its role in heme oxidation/reduction processes in nature and, more generally, the ease with which it can undergo changes in valency. Despite this, there have been few examples in the literature of Fe-containing  $\text{O}_2$  evolving complexes, only the works of Elizarova (47), and more recently Ellis (48) and Fillol (49) have demonstrated  $\text{O}_2$  evolution in the presence of chemical oxidants

Trisbipyridylruthenium  $[\text{Ru}(\text{bpy})_3]^{+3}$  and Ceric ammonia nitrate (CAN). The use

of chemical oxidants allows for proof-of-concept and an investigation of the mechanism via a single electron donor oxidant; however, these studies are limited by low turnover numbers and the exclusion of more complicated alternative reaction pathways evolving multi-electron transfer. Because of these limitations, it is preferential to utilize these molecular complexes as electrocatalysts for the OER, where the reaction driving force is provided by electrochemical potential rather than chemical potential.

Our approach utilizes an  $\text{Fe}^{\text{III}}$ -tetra amido macrocyclic ligand (TAML) derivative molecular complex as an electrocatalyst for the OER. TAML is first examined as a potential homogeneous electrocatalyst. The TAML powder is dissolved into an electrolyte and 3-electrode electrochemical experiments are carried out in the resulting solution, with the experimental results compared to a control with no addition of TAML to the solution. We also investigate TAML as a heterogeneous electrocatalyst. Here, TAML is immobilized onto activated carbon and incorporated into an electrode by painting catalyst-containing inks onto either 1  $\text{cm}^2$  strips of carbon paper or a glassy carbon electrode. The electrochemical activity is quantified using 3-electrode electrochemical experiments. The product gases in the headspace are also monitored using both gas chromatography and a fluorescent oxygen probe to determine both the Faradaic efficiency of the OER and what side reactions may persist.

While Fe-containing molecular catalysts, including TAML, have been demonstrated to oxidize water in the presence of a chemical oxidant, to our

knowledge, this is the first time it has been demonstrated to electrochemically evolve oxygen.

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## 2. Electrochemical Methods and Analysis

### 2.1 Electrochemical Introduction

Much of the work discussed in the proceeding chapters will involve electrochemical experiments. This chapter will discuss the fundamentals of electrochemistry that are used throughout the work in experimental synthesis and data analysis.

### 2.2 Thermodynamics of the Oxygen Evolution Reaction

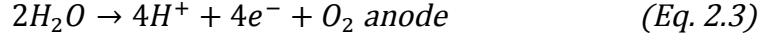
The net reaction for splitting water into hydrogen and oxygen is seen in Equation 2.1.



In order to describe the thermodynamics of this reaction, one must first define the electrochemical potential,  $\mu_i$ . The chemical potential is insufficient to describe the mechanics of the process because it does not account for the charge of species  $i(I)$ . The electrochemical potential is defined as

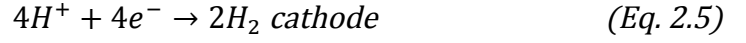
$$\mu_i = RT\lambda_i \quad (Eq. 2.2)$$

where  $\lambda_i$  is the activity of the charged species  $i$ . Now the reaction can be written in terms of the electrochemical potentials of the species at each electrode, where the two half reaction occur.



*becomes*

$$2\mu_{H_2O} = 4\mu_{H^+} + 4\mu_{e^-}^{\alpha'} + \mu_{O_2} \quad (Eq. 2.4)$$



*becomes*

$$4\mu_{H^+} + 4\mu_{e^-}^{\alpha} = 2\mu_{H_2} \quad (Eq. 2.6)$$

summing equations 2.4 and 2.6 leads to

$$(\mu_{e^-}^{\alpha} - \mu_{e^-}^{\alpha'}) = \frac{1}{2}\mu_{H_2} + \frac{1}{4}\mu_{O_2} - \frac{1}{2}\mu_{H_2O} \quad (Eq. 2.7)$$

In this form, the electrochemical potential difference between the electrons at each electrode is equal to the sum of the chemical potentials of the product gases less the chemical potential of water. By choosing a standard state of 25 °C and 1 atm, the chemical potential of the two gases becomes zero and the chemical potential of water is -237 kJ/mol, which leads to the following relationship.

$$FE^0 = (\mu_{e^-}^{\alpha} - \mu_{e^-}^{\alpha'}) = -\frac{1}{2}\mu_{H_2O}^0 \quad (Eq. 2.8)$$

where  $F$  is the Faraday constant, 96,485 coulombs/mol  $e^-$ ; thus,  $E^0$  is equal to 1.23 V, the standard cell potential for water splitting.

## 2.3 Electrochemical Kinetics

Electrochemical reactions are thus controlled by applying an electrical potential,  $E_{appl}$ . When this value is raised above (for oxidation) the standard cell potential,  $E^0$ , the reaction becomes exothermic and typically follows Butler-Volmer kinetics (Eq. 2.9), with the current increasing exponentially with increases in potential.

$$i = i_0 \left[ e^{\frac{\alpha_a \eta_s F}{RT}} - e^{\frac{\alpha_c \eta_s F}{RT}} \right] \quad (\text{Eq. 2.9})$$

where  $\eta_s$  is the overpotential,

$$\eta_s = E_{\text{appl}} - E^0 \quad (\text{Eq. 2.10})$$

$i_0$ , the exchange current density,  $\alpha_a$  and  $\alpha_c$ , anodic and cathodic charge transfer coefficients, are material dependent constants. At large overpotentials, Eq. 2.9 becomes

$$\lim_{\eta_s \gg E^0} i = i_0 * e^{\frac{\alpha_a \eta_s F}{RT}} \quad (\text{Eq. 2.11})$$

It is in this high overpotential regime where the oxygen evolution reaction typically takes place. Experiments are thus designed to understand the nature of the electrode surface at these potentials. From inspection of Eq. 2.11, taking the logarithm of both sides leads to a linear relationship between the log of current and the overpotential.

$$\log \frac{i}{i_0} = 2.3 * \frac{\alpha_a F}{RT} * \eta_s \quad (\text{Eq. 2.12})$$

$$\text{or } \eta_s = a + b \log (i) \quad (\text{Eq. 2.13})$$

Eq. 2.13 is known as the Tafel equation, and the constant  $b$  is known as the Tafel slope. The Tafel slope is an intrinsic kinetic parameter(2) of the electrode

surface, which relates the amount of overpotential required to increase the current by an order of magnitude. Thus, other things being equal, a decrease in the Tafel slope is indicative of a more active electrode. The other information that can be gleaned from the Tafel slope is the nature of the rate determining step of the reaction(2). Experimentally observed changes in the Tafel slope can thus give more insight into the activity and the reaction mechanism.

However, this type of analysis is only applicable to systems with sluggish kinetics where there is essentially no contribution from the reverse reaction(3). The oxygen evolution reaction exemplifies this behavior, and an example of the analysis is shown below.

In order to experimentally determine the Tafel slope, the potential region just beyond the onset of O<sub>2</sub> evolution must be examined. In order to determine the onset potential, the effects of pH and the choice of reference electrode must be considered, as the value of 1.23 V vs. normal hydrogen electrode (NHE) is defined at pH of 0. A sample calculation of the conversion is shown below (Eq. 2.14) for a Ag/AgCl reference electrode, 0.197 V vs. NHE, in 0.1 M KOH (pH = 12.8).

$$E^0 = 1.23 \text{ V} - 0.197 \text{ V} - 0.059 \frac{\text{V}}{\text{pH}} * 12.8 = 0.278 \text{ V} \quad (\text{Eq. 2.14})$$

In order to mitigate the effect of nonfaradaic current due to capacitive charging of the double layer, either steady-state constant potential experiments or slow scan cyclic voltammetry (example shown in Figure 2.1) experiments are performed.

A slow scan cyclic voltammetry experiment is performed from  $\sim 0$  to 0.4 V of overpotential, results shown in Figure 2.1. During the positive scan (top line) the current behavior falls into three distinct regions. The first (0 to  $\sim 0.28$  V) shows small increases in the current with increasing potential, which is attributable to double layer charging. The second region ( $\sim 0.28$  to 0.34 V) is where the electrode is undergoing a surface oxidation, and the last region ( $\eta > 0.34$  V) is the Tafel region, where the current increases exponentially with increases of  $\eta$ .

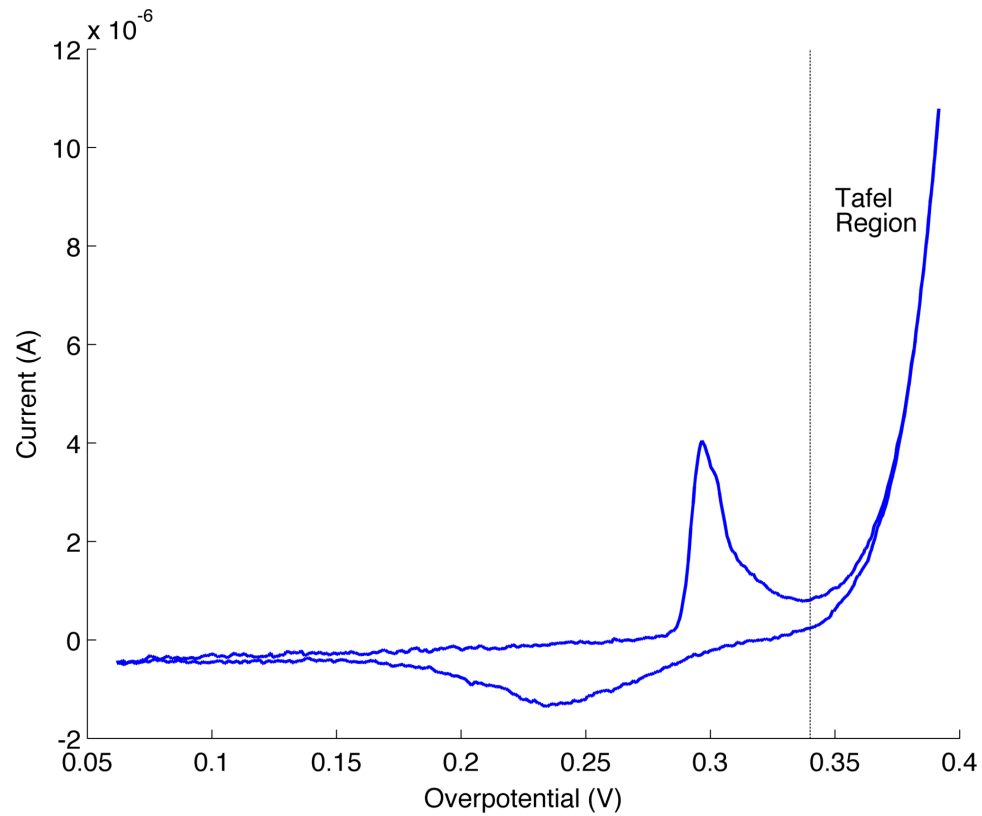


Figure 2.1. Example slow scan cyclic voltammogram. The Tafel region is highlighted by the exponential relationship between potential and current. Scan rate is set to 1 mV/s.

Next, for the data in the Tafel region, the logarithm of the current is plotted as a function of overpotential, shown in Figure 2.2.

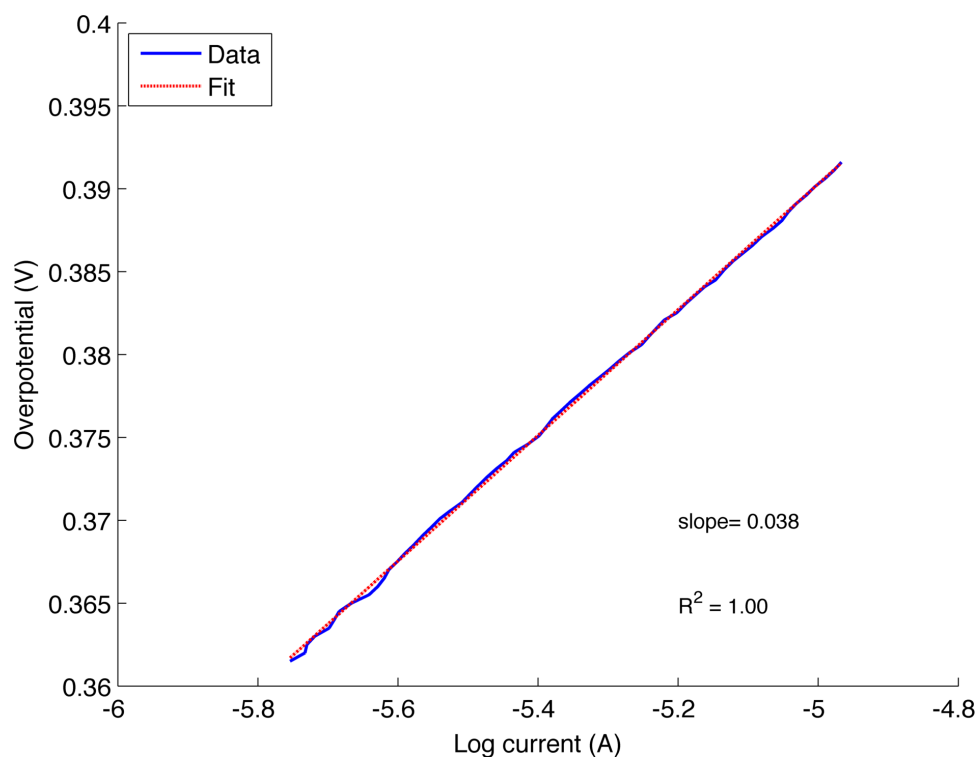


Figure 2.2. Tafel analysis produced by plotting the logarithm of the current as a function of overpotential of the data in the Tafel region in Figure 2.1.

In this region, the fit to the data is near exact, with an  $R^2$  value of  $\sim 1$ . The resulting slope of 0.038, or 38 mV/decade current would be the experimentally determined Tafel slope for this electrode.

The other constant in the Butler-Volmer equation (Eq. 2.9) is the exchange current density,  $i_0$ , which can similarly be determined by extrapolating the Tafel plot to the equilibrium potential ( $\eta = 0$  V). By extracting each of these values, the Tafel slope and exchange current density, polarization curves (current vs. potential) of the oxygen evolution reaction can be modeled for the system, thus avoiding contributions from other sources of current. The modeled curves can then be used to compare relative activities among a set of electrodes.

## 2.4 Comparing Electrochemical Activity

For the comparison of  $O_2$  evolution activity, the system is either modeled as previously described or the steady-state performance of the electrode is experimentally measured using constant potential experiments (chronoamperometry). Here the potential is set to values ranging from just above the onset potential for  $O_2$  evolution, and stepped up to highly oxidizing conditions. The potential is held for at least 10 minutes prior to stepping to the next value, with an example set of experiments shown in Figure 2.3.

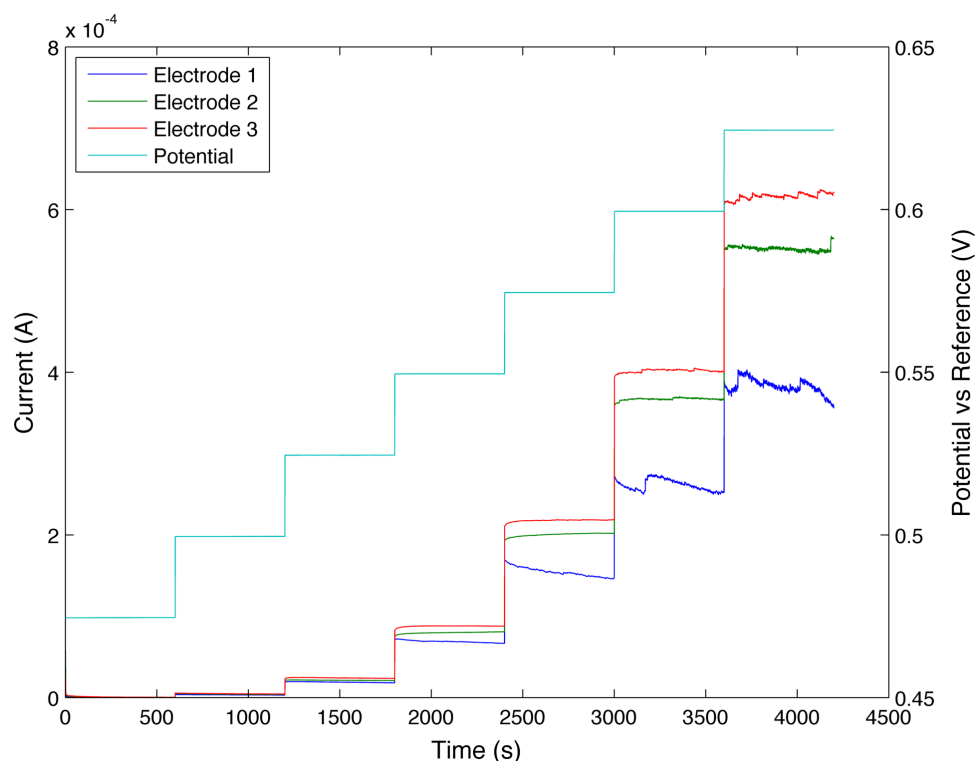


Figure 2.3. Example raw data from multi-step chronoamperometry experiments. The current is plotted as a function of time on the primary axis and the potential steps are plotted on the secondary axis (teal). The jagged behavior at high  $\eta$  is the result of bubble formation on the electrode surface blocking a portion of the active sites.

The raw current data in Figure 2.3 are then averaged at each potential step to give a measure of the steady-state activity of the electrode (current and activity



are synonymous). Plotting the time-averaged currents as a function of the applied potential gives a steady-state polarization curve, which allows for activity comparisons across multiple electrode systems.

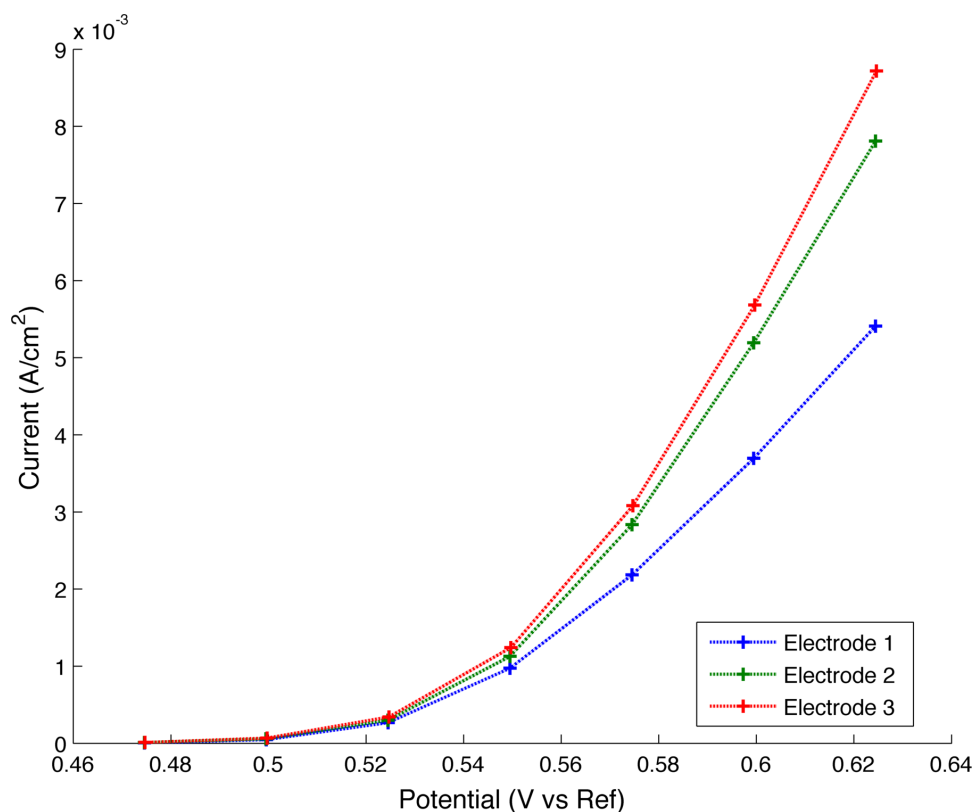


Figure 2.4. Time averaged current plotted as a function of the applied potential for the example data shown in Figure 2.3.

When comparing large sets of data for multiple electrode systems, choosing a single potential to report each of the currents allows for easier discussion of trends throughout the data set.

## 2.5 Constant Current Experiments

Though current and potential are correlated, there are times when it is beneficial to set a current, rather than the potential. Generally speaking, these instances arise when the total amount of product (i.e. gas evolved or material deposited) is

desired. In the case of product gas quantification, the theoretical maximum amount of O<sub>2</sub> evolved is directly proportional to the current through Eq. 2.15.

$$1\text{ mA} = \frac{\frac{1}{1000}\text{Coulombs}}{\text{s}} * \frac{1\text{ mol } e^{-}}{96485\text{ Coulombs}} * \frac{1\text{ mol O}_2}{4\text{ mol } e^{-}} = \frac{2.6\text{nmol}}{\text{s}} \quad (\text{Eq. 2.15})$$

Using this relation, the experimental rate of oxygen production, measured by the fluorescent oxygen probe, and the total quantity of oxygen produced, measured by gas chromatography, can be compared to the theoretical maximum (i.e. the coulombic efficiency of the process).

## References

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- (2) Bockris, J. O. Kinetics of Activation Controlled Consecutive Electrochemical Reactions - Anodic Evolution of Oxygen. *J Chem Phys* **1956**, *24*, 817–827.
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### **3. The Role of Alkali Cation Choice on the Electrochemical Oxygen Evolution Reaction on Nickel Oxide**

#### **3.1 Introduction**

While there has been much work focused on understanding and improving the catalysis of the electrode materials (1-4), there has been little done to understand the role the electrolyte can play on the catalysis of the reaction. The primary role of the electrolyte is that of a charge-transferring medium, used to maintain charge neutrality while conducting ions between the electrodes. However, at the charged electrode surface, and in the double layer beyond, the counter ions must interact with and facilitate the movement of reactant molecules to the charged surface. Thus the presence of these spectator ions can influence both the mobility and the specific adsorption of the reactant species to the charged surface. Furthermore, the electrolyte may affect the structure and composition of the electrode. For example, the Nocera group(5, 6) have reported that certain proton-accepting anions in electrolytes, e.g. inorganic borate and phosphate, could form very active Ni and Co thin film electrocatalysts that have incorporated the anions into their structure. Experiments with identical pH and metal concentrations, but nitrate anions resulted in no film growth, and thus, no catalysis.

Recent work has shown that alkali metal cations, in the series of alkali hydroxides (Li, Na, K, and Cs), have significant effects on the electrochemical hydrogen oxidation, methanol oxidation and oxygen reduction reactions at the Pt(111) single crystal surface(7). For each reaction, the activity increases as one moves down the periodic table of alkali cations, i.e. as the cations get larger and softer. That work concludes that the decrease in hydration energy of the cations explains the majority of the corresponding increase in activity. It is notable that these reactions occur at potentials where it is likely that the electrocatalyst is in a metallic state, or at most has a high coverage of hydroxyl/oxygen adsorbates. It has not been shown to our knowledge whether similar promotion effects would be observed at more oxidizing potentials where most metals become metal oxides. These conditions are highly relevant under oxygen evolution conditions, for example.

Clearly, electrolytes can play non-trivial roles in promoting, or enabling electrocatalysis in ways that are not fully understood yet. Based on the previous reports, we hypothesized that it would be possible to promote oxygen evolution electrocatalysis by selective choice of electrolytes. If this were true, it may be possible to promote, or enhance the activity of cheaper base metal electrocatalysts so they more closely resemble the activity of more expensive oxides such as ruthenium or iridium oxides. Those expensive oxides are used because, in addition to their high activity, they are stable in strongly acidic electrolytes. The stability of cheaper metal oxides, e.g. nickel oxides, increases at high pH, making alkaline electrolytes an attractive possibility for water splitting.

Nickel oxide materials have been of great interest, both industrially and academically, for their moderate activity(2), superior stability in alkaline environments(8), and low cost. While much work has focused on understanding the oxidation-reduction behavior, and ways to increase the activity of NiO anode materials, little work has looked into possible interactions between the electrode surface and the electrolyte. The works of Bernard (9) and Cheek(10) both employed the use of quartz crystal microbalance techniques in conjunction with electrochemical characterization to better understand the redox cycling behavior of Ni(OH)<sub>2</sub> film materials. Their findings both indicate incorporation of the alkali cations into the film material during oxidation; however, neither discussed the effects of the cation on the OER activity. While Bernard found the choice of cation affected the amount of water uptake during oxidation, Cheek found that water was expelled during oxidation and only observed differences in the frequency corresponding to the different molecular weights of the cations (10).

More recently, Yeo and Bell (11) studied both bulk and thin film nickel electrodes using a combination of electrochemistry and Raman spectroscopy. Their work focused on the differences between the  $\alpha$ -Ni(OH)<sub>2</sub>  $\rightarrow$   $\gamma$ -NiOOH and  $\beta$ -Ni(OH)<sub>2</sub>  $\rightarrow$   $\beta$ -NiOOH electrochemical phase transitions and the corresponding effect on activity. While the bulk electrodes showed higher activity for the  $\beta$ -NiOOH phase, the thin films exhibited much higher specific activities (turnover frequency) and their corresponding Raman spectra more closely resembled the  $\gamma$ -NiOOH phase at elevated potentials. The different phases and enhanced catalytic activity of thin-film Ni electrodes make them ideal candidates for further study.

Given the evidence that different electrolytes affect the structure and potentially the water uptake on NiO anodes, and that they can impact electrochemical activity, in this work, we examined the OER in Li, Na, K and Cs hydroxide electrolytes using cyclic voltammetry, chronoamperometry and in situ Raman spectroscopy. We find that the NiO surface is not the active surface under oxygen evolution conditions as shown in the literature(12, 13), but rather a nickel oxy-hydroxide phase is present under high OER rates. The potential at which this phase forms is cation dependent, and the relative amounts of the beta and gamma forms of this phase appear to be cation dependent. We show clear evidence that the activity of NiO-based electrodes can be enhanced by up to a factor of two in CsOH electrolytes compared to the activity in the LiOH electrolytes.

## **3.2 Experimental Methods**

### **3.2.1 Electrode Preparation**

Electrodes were prepared via constant current electrodeposition. First, the gold disk electrode (Pine Instruments) was electrochemically roughened in a 0.1 M KCl solution according to the method described by Weaver et al(14, 15). 0.01 M  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution in water was used as the plating solution. For Raman active films, 1 mM  $\text{Ag}(\text{NO}_3)_2$  was added to the solution to utilize the surface-enhanced Raman (SERS) effect created by the Ag particles.(16) A cathodic current of  $8 \text{ mA/cm}^2$  was applied for 10 s to generate a thin film of  $\text{Ni}(\text{OH})_2$  on the gold surface. A single linear sweep voltammogram, from 0-0.8 V vs open

circuit, was then performed to oxidize the film prior to rinsing and use in electrochemical OER testing.

### **3.2.2 Electrochemical Tests**

All electrochemical experiments were carried out in 0.1 M alkali hydroxide solutions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ). The reference electrode was a saturated Calomel electrode (SCE), 0.244 V vs NHE, and the auxiliary electrode was a Pt wire. A Gamry Ref600 potentiostat was used to control the experiments and data acquisition. Electrodes were first cycled 25 times from -0.2 to 0.65 V at a 50 mV/s scan rate. Constant potential experiments were then conducted in 25 mV steps from overpotentials of 200 up to 500 mV, with respect to the onset potential of  $\text{O}_2$  evolution (232 mV vs. SCE).

### **3.2.3 in situ Raman Spectroscopy**

Raman spectra were collected using a Horiba LabRAM HR Raman microscope fitted with a 50x LWD objective, 1800 g/mm, and a CCD detector. 532 nm laser excitation was provided by a Spectra Physics Nd:YAG laser. The laser power was set to 20 mW and each sample spectrum is the average of ten 5-second scans. Constant potential electrochemical experiments (from 250 to 700 mV) were allowed to reach a steady state prior to the collection of Raman spectra.

### **3.2.4 Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS)**

The chemical composition of the deposited thin-films was analyzed with an Agilent Technologies 7700 Series ICP-MS. The electrodes were rinsed, and then dissolved in 1 M Fisher Trace metals grade  $\text{HNO}_3$  collected and stored. A 50 ppb

spike of internal standard solution (ISTD) was added to each sample for quantitative analysis. The stock ISTD solution contained 10 mg/L of Li, Sc, and Ge. Calibration standards (CalStd) containing 1, 10, and 100 ppb of the analytes along with the 50 ppb ISTD were also prepared. The sample probe was rinsed in two sequential clean 2% HNO<sub>3</sub> solutions for 30 s each prior to each experimental collection. Each mass/charge ratio (m/z) of interest was collected for 0.6 s and repeated 3 times. The concentration was calculated from the linear calibration curve obtained for the calibration standard solutions. After every 5 unknown samples, the probe was sent back to the 10 ppb CalStd.

### 3.3 Results and Discussion

The results from a single cycle of a cyclic voltammetry experiment on a NiO electrode in 0.1M KOH are shown in Figure 3.1. The plot has been divided into 3 distinct regions of the positive sweep of the cycle. Region I is the ideally polarizable region, Region II is where the electrodeposited film undergoes a change in oxidation state from Ni<sup>2+</sup> to Ni<sup>3+</sup>, and Region III is where the OER catalysis takes place.



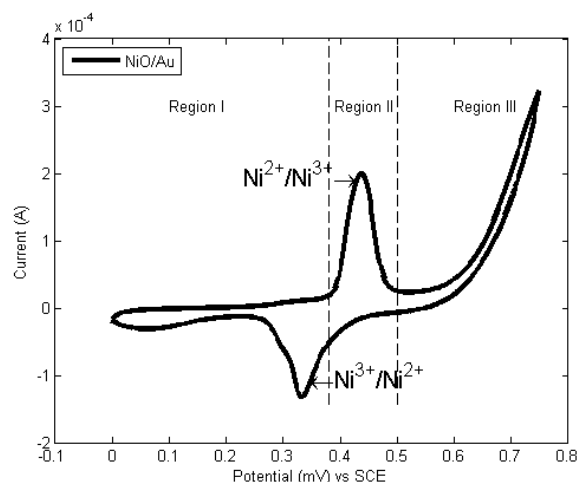


Figure 3.1. Cyclic voltammogram of the as-deposited NiO/Au electrode. The scan rate is 50 mV/s and the electrolyte is 0.1 M KOH. The 10<sup>th</sup> cycle after deposition is shown.

Region II in Figure 3.1 corresponds to the transient oxidation of Ni centers in the surface, and does not contribute to the overall oxygen evolution activity. To more cleanly compare the electrochemical activities of NiO electrodes in different electrolytes, we measured the steady state currents, which do not include this transient oxidation current, for the electrode at different potentials in the different electrolytes. The results from the constant potential experiments for the NiO/Au electrodes in each of the alkali hydroxide electrolytes are summarized in Figure 3.2. From these data it is seen that for a given potential, the activity depends on the solvated cation with  $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ . These data suggest that simply changing the solvated cation present can significantly change the activity of the OER. For example at a 450 mV overpotential, simply switching from LiOH to CsOH more than doubles the current.

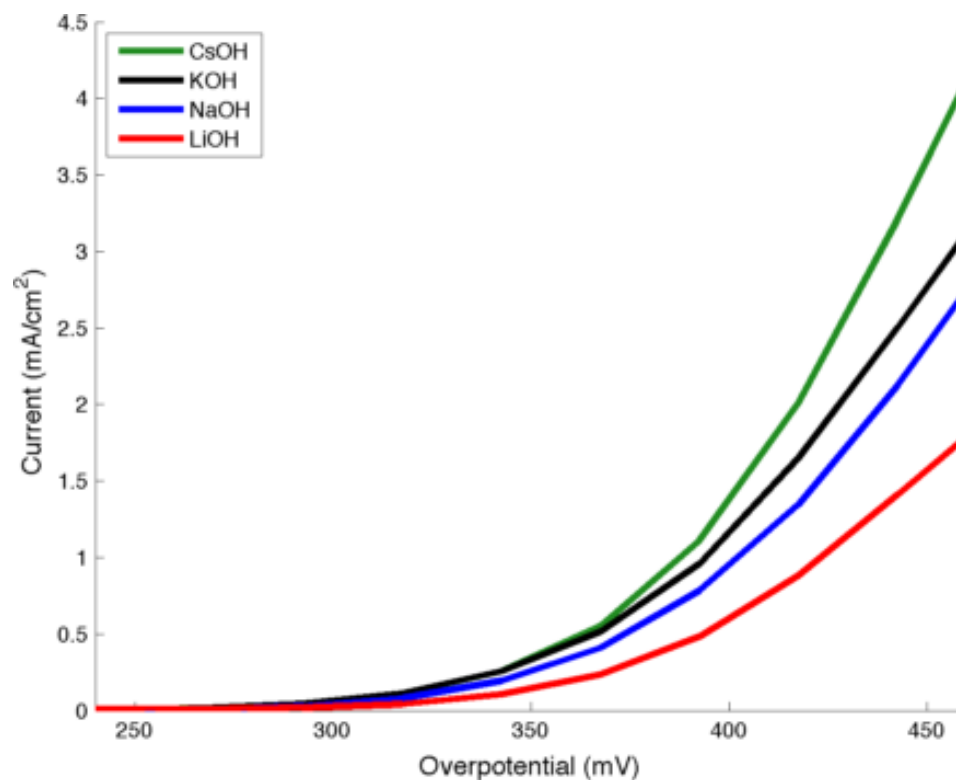


Figure 3.2. Plot of the steady-state activity as a function of potential in each of the 0.1 M hydroxide solutions. The overpotential is with respect to the equilibrium oxygen evolution potential. The current is normalized by the geometric area of the electrode.

Tafel analysis was performed on these data to test whether there is any change in the reaction mechanism, and a summary of this analysis is shown in Table 3.1, where it is evident there is no statistically relevant difference in the Tafel slopes in the different electrolytes. Thus, we cannot conclude with confidence that a mechanism change is responsible for the increased activity.

Table 3.1. Experimentally observed Tafel slope computed from the steady-state data shown in Figure 3.2.

| Electrolyte             | LiOH           | NaOH            | KOH           | CsOH            |
|-------------------------|----------------|-----------------|---------------|-----------------|
| Tafel Slope (mV/decade) | $79.3 \pm 9.4$ | $72.6 \pm 14.4$ | $80.8 \pm 14$ | $76.6 \pm 11.3$ |

The effects of the cations on OER activity are reversible. We performed electrolyte switching experiments where we measured the electrochemical performance of a single electrode in CsOH, then LiOH, and then again in CsOH shown in Figure 3.3. From *CsOH 1* to *LiOH*, there is both a shift of the Ni oxidation wave to more anodic potentials and a substantial decrease in the current in the OER region. Upon switching back to CsOH, *CsOH 2*, the oxidation wave shifts almost back to its original location and the activity is restored. These results give evidence that the changes in electrochemical behavior are a direct result of electrolyte. We next consider the possibility of cation intercalation and its effect on catalytic activity. As the NiOOH structure forms, water enters the electrode, and the water can drag cations with it. The presence of cations may have a promoting or deleterious effect on the electrode. We next attempt to quantify the intercalation of cations into the electrodes using ICP-MS.

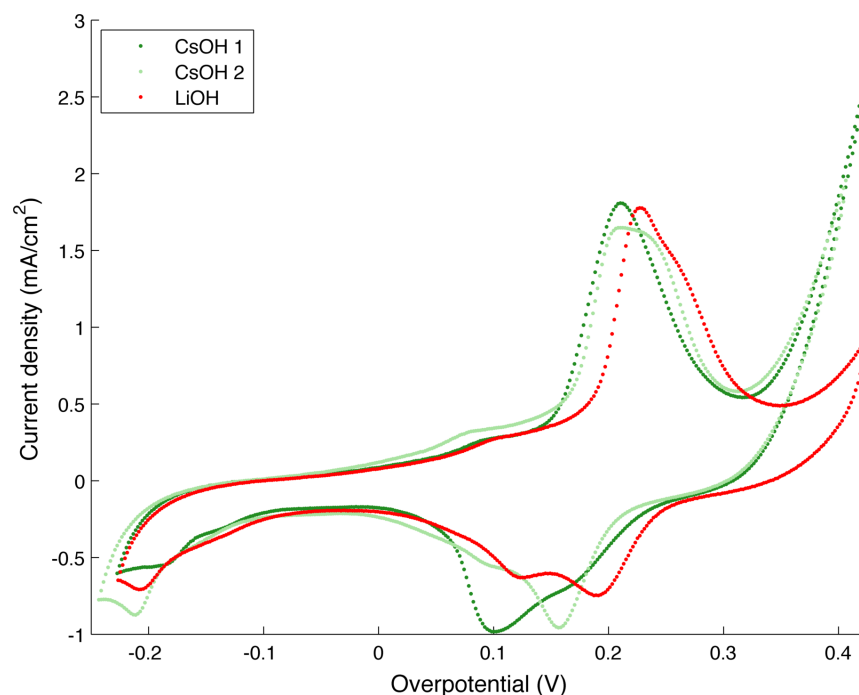


Figure 3.3. Final cycle of cyclic voltammograms of NiO/Au electrode placed first in 0.1 M CsOH (CsOH 1), then switched to 0.1 M LiOH, and back to 0.1 M CsOH (CsOH 2). The scan rate was 50 mV/s.

The experiments were designed to minimize contamination of the measurements by residual electrolyte on the electrodes, and to determine if the cation intercalation was reversible. All electrodes were oxidized at 100  $\mu$ A for 1 hr in the electrolyte. Half were then reduced for 100 s at -100  $\mu$ A, and then all were rinsed with deionized water prior to film dissolution. Half of the films were rinsed for 10 s and the other half for 100 s. After rinsing the electrode films were dissolved in 1 M HNO<sub>3</sub> for analysis.

The results from the ICP-MS experiments are shown in Figure 3.4, where the cation concentration is plotted as a function of the different rinse times. The results collected from experiments conducted in LiOH and NaOH are excluded because Li is used as an internal standard and thus diminishes the confidence of

the LiOH data and Na readings are excluded due to instrument sensitivity issues. The results in Figure 3.4 help explain the results from the electrolyte switching experiments. The cations are loosely bound to the surface and easily rinsed away. These results are observed regardless of whether the electrode was oxidized or reduced prior to the rinse. The results show higher concentrations of K cations relative to Cs, but rather than increased intercalation of K, the Cs cations are more easily rinsed away.

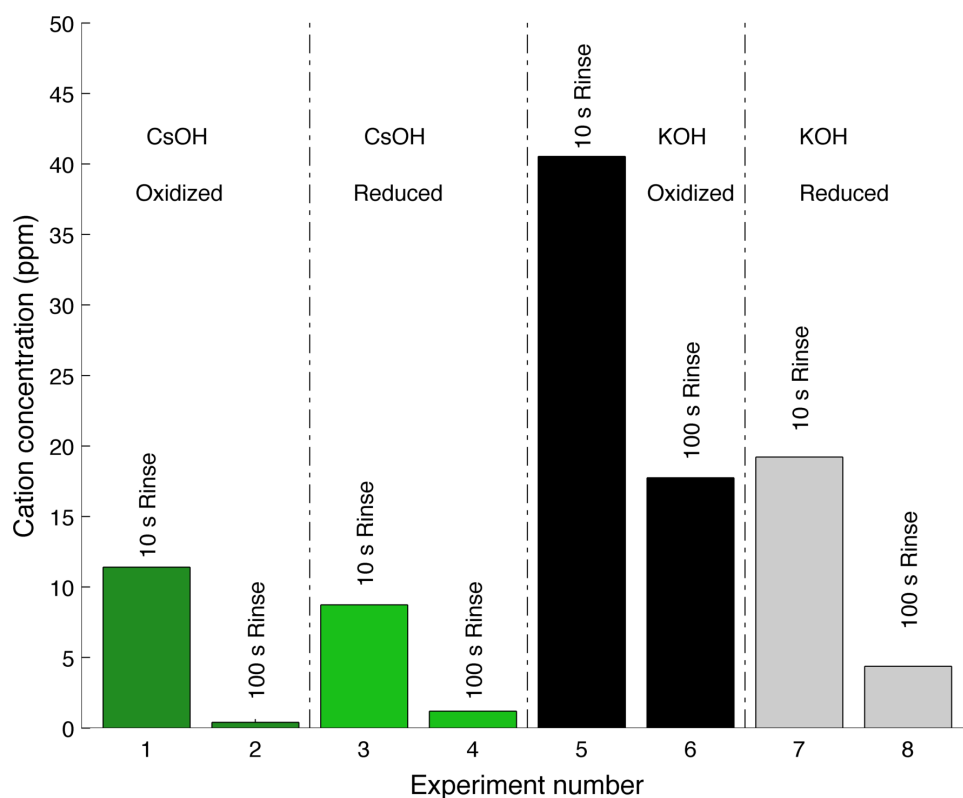


Figure 3.4. ICP-MS results for experiments conducted in Cs (green) and K (black) hydroxide solutions. Concentrations in parts per million are plotted for the oxidized (darker) and reduced (lighter) films. Films were rinsed for either 10 (odd numbers) or 100 (even) seconds with deionized water prior to dissolution.

Iron is both a common impurity in hydroxides and is also known to increase the activity of Ni electrodes for OER (17-19). The Fe content of the dissolved films

was found to be of order 10-100 ppb for each of the experiments, which is comparable to the level for Ni after dissolution. Due to the differing concentrations of Fe evidenced by the ICP-MS data, we next examine the effect of Fe impurity in the electrolyte by spiking the Fe concentration to much higher levels than those found in the clean electrolyte solutions. Fresh electrodes were tested in as-prepared 0.1 M hydroxide solution, then the Fe content was spiked to a level of 250 ppm and the experiments repeated, then returned to an as-received hydroxide solution for a final experiment.

From the Fe-spiked experiments (Figures 3.5 and 3.6), it is evident in the case of LiOH that Fe-spiking results in an increase in the electrochemical activity. (The 250 ppm amount is a substantial increase compared to the Fe content in the clean hydroxide solutions, which is of order 10-100 ppb.) After completion of the Fe-spiked experiments, the cell and all parts were thoroughly rinsed and the experiments were repeated in 0.1 M LiOH, *LiOH 2*. The behavior of the rinsed electrode was still better than the initial data set, suggesting that the Fe had adsorbed onto the Ni electrode; however, it is also clear that the activity has decreased from the Fe-spiked experiment to *LiOH 2*. This suggests that the Fe atoms may leach and be released back into the solution during the redox cycling.

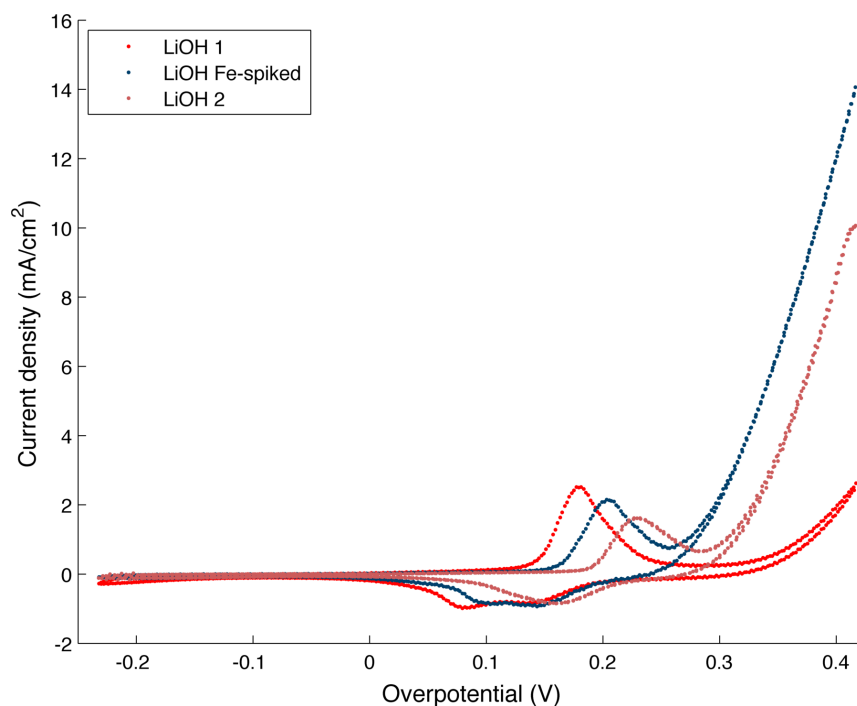


Figure 3.5. Final cycle (of 20) of cyclic voltammograms of NiO/Au electrode in 0.1 M LiOH (LiOH 1). Following the final scan, 250 ppm  $\text{Fe}(\text{NO}_3)_3$  was added to the electrolyte and the cyclic voltammetry experiment repeated (LiOH Fe-spiked). After rinsing, the electrode was placed in fresh 0.1 M LiOH and the experiment repeated a final time (LiOH 2). Scan rate is 50 mV/s.

The results from identical experiments conducted in CsOH are shown in Figure 3.6. The first experiment, *CsOH 1*, in the unspiked 0.1 M CsOH shows higher activity than even the Fe-spiked LiOH experiment. However, when the Fe spike is added, the CV shows a shift of the Ni oxidation wave to more anodic potentials and lower currents in the OER region of the CV. These results are corroborated in the chronoamperometry experiments where currents of 1 mA @ 625 mV were seen prior to the Fe spike, compared to 0.87 mA after the spike. After the parts were rinsed and cleaned, the activity returned to that seen in *CsOH 1*, though the redox potential remains shifted to a more anodic value.

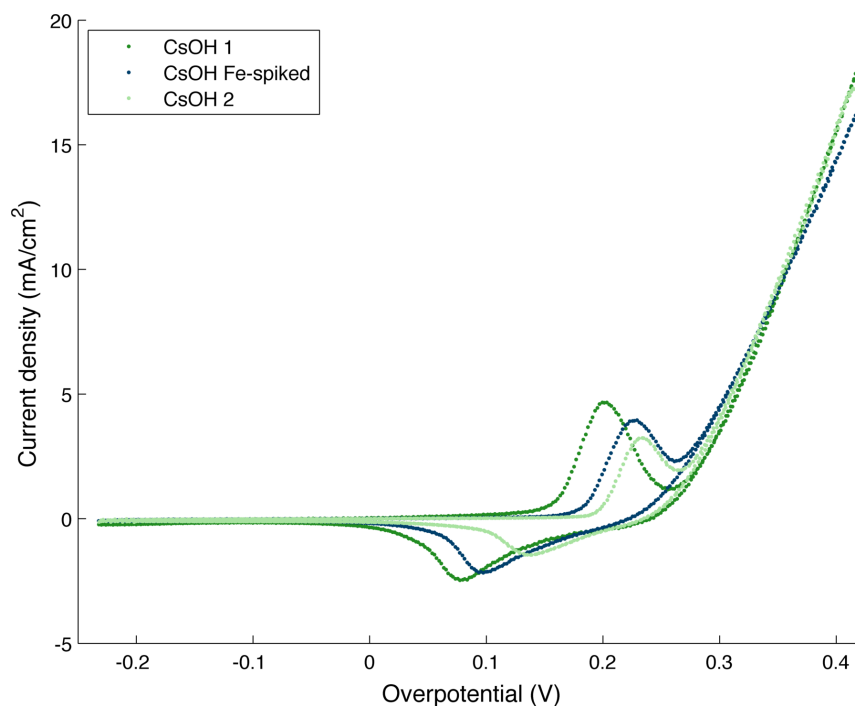


Figure 3.6. Final cycle (of 20) of cyclic voltammograms of NiO/Au electrode in 0.1 M CsOH (*CsOH 1*). Following the final scan, 250 ppm  $\text{Fe}(\text{NO}_3)_3$  was added to the electrolyte and the cyclic voltammetry experiment repeated (*CsOH Fe-spiked*). After rinsing, the electrode was placed in fresh 0.1 M CsOH and the experiment repeated a final time (*CsOH 2*). Scan rate is 50 mV/s.

The results from the Fe-spiked experiments are similar to those seen by Krejci (19), except that the  $\text{Ni } 2^+/3^+$  redox potential in our experiments did not shift to more cathodic potentials after rinsing and placement into the fresh electrolytes. It is also important to point out the positioning of the oxidation wave. For both electrolytes, the addition of iron shifts the oxidation wave to higher potentials, but in comparison to Figure 3.3, it is clear that switching the electrolyte from LiOH to CsOH results in a shift to lower potentials. This indicates that the role of the cations has a greater impact on the redox behavior than the trace levels of iron impurities in the hydroxide materials.



To further demonstrate the significance of the electrolyte effects, a mixed NiFe electrode was prepared via electrodeposition from a 0.01 M nitrate solution containing nominally 15% Fe(III) with the balance Ni(II). The as-deposited electrode was placed in a clean 0.1 M CsOH solution and 40 cycles from 0-0.65 V vs SCE were run at a scan rate of 50 mV/s. Upon completion of these CVs, multi-step chronoamperometry was run to complete the initialization of the electrode. A further 40 cycles under the same conditions were run, and cycles 1 and 40 are shown in Figure 3.7, *CsOH 1* and *CsOH 40*, respectively. The cell was then disassembled, rinsed, and reassembled with the electrolyte switched to 0.1 M LiOH. The first and last cycles are shown in the above figure, *LiOH 1* and *LiOH 40*.

While there is no appreciable difference between the behavior and activity seen in the CsOH electrolyte, there is an immediate shift of the Ni oxidation wave to more anodic potentials and the total current is lower upon switching the electrolyte to 0.1 M LiOH. As the residual Cs cations are displaced by Li cations the current continues to decrease to the value seen in *LiOH 40*. From the preceding set of experiments, we have shown that while there is a large effect with the addition of Fe to the system (17), there is still an appreciable effect to the catalytic behavior upon switching the electrolyte used in the NiFe electrode experiments, and on this evidence, we conclude that the increase is due to effects of the cation rather than due to Fe impurities in the electrolytes.

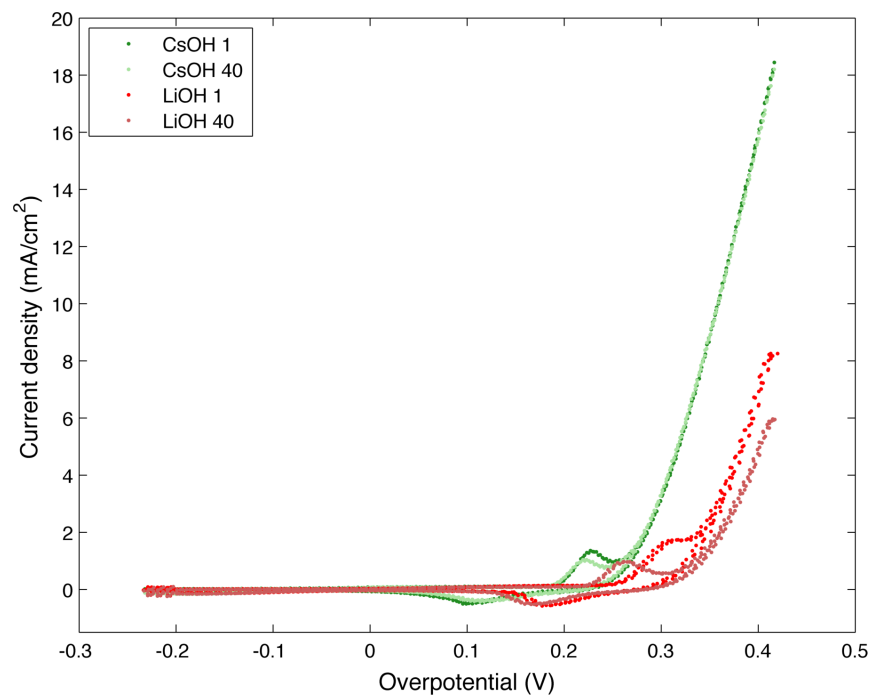


Figure 3.7. First and last cycles of cyclic voltammetry experiment on  $\text{Ni}_{0.85}\text{Fe}_{0.15}\text{O}_x/\text{Au}$  electrode placed first in 0.1 M CsOH, then rinsed and placed in a 0.1 M LiOH solution. Scan rate is 50 mV/s.

Finally, we consider the structure of the electrodes under the OER conditions using in situ Raman spectroscopy. The Raman cross section of the NiO films is sufficiently small that Ag particles(16) must be co-deposited with the Ni in order to get a measurable signal in our spectroelectrochemical cell.

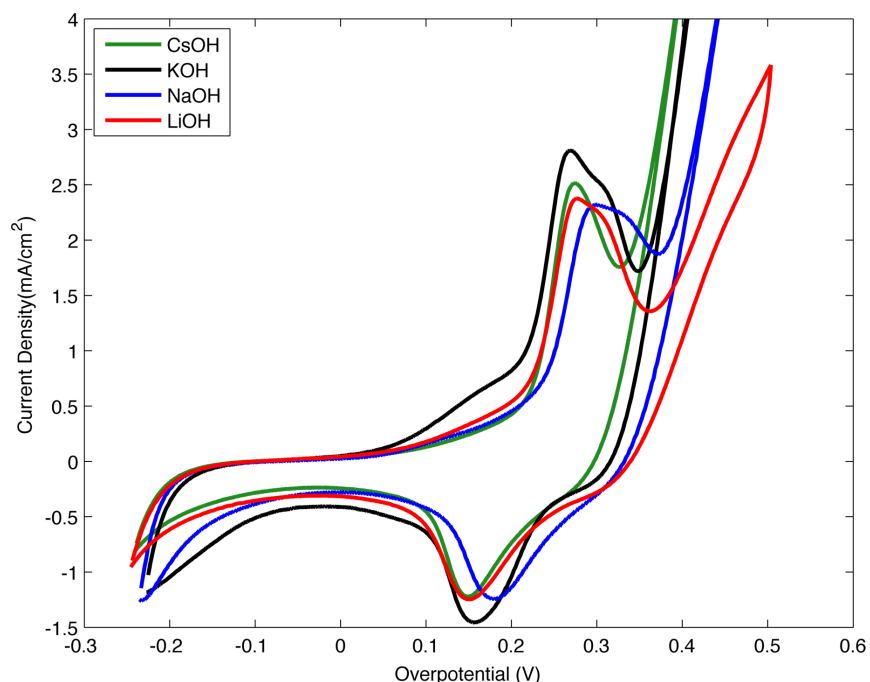


Figure 3.8. Cyclic voltammetry experiments conducted on Ni + Ag oxide films on gold. The behavior matches well with that observed on films without Ag coprecipitation.

Control experiments were carried out to ensure the Ag did not affect the electrochemical behavior of the surface. The results from these experiments show that electrodes prepared with and without Ag are electrochemically identical, as seen in Figure 3.8, with no evidence of electrochemically active Ag.

The *in situ* Raman spectra were collected throughout the 3 regions of the CV and are compiled in Figures 3.9-12. The spectra are normalized to the intensity of the  $480\text{ cm}^{-1}$  peak and the potential increases from the bottom (300 mV) to top (675 mV).

At low potentials, Region I, there are no clear peaks evident; however, as the potential is increased, two peaks begin to form at  $480$  and  $560\text{ cm}^{-1}$ . These peaks are associated with the Ni-O stretching modes indicating the formation of a Ni

oxy-hydroxide phase that forms during the OER (11, 12, 16). As the potential is increased further, the surface continues to oxidize further and the two peaks become more well-defined and larger in magnitude. These increases continue until the potential is increased up to ~575 mV, a potential just beyond the transition from region II to region III in the CV, indicating all of the Ni atoms have been oxidized to the >3+ oxidation state. In the CsOH and KOH spectra (Figures 3.9 and 3.11, respectively), a third peak ( $\sim 430\text{ cm}^{-1}$ ) appears at elevated potentials due to the oxidation of the Ag particles. Upon raising the potential beyond this point, the surface is readily evolving oxygen, but no further changes to the Raman spectra are observed. This suggests that the NiOOH material is the active phase undergoing catalytic turnover, and is similar to the findings in the literature(11).

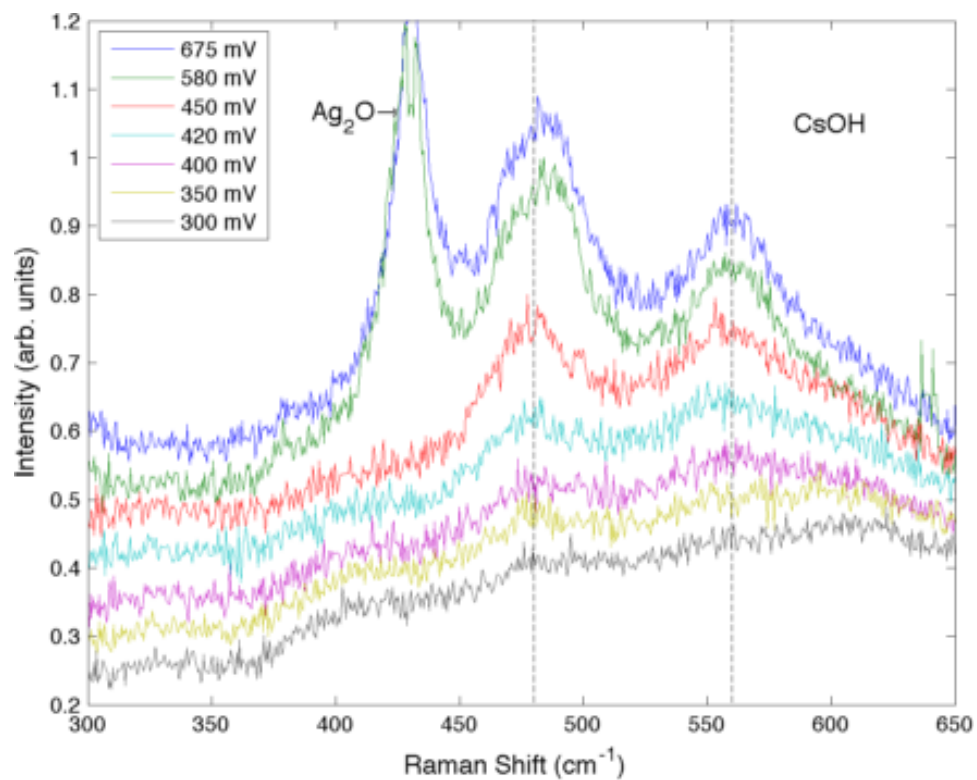


Figure 3.9. In situ electrochemical Raman spectra collected in 0.1 M CsOH. The spectra are normalized to the intensity of the 480 cm<sup>-1</sup> peak and offset for clarity. Potentials are listed relative to SCE reference electrode.

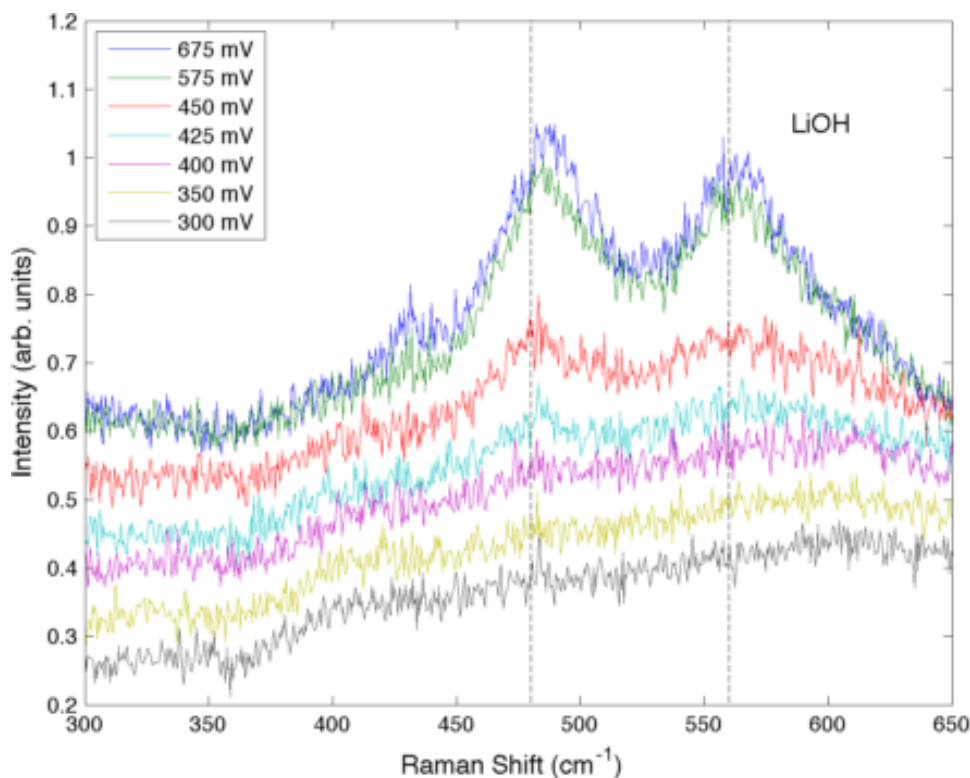


Figure 3.10. In situ electrochemical Raman spectra collected in 0.1 M LiOH. The spectra are normalized to the intensity of the 480  $\text{cm}^{-1}$  peak and offset for clarity. Potentials are listed relative to SCE reference electrode.

There are distinct differences in the spectra collected in CsOH (Figure 3.9) and LiOH (Figure 3.10). Most importantly, the peaks associated with the formation of the NiOOH phase appear at a much lower potential (350 mV) in CsOH compared LiOH (425 mV). This observation suggests a correlation between the solvated cation present in the electrolyte and the energy required to form the oxidized NiOOH species. Given the evidence that a) the OER reaction proceeds much more favorably in CsOH, b) the NiOOH phase is present during the reaction, and c) this phase is formed at lower potentials in CsOH, we propose that the promotion effect of the electrolyte is related to the number of active sites present, or equivalently to the formation of the active phase. Since the NiOOH phase

forms at a lower potential in CsOH than in LiOH, there are more active sites present in the CsOH electrolyte at lower potentials, and hence we observe higher activity. It is not possible to count the number of active sites, however, because they only exist under OER conditions.

From the literature there are two proposed forms of the Ni oxyhydroxide phase,  $\gamma$  and  $\beta$  (20). The two differ in the inter-layer stacking,  $\beta$  is more close packed compared to the more disordered  $\gamma$ , and in their respective Ni valencies (21). The average valency in the  $\beta$  phase is  $\sim 3$ , while the average Ni valency in the  $\gamma$  phase is  $\sim 3.7$  (22, 23). The higher valency is the result of more +4 Ni sites, and higher valence state materials are found to play an important role in water oxidation. Raman can be used to differentiate the two by careful inspection of the peak locations and relative intensity of the two oxyhydroxide peaks (11, 16).

In CsOH, the peaks are centered around the 480 and 560  $\text{cm}^{-1}$  lines, and the intensity of the 480  $\text{cm}^{-1}$  peak is considerably larger than the 560  $\text{cm}^{-1}$  peak. Contrasting this to the same data in LiOH, the two peak centers are blue shifted, and the relative intensity is much lower than the CsOH spectra. The shift to higher frequencies is indicative of shorter bond lengths (24), which would be expected for the lower valence state of Ni and more dense  $\beta$  phase. The relative intensities have been noted by both Yeo (11) and Kostecki (16) as evidence of phase differentiation. Yeo prepared  $\gamma$  and  $\beta$  electrodes and noted these differences, while Kostecki noted coupled decay of the 480  $\text{cm}^{-1}$  peak with growth of the 560  $\text{cm}^{-1}$  peak after 60 potential cycles, which is evidence of the  $\gamma$  to  $\beta$  aging process. From this evidence in conjunction with the data in Figure 3.5, we conclude that

the  $\gamma$  phase is promoted in CsOH, while the less active  $\beta$  phase is promoted in LiOH for these thin-film electrodes.

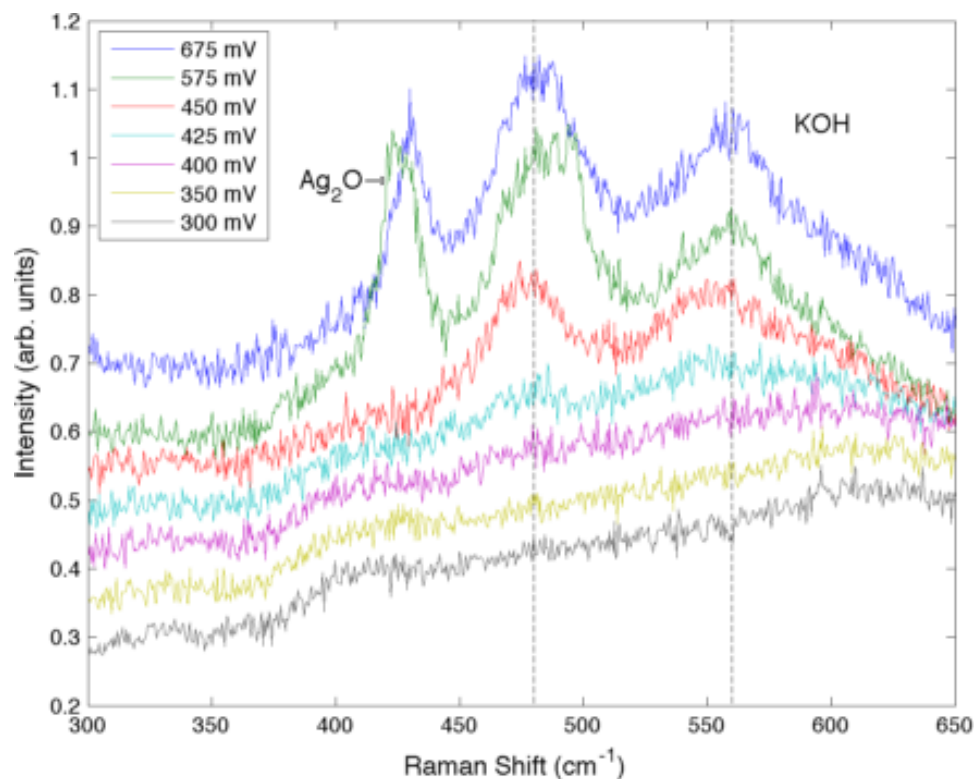


Figure 3.11. In situ electrochemical Raman spectra collected in  $0.1\text{ M KOH}$ . The spectra are normalized to the intensity of the  $480\text{ cm}^{-1}$  peak and offset for clarity. Potentials are listed relative to SCE reference electrode.



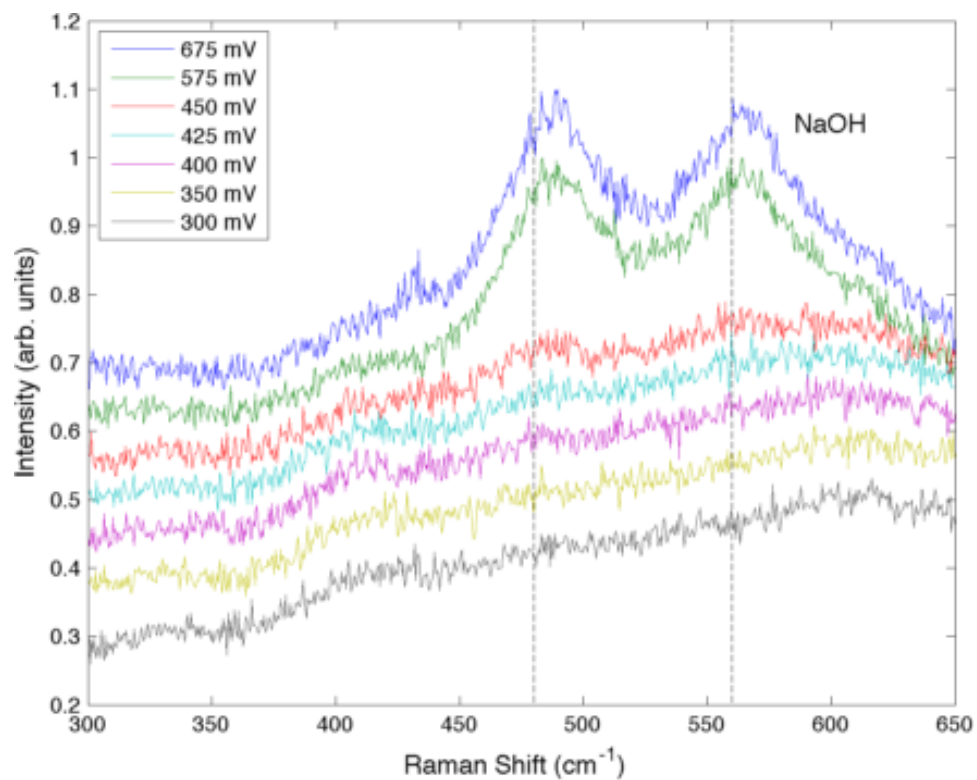


Figure 3.12. In situ electrochemical Raman spectra collected in 0.1 M NaOH. The spectra are normalized to the intensity of the 480 cm<sup>-1</sup> peak and offset for clarity. Potentials are listed relative to SCE reference electrode.

We also observed different behavior in the electrolytes with respect to formation of  $\text{Ag}_2\text{O}$ . It is important to note that we do not see any electrochemical evidence of Ag in the electrode surface in the cyclic voltammetry. Ag readily corrodes and strips away at high oxidizing potentials, so we believe the surface is Ag free and that all the Ag is buried under the surface. Yet, we see formation of  $\text{Ag}_2\text{O}$  in CsOH and KOH (Figures 3.9 and 3.11, respectively), but hardly any formation in NaOH and LiOH (Figures 3.10 and 3.12, respectively). We hypothesize that as the NiOOH forms, the thickness of the layer is electrolyte dependent. Our hypothesis is that the more open  $\gamma$ -NiOOH layer formed in CsOH and KOH allows access to subsurface Ag particles, which oxidize on exposure to water. In LiOH and NaOH, the  $\beta$ -NiOOH layer is more close-packed, and does not facilitate the hydration of subsurface Ag particles, which in turn, are not oxidized. Again, the type of NiOOH layer affects the number of higher valence Ni sites, which could be responsible for the increased activity.

### 3.4 Conclusions

We have shown that for the series of alkali hydroxides ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$ ) there is an increase in OER activity of nickel oxide based electrocatalysts going down the periodic table. The cation promotion effects are reversible. From *in situ* spectroscopic experiments, there is evidence that the NiOOH species is the phase present during the electrocatalytic oxygen evolution reaction and that the more active  $\gamma$ -NiOOH phase is more readily formed in CsOH compared to LiOH. Thus,

there is a correlation between the electrolyte cation present and the promotion of the oxidized NiOOH phase, and by extension to the overall activity of the electrode for the OER catalysis.

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## **4. Mixed Nickel-Iron Catalysts for the Oxygen Evolution Reaction**

### **4.1. Introduction**

Corrigan's work in the 1980s clearly showed that the rate of the oxygen evolution reaction (OER) on NiO could be greatly increased by co-precipitating small amounts of either cerium or iron(1, 2). Iron is a particularly interesting case because of its earth abundance and benign environmental characteristics. Though Corrigan's work touched off an immediate interest in the Ni-Fe system(3-7), questions remained as to how Fe promoted the reaction.  $^{57}\text{Fe}$  Mossbauer spectroscopy suggested high valency Fe ions (+4 or +6) were present during electrochemical water splitting(8, 9); however, these results were contradicted by X-ray absorption spectroscopy (XAS) measurements that showed Fe was predominantly in the +3 oxidation state(10), both at open circuit and at the elevated potential required for oxygen evolution.

Our group first approached this research area wanting to better understand the role of Fe in the promotion of NiO. In an effort to have better control over the catalyst material synthesized, catalyst powders were prepared through thermal treatment of pre-cursor metal salts, rather than through electrodeposition techniques. The choice of these synthesis routes also allowed for the facile use of many ex situ characterization techniques, which we hypothesized would elucidate

a structure-function relationship between the catalyst powder materials and the increased OER activity.

The full account of our findings is published in *ACS Catalysis* 2012 Vol 2 (8) pp 1793-1801.

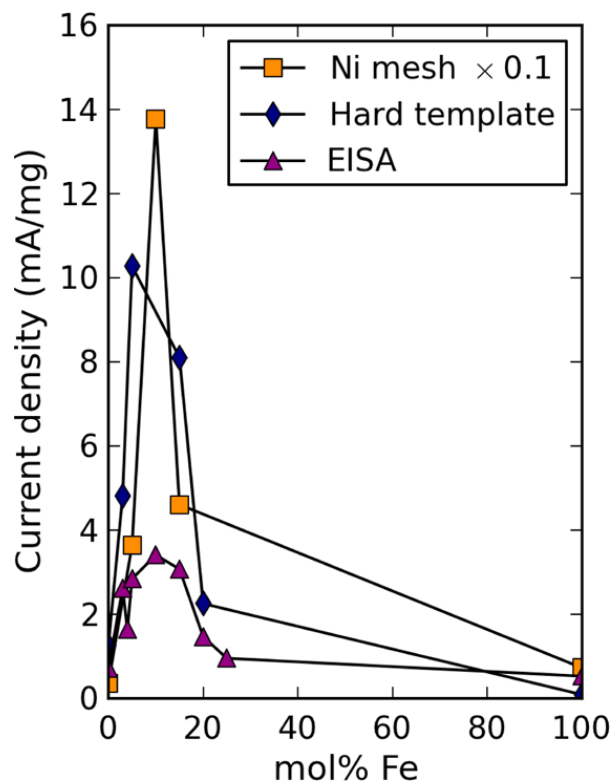


Figure 4.1. Current density at a given overpotential plotted as a function of iron loading. The mixed metal oxides were produced via 3 separate techniques, with the maximum in activity found near 10 mol% Fe for each. Reprinted with permission from Landon, J.; Demeter, E.; Inoglu, N.; Keturakis, C.; Wachs, I. E.; Vasić, R.; Frenkel, A. I.; Kitchin, J. R. Spectroscopic Characterization of Mixed Fe–Ni Oxide Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Electrolytes. *ACS Catalysis* 2012, 2, 1793–1801. Copyright 2012 American Chemical Society.

Briefly, for each of the three synthesis techniques, a peak in OER activity was found at ~10 mol% Fe loading, as seen in Figure 4.1. The increase in activity was accompanied by a decrease in the measured Tafel slope and no appreciable change in the electrochemically active surface area (as calculated by double layer

charging), which indicates the surface was intrinsically more active, rather than producing a higher current as a result of a higher surface area.

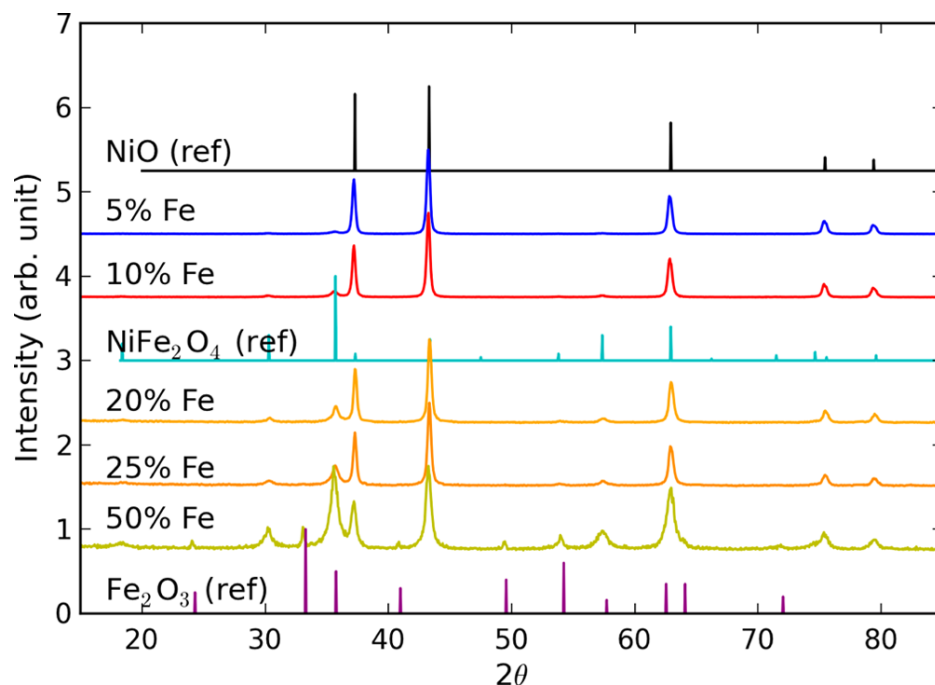


Figure 4.2. Experimental X-Ray diffraction patterns for 5 Ni-Fe oxide powders along with 3 reference patterns from JCPDS. Reprinted with permission from Landon, J.; Demeter, E.; Inoglu, N.; Keturakis, C.; Wachs, I. E.; Vasić, R.; Frenkel, A. I.; Kitchin, J. R. Spectroscopic Characterization of Mixed Fe–Ni Oxide Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Electrolytes. *ACS Catalysis* 2012, 2, 1793–1801. Copyright 2012 American Chemical Society.

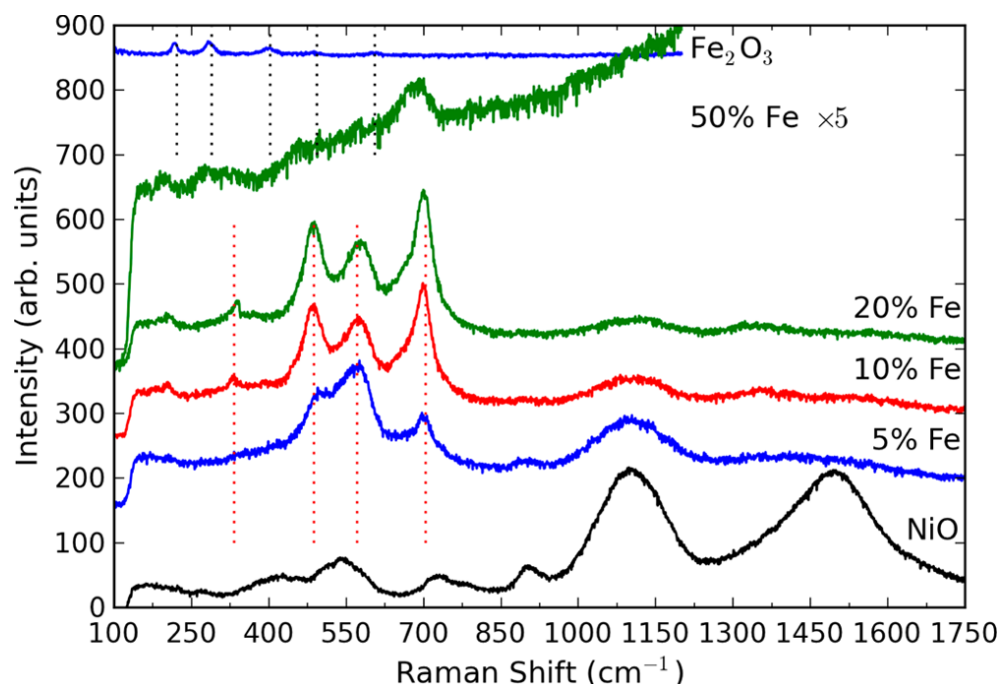


Figure 4.3. Powder Raman spectroscopy of NiO Fe<sub>2</sub>O<sub>3</sub> and 5, 10, 20, and 50 mol% Fe Ni-Fe oxides. Red dotted lines correspond to NiFe<sub>2</sub>O<sub>4</sub> spinel phase and black dotted lines correspond to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Reprinted with permission from Landon, J.; Demeter, E.; Inoglu, N.; Keturakis, C.; Wachs, I. E.; Vasić, R.; Frenkel, A. I.; Kitchin, J. R. Spectroscopic Characterization of Mixed Fe–Ni Oxide Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Electrolytes. *ACS Catalysis* 2012, 2, 1793–1801. Copyright 2012 American Chemical Society.

Ex situ characterization of the catalyst powders using X-ray diffraction (XRD), Figure 4.2, and Raman Spectroscopy, Figure 4.3, both suggested the formation of a NiFe<sub>2</sub>O<sub>4</sub> spinel phase in the Fe-containing materials. While NiFe<sub>2</sub>O<sub>4</sub> spinel is known to be a better catalyst than NiO, our results indicated increasing amounts of the spinel were formed with increased Fe content up to 50 mol% Fe. Were the spinel phase responsible for the increase in activity, the catalysts with higher loadings of Fe would have been expected to also have higher activities, yet the electrochemical OER activity falls greatly at Fe loadings above 10 mol%.



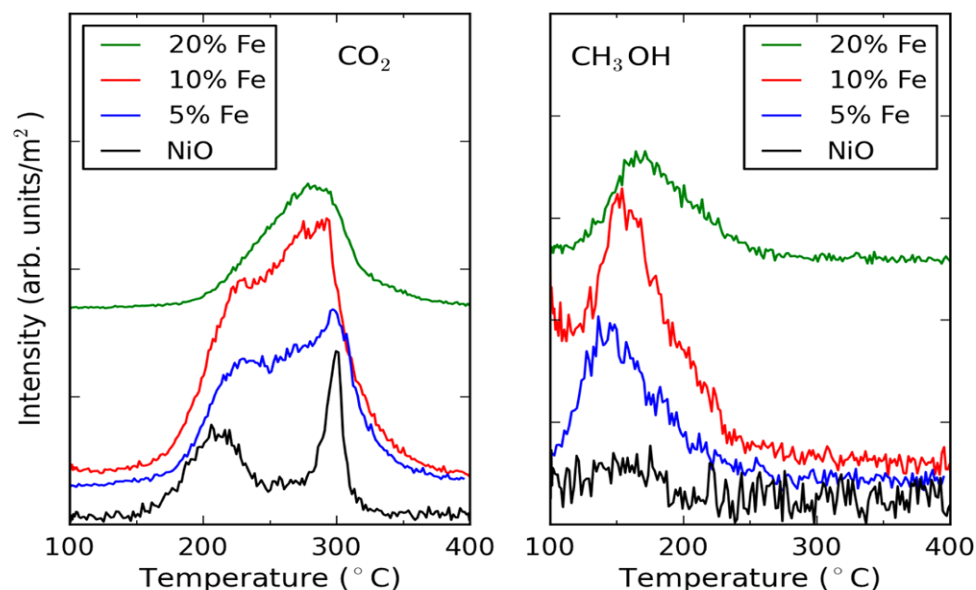


Figure 4.4. Methanol temperature programmed reaction spectroscopy data for product species  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$ . Methanol was adsorbed to the surface and slowly heated with the effluent gas monitored via mass spectrometer to quantify product gas speciation. Reprinted with permission from Landon, J.; Demeter, E.; Inoglu, N.; Keturakis, C.; Wachs, I. E.; Vasić, R.; Frenkel, A. I.; Kitchin, J. R. Spectroscopic Characterization of Mixed Fe–Ni Oxide Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Electrolytes. *ACS Catalysis* 2012, 2, 1793–1801. Copyright 2012 American Chemical Society.

Further examination of the catalyst powder materials using temperature programmed reaction spectroscopy (TPRS), Figure 4.4, revealed that increasing the Fe content to 5 and 10 mol% resulted in an increase in the amount of  $\text{CO}_2$  produced; hence, the number of basic sites available had increased. Increasing the Fe loading beyond 10 mol% resulted in a decrease in the amount of  $\text{CO}_2$  produced. Thus, there was a correlation between the number of basic sites and the OER activity of the material. Also of note was that in the 10 mol% Fe experiment, desorbed  $\text{CH}_3\text{OH}$  was also observed, indicating that there were Fe sites available on the surface.

These results led us to two new hypotheses (1) that the Fe preferentially segregated to the surface and (2) that in order to understand the nature of the

active phase and the role of Fe in the promotion of the OER, in situ spectroscopic techniques would be required. To test these hypotheses, this chapter will discuss Ni@Fe core/shell catalyst materials were prepared with varying loadings, from sub monolayer up to 10 atomic layers of Fe, to geometrically restrict Fe to the surface. Later, thin film electrodes are utilized to collect Raman spectroscopy of mixed Ni-Fe oxide materials during the electrochemical oxygen evolution reaction.

## **4.2 Experimental methods**

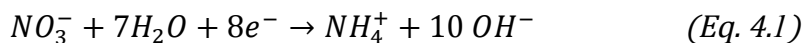
### **4.2.1 Ni@Fe Core Shell Synthesis**

The core shell catalyst materials were prepared via a two-step synthesis. First, NiO particles were formed using a hydrothermal polyol process. NiCl<sub>2</sub> was dissolved using ethylene glycol (EG) in a 200 mL round bottom flask. 1 M NaOH in ethylene glycol was then added to the flask to stoichiometrically hydroxylate the Ni atoms to Ni(OH)<sub>2</sub>. This reaction was almost instantaneous upon addition of the hydroxide, which was evident by a rapid color change from green to gray/black. The flask was then placed into a 160 °C wax bath for 1 hr in order to facilitate more complete conversion to Ni(OH)<sub>2</sub>. The flask was removed from the bath and allowed to cool to room temperature, at which time the particles had settled to the bottom of the flask. The glycol was decanted and the remaining particulate suspension was collected in a beaker and fired at 300 °C for 4 hr to produce the NiO powder.

The Fe shell was deposited by first producing a 10 mg/mL solution of  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$  in water. The solution was then sonicated for 1 hr to ensure homogeneity. The NiO was weighed into a glass vial, and the Fe solution was added to the desired molar amount using a micropipette. The resultant slurry was then sonicated briefly to ensure even dispersion and moved to a vacuum oven to slowly evaporate the solution at 120 °C. Once dried, the coated powder was calcined at 350 °C to decompose the acetate to iron oxide.

#### **4.2.2 Ni-Fe Thin Film Electrode Synthesis**

Thin film materials allow for an easier description of the surface-active material during experiments. To produce thin film electrode materials an electrodeposition technique was utilized. The gold substrate was polished to a mirror finish using 0.05  $\mu\text{m}$  polishing suspension. After polishing, the electrode was sonicated in deionized water, and rinsed to remove the alumina fine particles. The electrode was then electrochemically pre-treated by potential cycling from -0.3 to 1.4 V vs. SCE at a scan rate of 1 V/s in 1 M  $\text{HNO}_3$  to ensure the surface was clean. The plating solution was prepared by dissolving nitrate salt solutions to a total concentration of 0.01 M, which allows for better deposition efficiency(11). A cathodic current of 0.8  $\text{mA}/\text{cm}^2$  (entered into Gamry software as  $-2.51 \times 10^{-5}$  A for the 2 mm ID Pine Instruments electrodes) was set for the 20 s and the metal atoms were deposited. A suggested mechanism of Ni deposition follows.



Thus, up to one Ni atom can be deposited per every 1.6 electrons transferred, and the film thickness can be controlled by changing the deposition time. Mixed Ni-Fe films were produced in a similar manner; the plating solution was kept at a total concentration of 0.01 M, but the precursor nitrate salt solutions are combined in the desired mole ratios.

### 4.2.3 Electrochemical Experiments

All electrochemical experiments were carried out in 1 M potassium hydroxide (KOH) solution for the core shell experiments and 0.1 M KOH for the thin film experiments. For the core shell experiments, a Hg/HgO electrode, 0.098 V vs. normal hydrogen electrode (NHE), was used as the reference along with a Pt wire as the auxiliary electrode. The thin film electrodes were deposited onto ceramic patterned gold electrodes from Pine Research Instruments, which utilize a Ag/AgCl reference, 0.197 V vs. NHE, and an extended gold surface as the auxiliary electrode. A Gamry Ref600 potentiostat was used to control the experiments and data acquisition.

Electrodes were first initialized via potential cycling experiments. Electrodes are cycled between -350 and 400 mV overpotential at a scan rate of 50 mV/s until the resulting voltammograms remained constant (typically between 60 and 100 cycles). Steady-state activity experiments were then conducted by setting the potential between 200 and 500 mV overpotential in 50 mV increments for 20

minutes at each step. The average value over the last ten minutes of the step is taken as the steady-state value.

Finally, slow scan cyclic voltammetry experiments were conducted to compute the Tafel slope and exchange current density of the electrodes. The potential is cycled between 0 and 400 mV of overpotential at a scan rate of 1 mV/s for 3 cycles. The final cycle was used to compute the Tafel slope and exchange current density, as discussed in Chapter 2.

#### **4.2.4 In situ Electrochemical Raman Spectroscopy**

Raman spectra were collected using a Horiba LabRAM HR Raman microscope fitted with a 50x LWD objective, 1800 g/mm, and a CCD detector. 532 nm laser excitation was provided by a Spectra Physics Nd:YAG laser. The laser power was set to 20 mW and each sample spectrum is the average of fifteen 5-second scans. Constant potential electrochemical experiments (from 0 to 550 mV) were allowed to reach a steady state prior to the collection of Raman spectra. The data are background subtracted and offset for ease of view.

### **4.3 Ni@Fe Core Shell results and discussion**

The results from the experiments conducted on Ni@Fe core shell catalysts supported on carbon paper are summarized in the following data sets. The first set of experiments was conducted by an undergraduate researcher, Rebecca McKeever, under my supervision. The change in activity with increasing Fe loading is monitored by measuring two intrinsic parameters of the system, the Tafel slope and the exchange current density,  $i_0$ . The data shown in Figures 5 and

6 track these values as a function of Fe loading. Generally speaking, higher activity is observed with decreasing Tafel slopes, (i.e. larger differential increase in current per increase in applied potential), and increasing values of the exchange current density, which is defined as the rate of the forward reaction at 0 V overpotential.

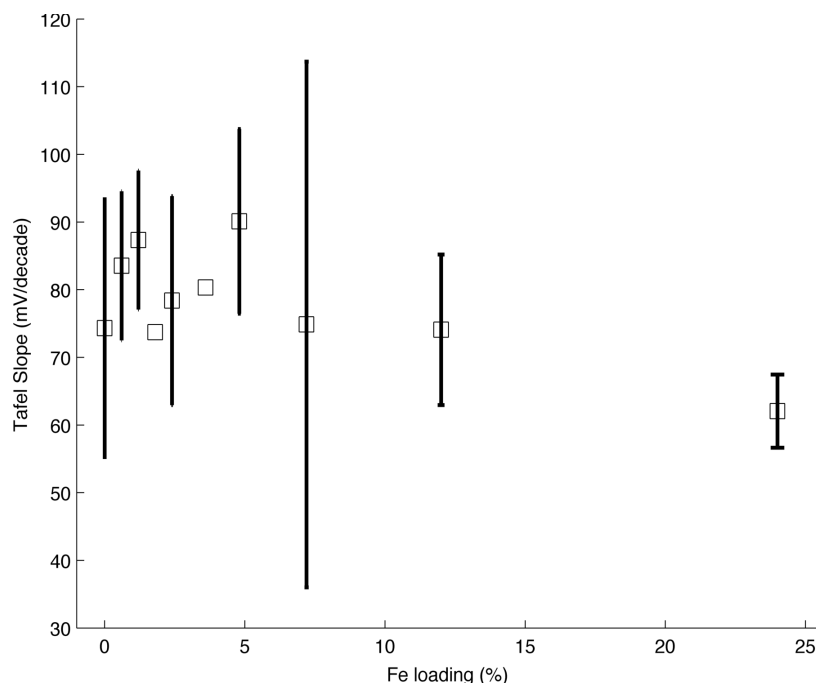


Figure 4.5. Experimental Tafel slopes computed from slow-scan cyclic voltammetry plotted as a function of iron loading from 0-25 % for a series of Ni@Fe core shell electrocatalysts. Other things being equal, a decrease in the Tafel slope indicates an increase in catalytic activity.

From inspection of Figures 4.5 and 4.6, there are no discernable trends in either metric as a function of Fe loading. The error bars represent 90% confidence intervals when at least 3 runs were performed and the points with no error bars are the mean of two experimental runs. Given the observed trend in Fe loading from the literature(2, 12), an increase in activity would have been expected at low loadings of Fe, were surface Fe to be the main cause of the activity enhancement.

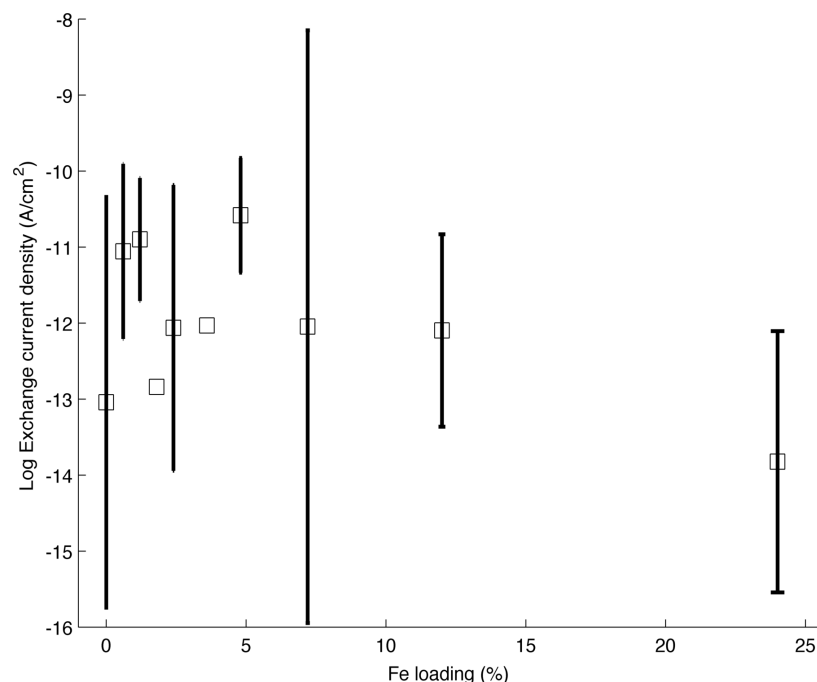


Figure 4.6. Experimental exchange current densities computed from slow-scan cyclic voltammetry plotted as a function of iron loading from 0-25 mol %. Generally speaking, a larger value of the exchange current density equates to a more active catalyst material.

To test the hypothesis further, a second set of experiments was performed focusing on only Fe loadings less than 10% mole. In Figure 4.7 the current density is plotted as a function of Fe loading at a potential of 700 mV vs. Hg/HgO, or an overpotential of 380 mV, where O<sub>2</sub> evolution readily occurs. The activity is the recorded average current measurement during a 20-minute chronoamperometry experiment held at the potential of interest. Again, as seen in the above analysis, there is no observed trend in activity with respect to Fe loading. These data suggest that adding Fe directly to the surface of NiO does not result in an increase in OER activity, such as the case when the mixed oxide material is made from concurrent oxide formation of mixed precursor materials.

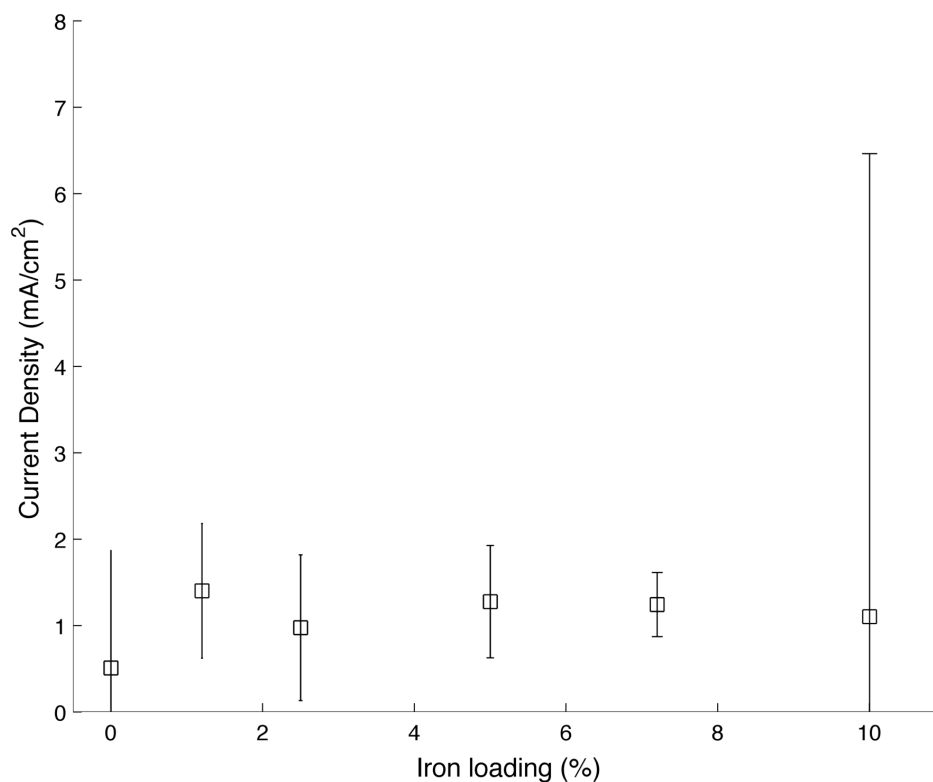


Figure 4.7. Average current density during a 20 minute constant potential experiment set to at an overpotential of 380 mV plotted as a function of iron loading for series of Ni@Fe core shell powder electrocatalysts. Current density is a direct measure of activity.

Inspection of the cyclic voltammograms in Figure 4.8 illustrate the effect of the addition of Fe onto the surface of NiO powders. The reduction wave during the cathodic sweep of the experiment indicates the point at which oxidized Ni atoms are reduced back to the +2 oxidation state. The area of this wave gives an indication of the number of redox active Ni sites electrochemically accessible, and this value greatly diminishes after the addition of 1.2% Fe to the surface, and continues to diminish with increasing Fe loading.



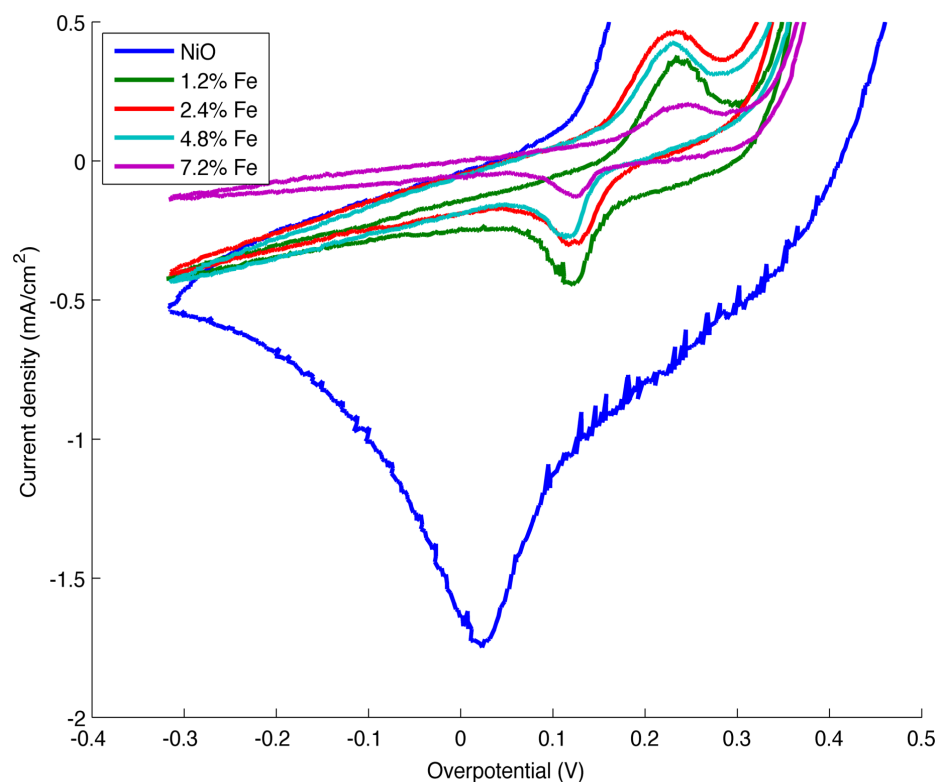


Figure 4.8. Characteristic cyclic voltammograms of Ni@Fe core shell catalysts focusing on the cathodic potential sweep. As the Fe content is increased the area of the reduction wave decreases, indicating fewer Ni sites electrochemically accessible. The scan rate was 100 mV/s.

On this evidence Ni@Fe core shells are no more active than NiO catalyst powders, which suggests that mixed Ni and Fe sites are more active for the OER than Fe covered Ni sites. To further probe the inter-relation between Ni and Fe responsible for the increase in catalytic activity for O<sub>2</sub> evolution, thin film electrode materials were produced with various mixed compositions of Ni and Fe. These thin films are experimentally advantageous because spectroscopic analysis will not suffer from interference due to bulk contributions, allowing for a studying of the active materials.

## 4.4 Ni-Fe thin film electrodes Results and Discussion

Thin film Ni-Fe electrodes were deposited onto a gold substrate in compositions varying between 0-100% Fe. Scanning electron micrographs of the cleaned gold electrode prior to film deposition and a characteristic film containing 10 mol% Fe are shown in Figure 4.9. The gold surface is not smooth as noted by the small black imperfections in the micrographs. In the case of the  $\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_x$  film, these imperfections are partially covered by the film. The image of the thin film also illustrates the evenness of the electrode surfaces created via electrodeposition.

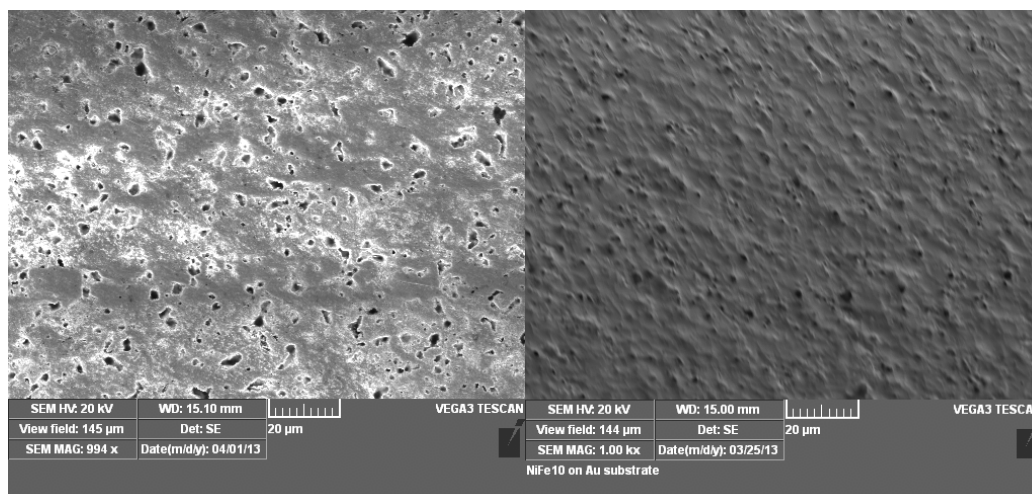


Figure 4.9. Scanning electron micrographs of clean (left) and as deposited  $\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_x$  (right) on gold electrode surfaces at 1000x magnification.

The thin film electrodes were tested for their electrochemical OER activity by use of slow-scan cyclic voltammetry. Under these conditions, the film will undergo an oxidation and then begin the OER (as seen in Figure 4.12). In order to decouple the surface oxidation event from the catalytic  $\text{O}_2$  evolution, the data are analyzed to determine the Tafel slope and the exchange current density. The data for these two intrinsic kinetic parameters are summarized in Figures 4.10 and 4.11, where they are plotted as a function of Fe content in the plating solution.

The content in the plating solution is used for the sake of precision, however; energy dispersive x-ray measurements and precedence in the literature(*1*) confirm nearly identical concentrations in the film.

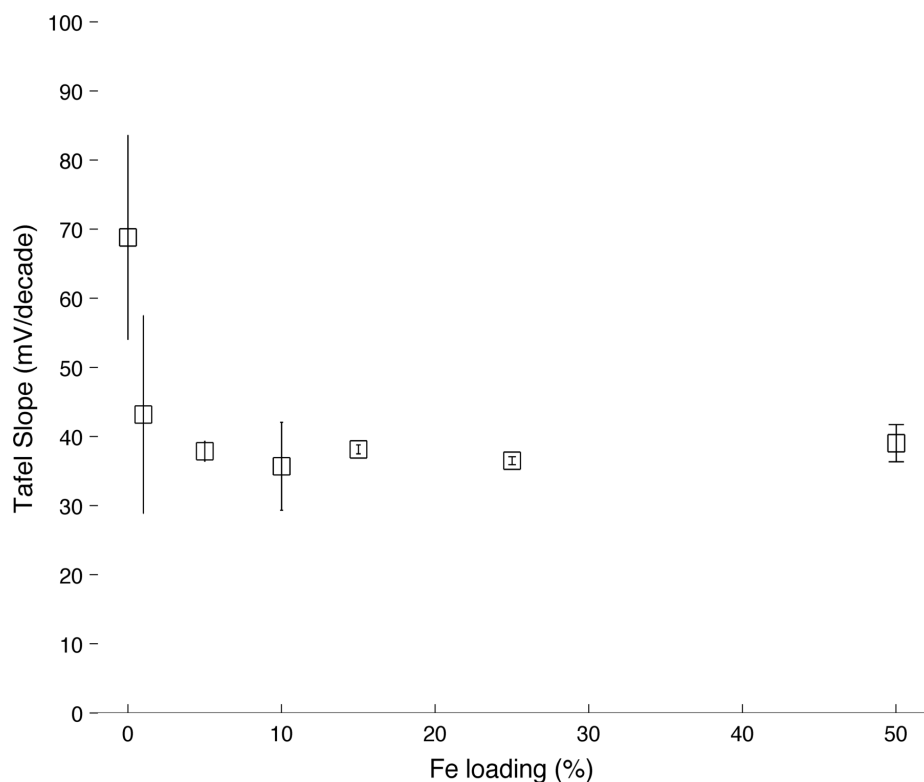


Figure 4.10. Experimental Tafel slopes computed from slow-scan cyclic voltammetry plotted as a function of iron content in Ni-Fe oxide thin film electrodes deposited onto gold. The Tafel slopes decrease sharply with a small amount of Fe added to the system, indicating improved kinetics of the reaction.

From inspection of these data, both the Tafel slope and the exchange current density are seen to decrease as the Fe content in the film increases. Because these two trends oppose one another with respect to catalytic activity, it is instructive to insert these values into the Butler-Volmer equation in order to model the kinetics of the reaction prior to discussion of relative activities.

$$i = i_0 * e^{\frac{\eta_s}{b}} \quad (Eq. 3)$$

where  $i_0$  is the exchange current density,  $b$  is the Tafel slope, and  $\eta_s$  is the overpotential.

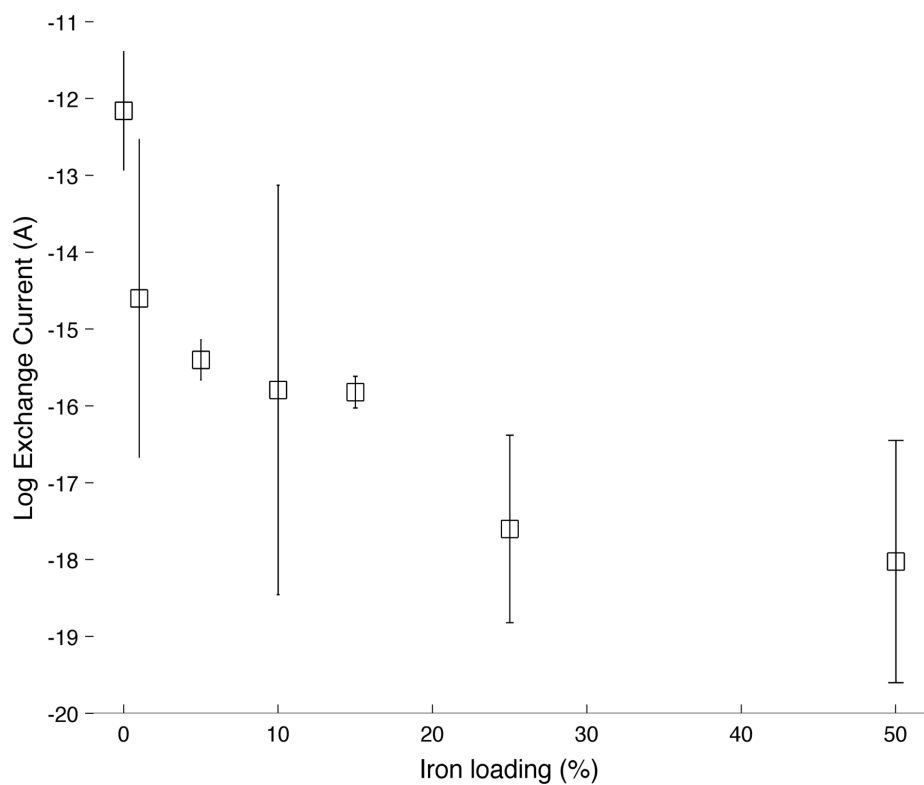


Figure 4.11. Experimental exchange current densities computed from slow-scan cyclic voltammetry plotted as a function of iron content. The decrease with increasing iron suggests an increase in the activation barrier of the reaction.

To demonstrate the validity of such an approach, the raw data from a typical experiment and the model using the kinetic parameters derived from 3 such experiments are compared in Figure 4.12.

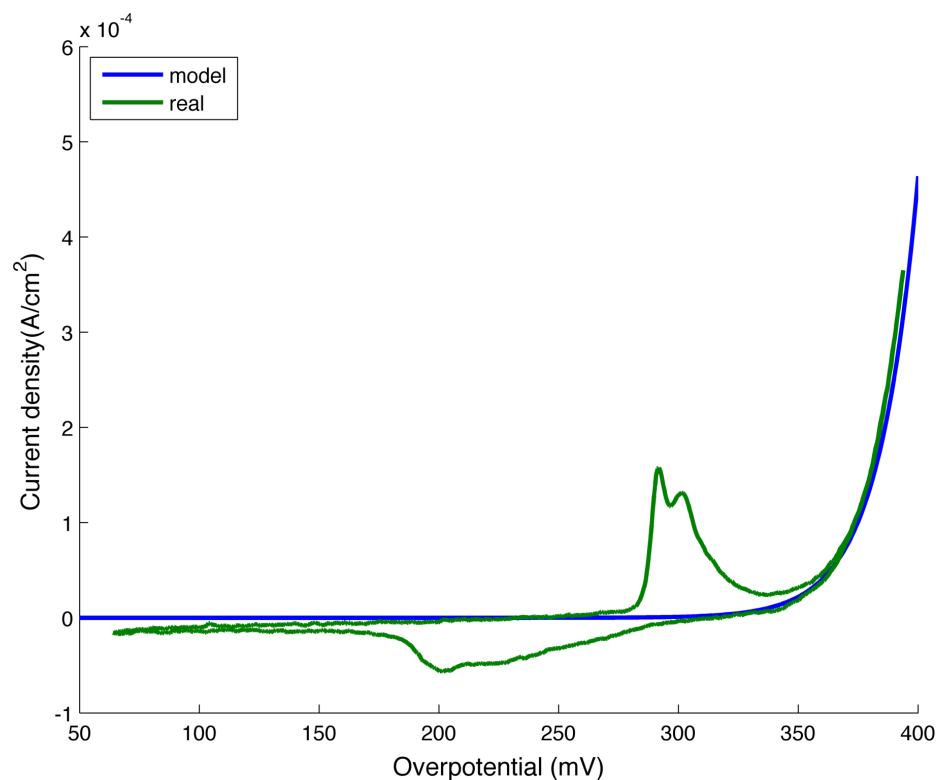


Figure 4.12. A single experimental voltammogram plotted with the modeled CV computed by using average values of the Tafel slope and exchange current density for the given iron content.

With this high level of agreement, all of the compositions are modeled and shown in Figure 4.13. From these data, it is clear that the Tafel slope has a more pronounced effect on the activity, illustrated by the fact that NiO was found to have the highest exchange current density, yet be one of the least active materials studied.

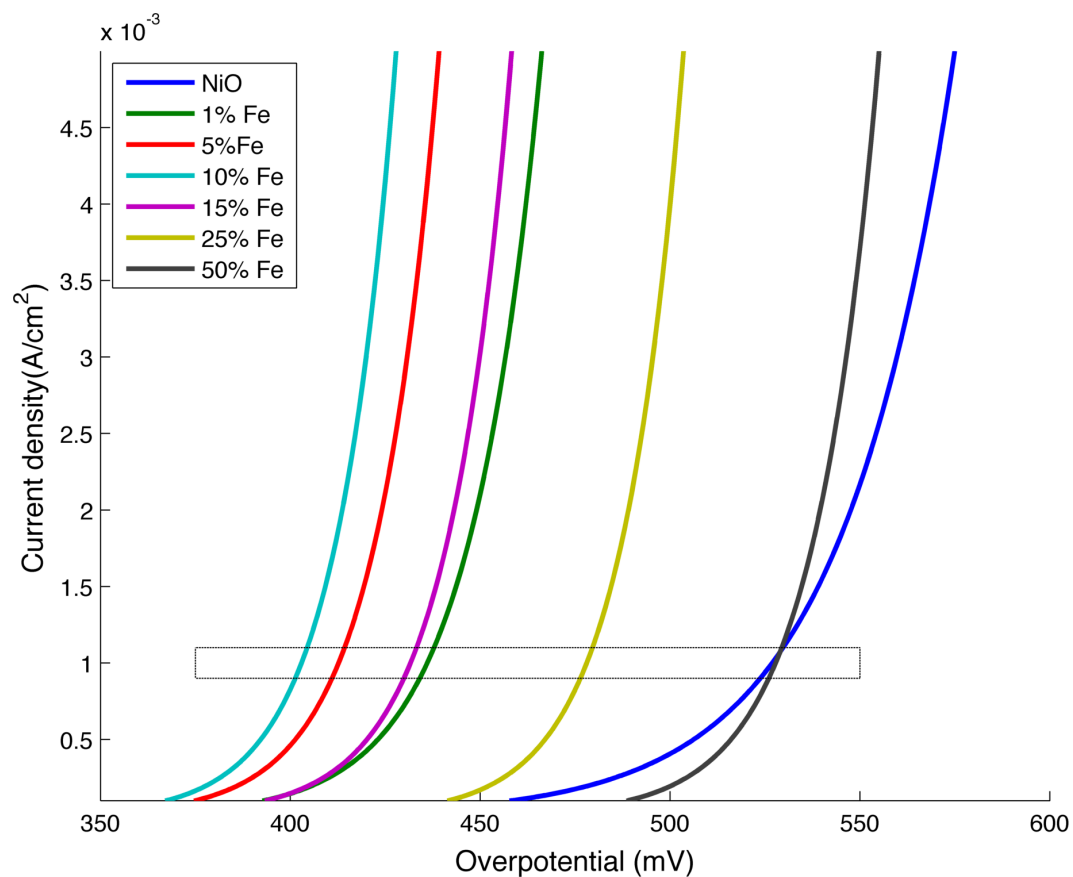


Figure 4.13. Modeled current-voltage data from experimental kinetic parameters for each of the iron loadings produced (0-50 mol%). For comparing activity selecting a single current and determining the corresponding value of the potential required is instructive, as seen in the gray box, with lower potentials indicating a more active material.

Comparing relative activities of the different electrode materials is done by considering a single current density and comparing the amount of overpotential required to achieve this current(13), as illustrated by the gray box in Figure 4.13. Plotting the resultant current values as a function of Fe loading gives rise to the “volcano” plot shown in Figure 4.14.

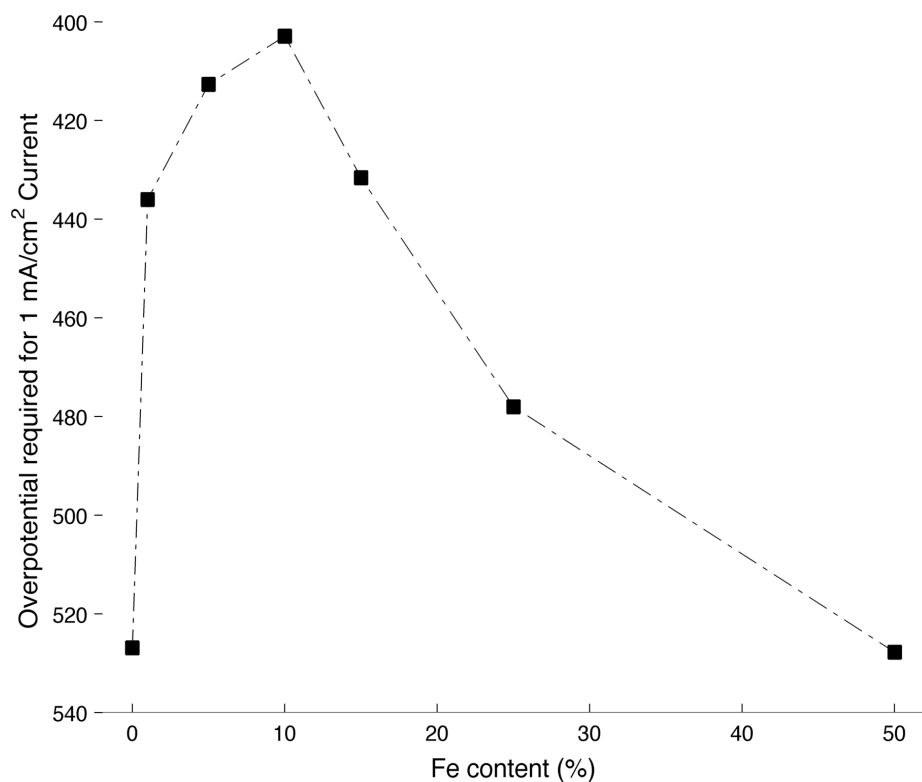


Figure 4.14. The required potential to achieve current density of 1 mA/cm<sup>2</sup>, as determined from modeled data. The plot results in a peak in activity for a value of 10 mol% Fe loading; lower overpotential indicates higher activity.

As can be seen in Figure 4.14, there is a peak in activity observed at an iron loading of 10 mol%. This amount matches well with both our previous results(12) and those in the literature (2). Having confirmed the peak in activity at low iron loadings on the thin film Ni-Fe system we are now interested in correlating the trend in activity with spectroscopically observable changes in the surface chemistry using in situ Raman spectroscopy.

Using Raman spectroscopy we can observe chemical changes to the catalyst surface during the electrochemical experiments. Electrodes were prepared containing 0, 10, 25, 50, and 100 mol% Fe for study. The electrodes were initialized by potential cycling from -300 to 400 mV overpotential for 60 cycles at a 50 mV/s scan rate prior to being moved to the Raman apparatus.

For collection of the Raman spectra, the electrode was set at a potential, allowed 60 s to equilibrate, and then the spectrum was collected. The potential range was set to encompass regions where the electrode is in its reduced state, oxidized state, and undergoing O<sub>2</sub> evolution.

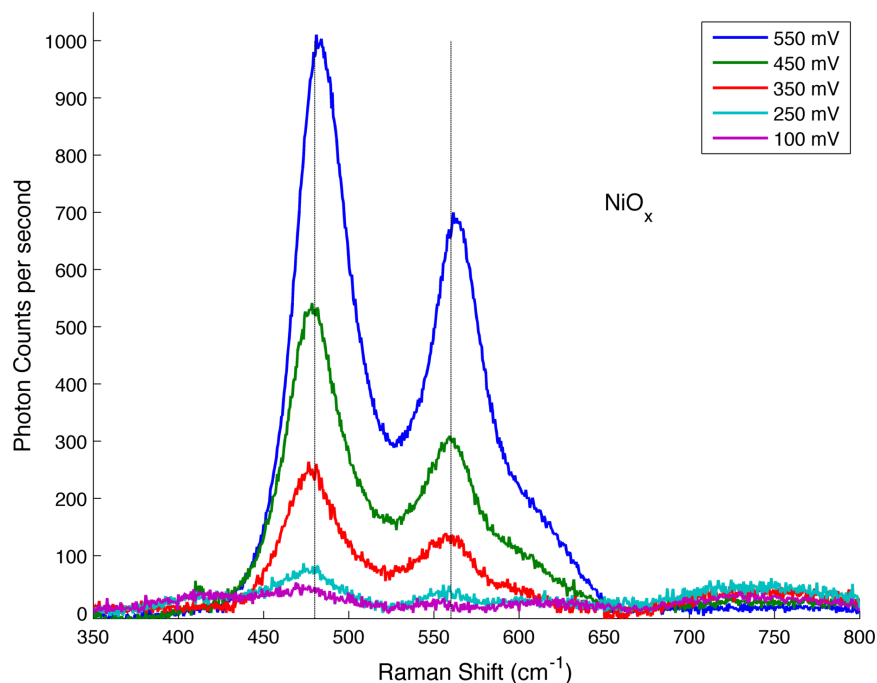


Figure 4.15. In situ electrochemical Raman Spectra of NiO on gold. Each Raman spectrum is a composite average of 15 five second exposures. Guidelines are shown at 480 and 560 cm<sup>-1</sup> indicative of Ni-O stretching modes of NiOOH species. Potentials are listed relative to Ag/AgCl reference.



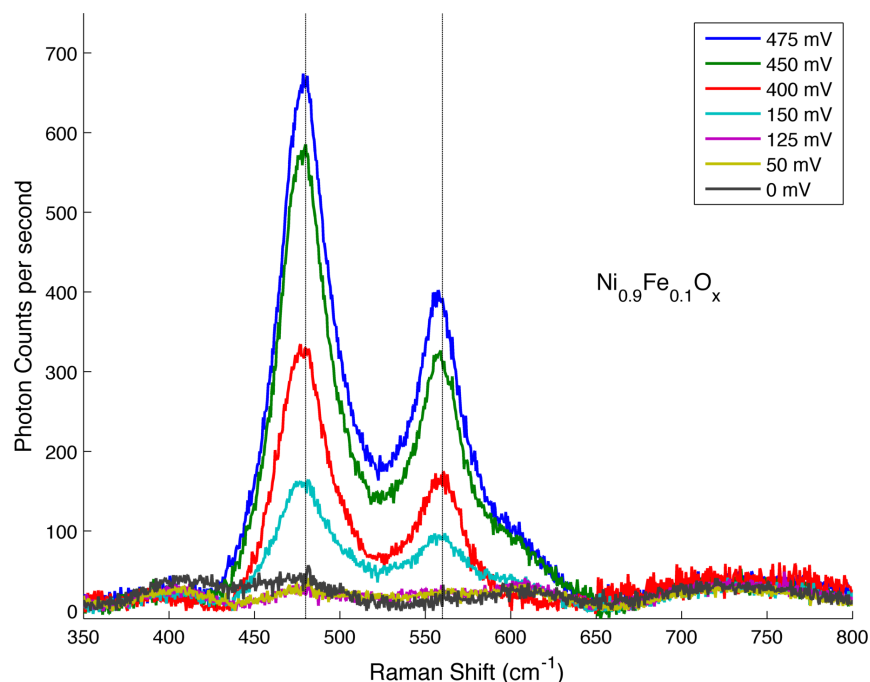


Figure 4.16. In situ electrochemical Raman spectra collected on NiFe10 oxide on gold. Guidelines are shown at 480 and 560  $\text{cm}^{-1}$  indicative of Ni-O stretching modes of NiOOH species. Potentials are listed relative to Ag/AgCl reference.

Figures 4.15 and 4.16 show the in situ electrochemical Raman spectra collected over NiO and the 10 mol% Fe mixed oxide. These guidelines on the figures are drawn to illustrate the differences of the Ni-O stretching modes<sup>(14)</sup> of the oxidized NiOOH state for pure NiO material and that of the film with the highest OER activity. In the spectra of both films strong peaks begin to form around 480 and 560  $\text{cm}^{-1}$  as the potential is raised and the Ni in the film oxidizes. Careful inspection of these spectra gives rise to important differences in the nature of the Ni atoms present in each film.

First, in the NiO spectra, the two peaks appear to be centered about 480 and 560  $\text{cm}^{-1}$  up to a potential of 450 mV. When the potential is raised beyond this potential to 550 mV, each of the peaks appears to shift to higher wave numbers, which is an indication of metal to oxygen bond contraction<sup>(15)</sup>. This is an

important distinction as it is indicative of film dehydration expected for the  $\beta$ -NiOOH phase(16, 17). Along with this observation is increase in the intensity of the  $560\text{ cm}^{-1}$  peak relative to the increase of the  $480\text{ cm}^{-1}$  peak at the highest potential. The continued growth of the  $560\text{ cm}^{-1}$  peak is another indication of  $\beta$ -NiOOH(14, 18).

Alternatively, inspection of the same peaks in  $\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_x$  indicates a less compact M-O spacing, with both peak centers shifted to lower wave numbers for all potentials examined(15). This less compact spacing is indicative of the  $\gamma$ -NiOOH phase(9, 16). The relative intensity of the  $480\text{ cm}^{-1}$  peak to the  $560\text{ cm}^{-1}$  peak is much larger than 1 and this value does not diminish under highly oxidizing conditions, which is again indicative of  $\gamma$ -NiOOH(18).

Both NiOOH phases are comprised of a mix of +3 and +4 oxidation state Ni atoms. However, the  $\gamma$ -NiOOH phase has a larger proportion of  $\text{Ni}^{+4}$  and an overall oxidation state of  $\sim 3.7$ (19-22). In contrast the  $\beta$ -NiOOH phase has far fewer  $\text{Ni}^{+4}$  centers and an overall oxidation state of  $\sim 3.1$ . The  $\text{Ni}^{+4}$  centers are believed to be responsible for OER activity(18, 19), and thus the addition of a small amount of iron that stabilizes the  $\gamma$ -NiOOH phase(23) at lower potentials is a plausible explanation for the enhancement mechanism. To further explore this hypothesis, subsequent examination of the Raman spectra will focus on the characteristic vibrational modes of Fe observed.

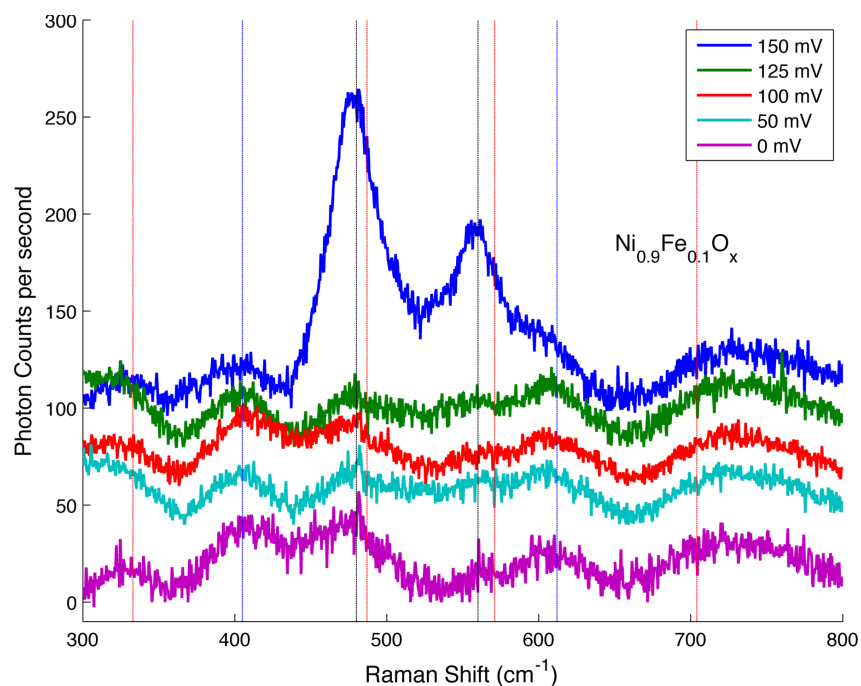


Figure 4.17. In situ electrochemical Raman spectra of 10% Fe mixed oxide on gold. Guidelines correspond to NiOOH (black), NiFe<sub>2</sub>O<sub>4</sub> spinel (red), Fe<sup>3+</sup>O<sub>x</sub>R (blue). Potentials are listed relative to Ag/AgCl reference.

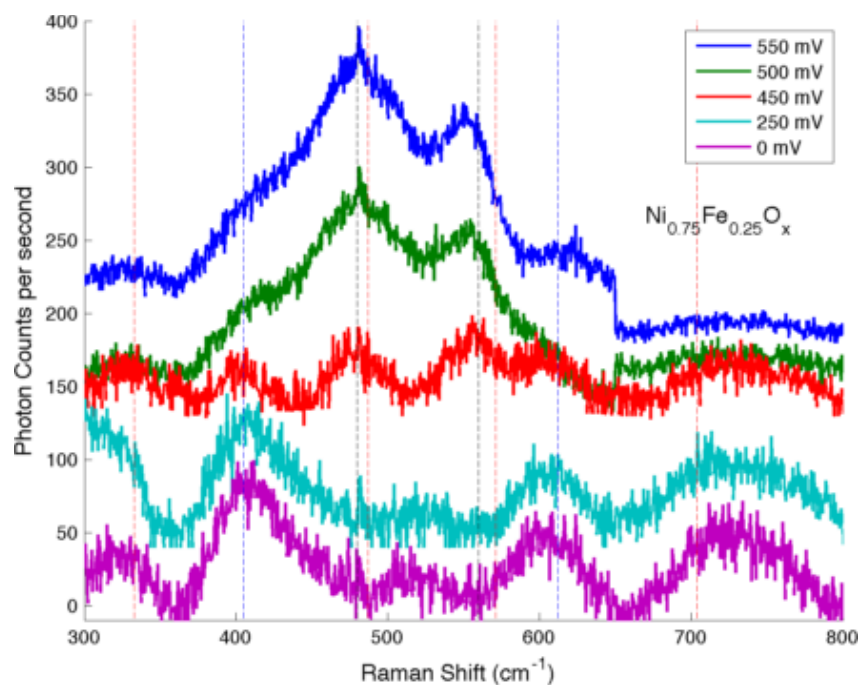


Figure 18. In situ electrochemical Raman spectra of 25% Fe mixed oxide on gold. Guidelines correspond to NiOOH (black), NiFe<sub>2</sub>O<sub>4</sub> spinel (red), Fe<sup>3+</sup>O<sub>x</sub>R (blue). Potentials are listed relative to Ag/AgCl reference.

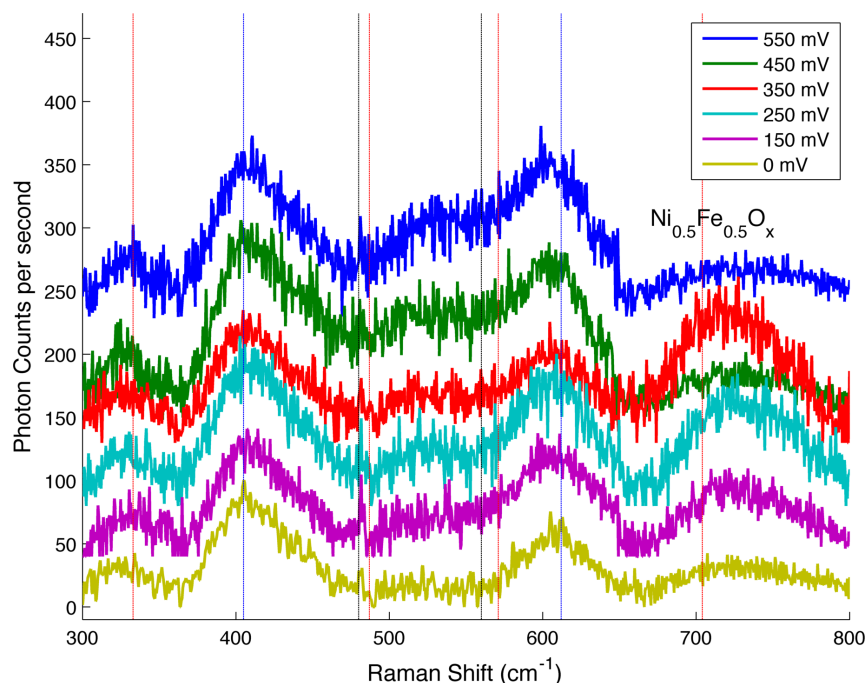


Figure 4.19. In situ electrochemical Raman spectra of 50% Fe mixed oxide on gold. Guidelines correspond to NiOOH (black), NiFe<sub>2</sub>O<sub>4</sub> spinel (red), Fe<sup>3+</sup>O<sub>x</sub>R (blue). Potentials are listed relative to Ag/AgCl reference.

Figures 4.17-19 show the evolution of the Raman spectra corresponding to films containing 10, 25, and 50 mol% Fe as a function of the applied potential.

Considering first the NiOOH peaks (black guidelines), it can be seen that with as much as 25 mol% Fe co-deposited with Ni, the Ni atoms are still electrochemically accessible and undergo oxidation to NiOOH at elevated potentials. The total amount of redox active Ni centers can also be quantified via integration of the reduction wave of the cyclic voltammogram(1), which can be seen to decrease with iron loading in Figure 4.20. Along with a decreasing number of redox active sites, a higher potential is required in order to begin the oxidation with increasing iron loading. For the 10 mol% Fe sample, Figure 4.17,

sharp peaks form as low as 150 mV, compared to much smaller peaks at 450 mV for the 25 mol% Fe sample in Figure 4.18. Increasing the iron content further to 50 mol% results in a complete suppression of the NiOOH peaks, and correspondingly there is a substantial decrease in OER activity at this loading.

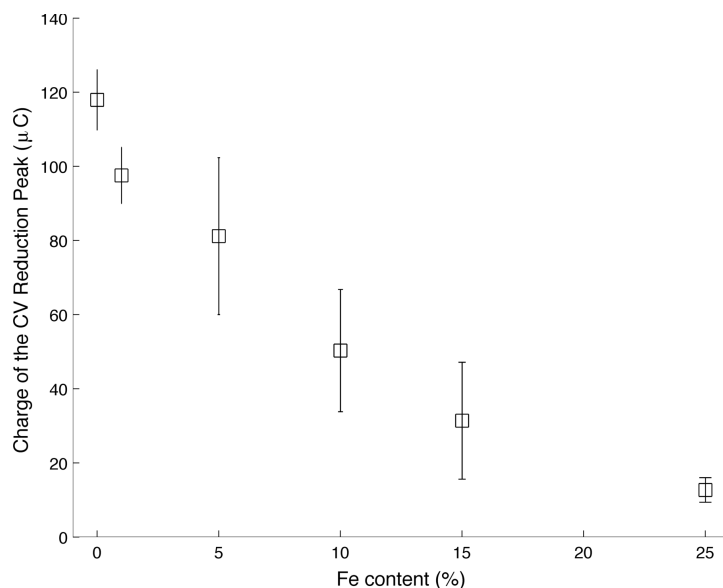


Figure 4.20. Area of the reduction wave of cyclic voltammetry experiments. The charge transferred provides a measure of the redox active Ni atoms. Increasing the Fe loading results in a decrease in charge transferred.

From our previous results,  $\text{NiFe}_2\text{O}_4$  spinel was found to be a significant bulk phase, seen in both XRD and Raman data(12). The red guidelines in Figures 4.17-19 correspond to the 4 significant Raman active modes ( $A_{1g} + E_g + 2F_{2g}$ ) of the  $\text{NiFe}_2\text{O}_4$  spinel(24). From inspection of the three figures, there is little evidence of spinel formation on the mixed oxide film materials under electrochemical conditions. This illustrates a key distinction between the ex situ powder Raman experiments that showed strong spinel peaks at low to moderate iron loadings.

The final set of guidelines, at 405 and 612  $\text{cm}^{-1}$  (blue), correspond to the Fe-O stretching modes of  $\text{Fe}^{3+}$  compounds,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-FeOOH}$ (25-27). At as low as 10 mol% Fe loading, there is evidence of the  $\text{Fe}^{3+}$  compounds, with the 405  $\text{cm}^{-1}$  peak observed at each of the potentials, while the 612  $\text{cm}^{-1}$  peak is washed out by the NiOOH peak at elevated potentials. For the 25% sample, the peaks have higher intensities, which leads to the observation of shoulders on either side of the NiOOH peaks upon oxidation of the Ni atoms. These data suggest that the Fe atoms are not undergoing oxidation at these potentials and instead remain in the 3+ state during electrolysis. These results are similar to the findings of Kim et. al(10) using in situ X-ray absorption near edge spectroscopy measurements to monitor the oxidation state of Fe during the electrochemical reaction. At the highest loading of iron measured (50%), a similar observation is made, with no discernable changes to the spectra seen throughout the set of potentials applied.

Taken as a whole, the data in Figures 4.17-4.19 suggest that iron is deposited in the +3 oxidation state and remains in this state throughout the series of potentials examined. Nickel, however, is seen to oxidize to NiOOH at loadings of iron up to 25 mol%. It has been suggested in the literature that the inclusion of up to 20% Fe with NiO stabilizes the redox transition to the  $\gamma\text{-NiOOH}$  phase(23). Our data would support this hypothesis based upon the 10 mol% Fe Raman spectra, where both the NiOOH peaks are shifted to lower frequencies, and the ratio of the 480  $\text{cm}^{-1}$  peak to the 560  $\text{cm}^{-1}$  peak is much greater than 1, which are both indicative of  $\gamma\text{-NiOOH}$ . Stabilization of the  $\gamma\text{-NiOOH}$  phase results in a higher proportion of  $\text{Ni}^{4+}$  sites available and could explain the increase in OER activity. Beyond 10

mol% Fe, the decrease in activity can be explained by detrimental blocking of Ni sites by Fe, as noted both by the decrease in reduction charge from cyclic voltammetry measurements and the decrease in intensity of the Ni-O bending modes in the Raman spectra of films with elevated Fe loading.

## 4.5 Conclusions

The promotion of base metal oxide materials for the oxygen evolution reaction is of importance if the technology is to become widely utilized. We have examined the promotion of NiO through the addition of Fe atoms to produce a more active mixed-metal oxide catalyst. Our previous work focused on the use of mixed-metal oxide powders that could be easily studied using surface characterization techniques. The results of that work showed the importance of low loadings of iron to produce higher OER activity. The characterization techniques indicated Fe was present at the surface and involved in the catalysis, with bulk characterizations indicating Fe incorporation into  $\text{NiFe}_2\text{O}_4$  spinel. This work sought to determine the effect of Fe deposition onto the surface of a NiO material as well as to characterize the nature of the active site through the use of in situ electrochemical Raman spectroscopy of thin-film electrodes of  $\text{Ni}_{1-x}\text{Fe}_x\text{O}_y$ .

Finally, the electrochemical results of the co-deposited  $\text{Ni}_{1-x}\text{Fe}_x\text{O}_y$  thin film electrodes on Au were shown to produce a peak in activity at a nominal loading of 10 mol% Fe. These results match well with our previous results(12) as well as those from the literature(2). The films were then examined using in situ electrochemical Raman spectroscopy to probe the surface during reaction

conditions. The spectra suggested that much lower potentials were required to oxidize the 10 mol% Fe film into the active phase, relative to the pure NiO. Additionally, the incorporation of Fe was shown to help promote the redox transition to the  $\gamma$ -NiOOH phase, which results in a higher number of quadrivalent Ni atoms that are thought to increase the catalytic activity(19). Contrary to the powder measurements, Fe is observed to exist as either  $\alpha$ -FeOOH or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and the incorporation of trivalent Fe atoms near Ni could explain the stabilization of the Ni<sup>2+</sup>/Ni<sup>4+</sup> oxidation.

This work provides an example of how a combination of spectroscopic data can be paired with empirical trends in activity to elucidate structure-function relationships. Better understanding of the nature of the active catalytic site can provide a pathway for engineers to create more active catalysts.

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## **5. Use of Fe-TAML Molecular Catalyst for the Electrocatalysis of the Oxygen Evolution Reaction**

### **5.1 Introduction**

Efficient energy storage is an important challenge to the further implementation of renewable energy generation due to intermittency and peak production/demand mismatch. The formation of chemical bonds is one energy storage strategy, as this would allow either direct utilization or further conversion into liquid fuels. One such technology is the electrochemical splitting of water, which couples the hydrogen and oxygen evolution reactions, HER and OER, respectively. (1) Of the two electrochemical reactions, the OER is considered the more demanding reaction, requiring four electron transfers and accounting for much of the overpotential needed for exergonic water splitting, as well as occurring at highly oxidizing potentials where material stability can be a concern. OER catalysis has been of particular interest lately, with promising studies involving thin transition metal oxide films(2-8) and transition metal complexes. (9-14) Metal oxide catalysts have been extensively investigated; (15-18) however, hypothesized correlations between the energetics of the distinct steps result in limitations of the minimum overpotential necessary for high rates of water oxidation. (19) There is a critical need for new classes of OER catalysts that could circumvent the limitations inherent in metal oxide catalysts. Molecular electrocatalysts offer a

path towards this goal due to the possibilities of combining active centers with ligands that can modify the reactivity.

Discovering more economical water oxidation catalysts is also of great interest. Fe is a particularly important option because it is not only one of the most abundant materials in the earth's crust, but it can also readily change its oxidation state change which makes it an attractive catalyst material for redox chemistries. (20) Iron oxides are not particularly efficient water oxidation electrocatalysts, although Fe has been used to promote other oxide based electrocatalysts. (21) At present, water oxidation by Fe complexes has only been sparsely demonstrated in the literature. (22-24) These previous works relied on the use of chemical oxidants, such as ceric ammonium nitrate or  $[\text{Ru}(\text{bpy})_3]^{3+}$  to drive the reaction. The use of chemical oxidants allows for proof-of-concept and reaction kinetics studies, but there remains a need to demonstrate electrochemical turnover of Fe-centered complexes for OER catalysis.

$\text{Fe}^{\text{III}}$  tetra-amido macrocyclic ligand (TAML) is one such complex that has recently been shown to homogeneously catalyze the OER through the use of the chemical oxidant, ceric ammonium nitrate. (23) TAML has historically been used as a molecular catalyst for the treatment (oxidative destruction) of water contaminants. (25-27) In this work, the FeB\* member (Figure 1) of the TAML family has been used as an electrocatalyst for the OER. We have examined the use of TAML as a homogeneous electrocatalyst and immobilized it onto a carbon support for use as a heterogeneous electrocatalyst.

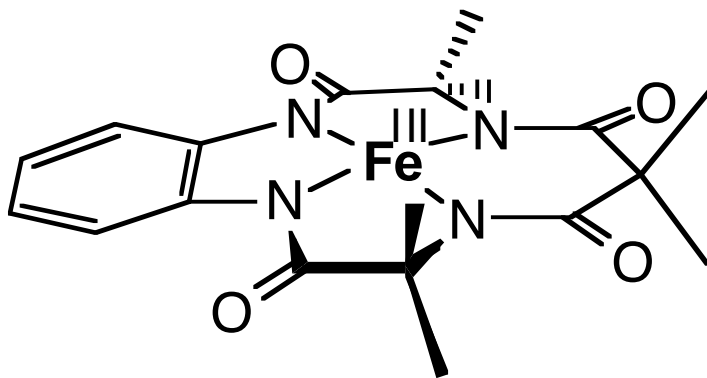


Figure 5.1. FeB\* member of the TAML family.

## 5.2 Methods

### 5.2.1 Homogeneous TAML Electrochemistry

TAML powder was used as received from the Carnegie Mellon University Department of Chemistry, specifically from the group of Terry Collins. In order to test its use as a homogeneous water oxidation electrocatalyst, the powder was dissolved in 0.1 M HNO<sub>3</sub> electrolyte to a concentration of 0.5 mg TAML/mL solvent. The solution was bright orange after dissolution. Three electrode experiments were conducted with a 3 mm ID glassy carbon electrode from Pine Research Inst as the working electrode, Ag/AgCl as the reference electrode and a Pt wire as the auxiliary electrode. Cyclic voltammetry experiments were performed by cycling the voltage from 0 to 1.4 V vs. Ag/AgCl at a scan rate of 100 mV/s to characterize the electrochemical behavior of the dissolved catalyst. The limits of polarization were set to encompass regions sufficiently above and below the theoretical potential for O<sub>2</sub> evolution (~0.95 V vs. Ag/AgCl).

### 5.2.2 Heterogeneous TAML Electrochemistry

The TAML/C electrocatalyst powder was produced by first making a solution of 20 mg TAML in 1 mL of H<sub>2</sub>O. After brief sonication to ensure dissolution, 1 g of Vulcan XC-72 Carbon Black was added to serve as the catalyst support. The resultant slurry was sonicated for 1 hour then filtered, washed, dried, and collected. The immobilized TAML was then incorporated into a catalyst ink by adding Nafion (Aldrich) as a binder and a 50:50 methanol: isopropanol mixture. After sonication for 30 minutes, the ink was deposited onto either a 3 mm glassy carbon disk electrode (Pine Instruments) or a 1 cm<sup>2</sup> piece of Toray carbon paper and dried at 120 °C. This cycle was repeated until the desired loading was achieved.

Cyclic voltammetry (CV) and constant current electrochemical experiments were performed in 0.1 M HNO<sub>3</sub> using a Gamry Ref600 potentiostat, a Pt wire counter electrode and an Ag/AgCl reference electrode. The counter electrode was housed in a glass compartment with a glass frit that allowed the evolved H<sub>2</sub> to escape to the atmosphere.

### 5.2.3 Quantification of Gas Evolution

In order to confirm the production of oxygen gas, the experiments were performed in a gas-tight cell (Figure 5.2). The composition of the headspace was measured two ways, using a fluorescent O<sub>2</sub> sensor (FOXY) from Ocean Optics and a Shimadzu GC-8A gas chromatograph with a 100 µL syringe for sampling. The FOXY sensor allowed for real-time monitoring of the O<sub>2</sub> content in the

headspace, while the GC can detect other gas species that may result from side reactions, such as  $\text{CO}_2$ .



Figure 5.2. Picture of gas-tight electrochemical cell. The five port cell is configured (starting at the left and working clockwise) with a Pt counter electrode, glassy carbon working electrode, Ag/AgCl reference electrode, Teflon plug fit to 100  $\mu\text{L}$  syringe, and FOXO sensor (center).

Previous uses of the fluorescent  $\text{O}_2$  sensor in this manner have been carried out in  $\text{O}_2$ -free environments using a vacuum apparatus to evacuate the cell before backfilling with inert gas. (28) In this work the concentration of  $\text{O}_2$  above the ambient atmospheric concentration in air was measured. The benefit of this approach is the amount of oxygen produced is not overestimated due to leakage of air into the cell. In contrast, in long experiments, the amount of oxygen produced can be underestimated due to oxygen leakage out of the cell. A baseline

measurement of  $O_2$  was established in the cell prior to the electrochemical experiments, and was subtracted from these data for clarity.

The experimental instrument settings for the GC measurements are as follows; Injector/Detector temperature, 100 °C, Column temperature, 45 °C, operating current, 120 mA, injection volume, 100  $\mu$ L. There are three gas species of interest in our GC experiments,  $O_2$ ,  $N_2$ , and  $CO_2$ .  $O_2$  and  $N_2$  have similar elution times, which results in an overlapping of their corresponding elution peaks. These two peaks are quantitatively decoupled using a method described by Goodman et al(29).

The  $CO_2$  peak takes far longer to elute, and the column temperature must also be increased for  $CO_2$  to elute. To accomplish this, the column is given sufficient time for the  $N_2$  elution peak to complete, ~6 minutes, then the column temperature is increased to 95 °C. Following this temperature increase, the  $CO_2$  is seen to elute at t~25 minutes.



## 5.3 Results and discussion

### 5.3.1. Homogeneous TAML Electrochemistry

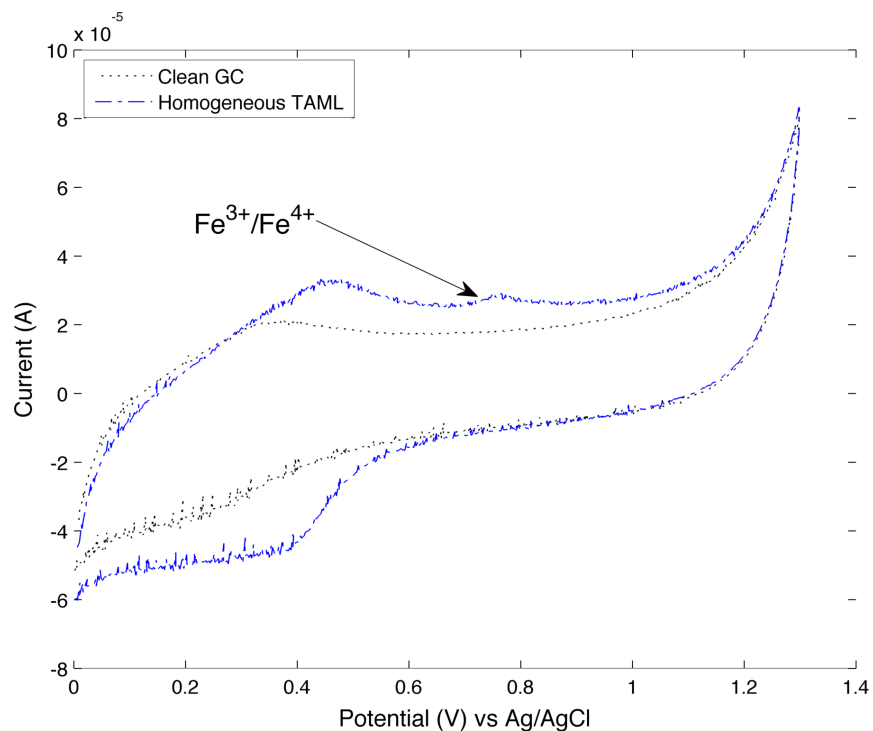


Figure 5.3 Cyclic voltammograms of glassy carbon electrode in 0.1 M  $\text{HNO}_3$  with (blue) and without (black) 0.5 mg TAML/mL dissolved in the electrolyte. The scan rate is 100 mV/s.

The results of the electrochemical characterization of dissolved TAML as a homogeneous OER electrocatalyst are shown in Figure 5.3. Here it is seen that there is evidence of Fe oxidation/reduction chemistry; however, at the elevated potentials required for  $\text{O}_2$  evolution, there is no clear distinction between the observed currents for experiments with and without TAML present. These results suggest that while the catalyst does undergo electrochemical redox chemistry, the currents achieved are not high enough for practical water splitting.

Immobilization of the catalyst could lead to more efficient utilization of the material through geometrically constraining TAML to the electrode surface.

### 5.3.2 Heterogeneous TAML Electrochemistry

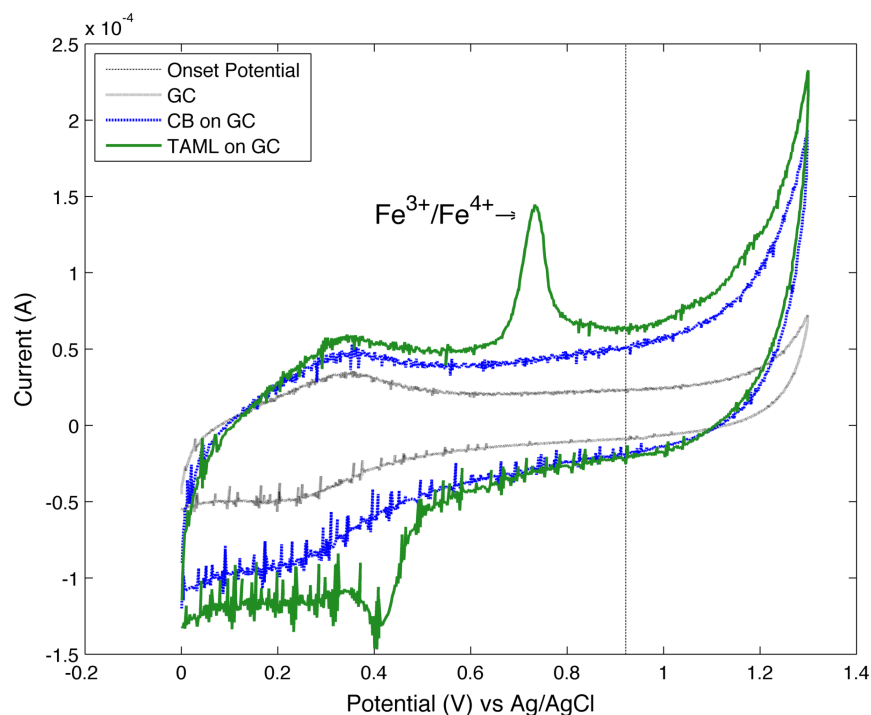


Figure 5.4. Series of cyclic voltammograms (100 mV/s) of clean glassy carbon (GC), 20  $\mu\text{L}$  XC-72 carbon (CB on GC), and 20  $\mu\text{L}$  immobilized TAML (TAML on GC).

The electrochemical results of the immobilized catalyst material are summarized in Figures 5.4, which is a set of cyclic voltammetry experiments comparing the electrochemical behavior of the TAML-modified electrode to that of the polished glassy carbon electrode and carbon black on glassy carbon electrode. The loading of 20  $\mu\text{L}$  corresponds to  $\sim 17$  nmoles of TAML. The ground oxidation state of the iron center is +3, and TAML has been shown to undergo a +3/+4 oxidation, which arranges into a  $\mu$ -oxo dimer conformation. (30) Based on the data shown in the CV, a similar oxidation cycle is observed electrochemically, with the +3/+4 oxidation occurring at 720 mV vs Ag/AgCl prior to the onset of  $\text{O}_2$  evolution at

~950 mV. Comparing the curves, it is clear that this oxidation wave is not present in the CVs without TAML added. The CVs also give an indication of activity, and here it is seen that at a given overpotential ( $\eta > \eta_{\text{onset}}$ ), the oxidative current is higher with TAML than without.

### 5.3.3 Quantification of Gas Evolution

Figure 5.5 shows the real-time production of O<sub>2</sub> gas as measured by FOXY probe in the foreground and the corresponding chronopotentiometric data in the inset. Constant current of 10 mA was applied for 30 min. O<sub>2</sub> was evolved for the duration of the experiment up to a maximum of ~22  $\mu\text{mol}$ . The empirical Faradaic efficiency was found to be ~45%; this value is a lower bound because evolved O<sub>2</sub> can leak from the reaction cell due to the partial pressure of O<sub>2</sub> in the cell being greater than that of ambient air. The inset shows the potential increasing gradually from ~2 V before leveling off at ~2.7 V towards the end of the experiment.

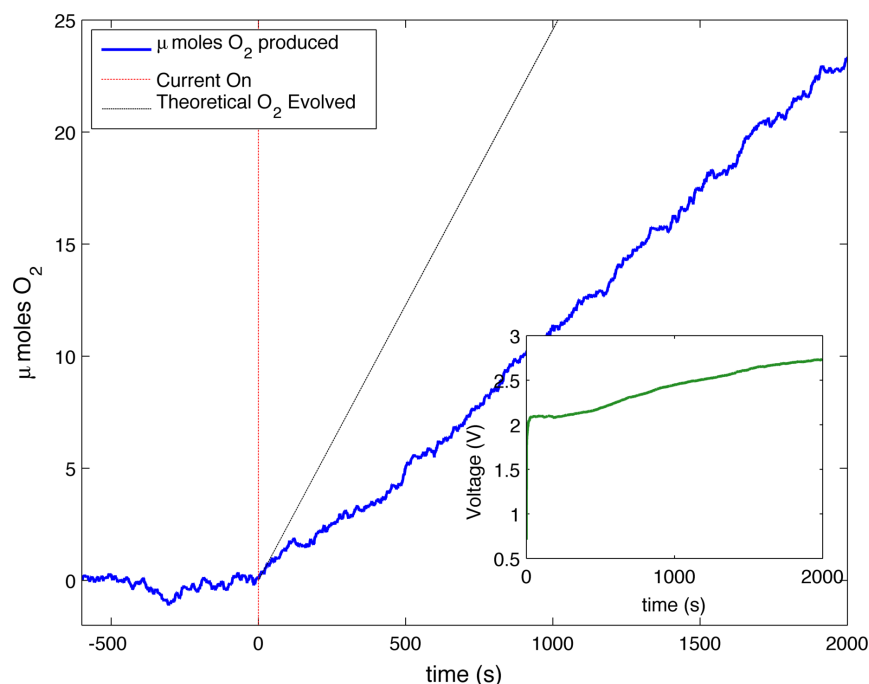
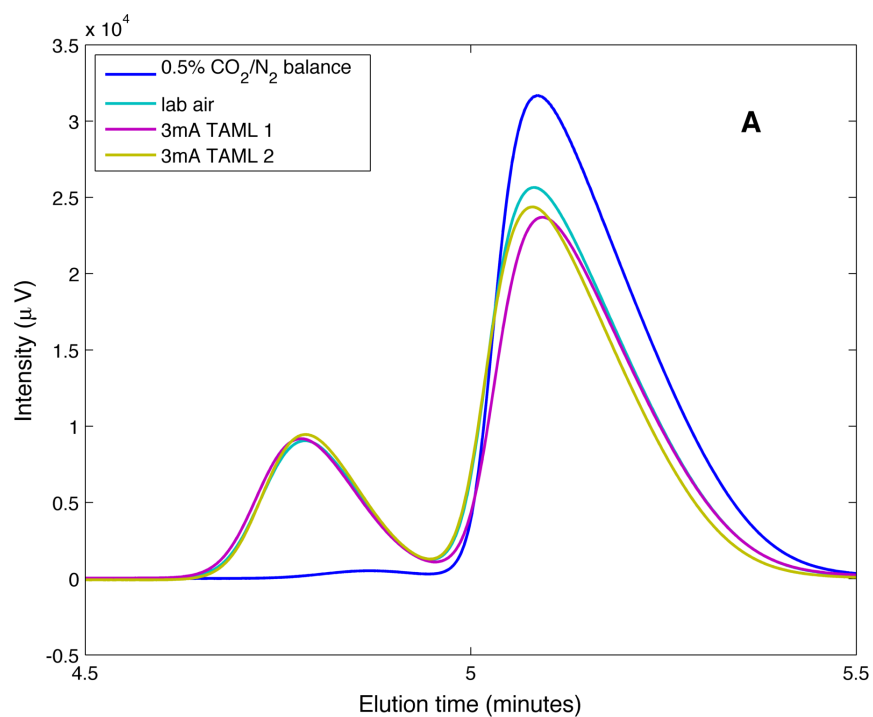


Figure 5.5. Real-time production of oxygen gas during 10 mA constant current experiment, as measured by the FOXY sensor in the head space. The inset shows the corresponding voltage response to maintain desired current.

The activity of each TAML can be estimated in the form of turnovers if we assume that electron transfer through TAML produced all of the oxygen (as noted above, about 45% of the current generated oxygen gas). Thus, we estimate that each TAML has on average participated in 620 electron transfers, or equivalently has generated 155 oxygen molecules at a turnover frequency of  $0.086 \text{ s}^{-1}$ . The turnover numbers here represent a large increase compared to the experiments with the chemical oxidant. (23) It should also be noted that we have only tested one derivative of Fe-TAML, and higher activities may be achieved with different functionalized end-groups.

The composition of the headspace in the electrochemical cell was determined before and after constant current experiments using gas chromatography as seen

in Figure 5.6. Due to the overlap of the  $O_2$  and  $N_2$  peaks, quantitative fits were produced according to the method described by Goodman, (29) and the compositions were calculated by comparison to calibration gas data. These data corroborate the results found with the  $O_2$  probe; mainly that  $O_2$  is concentrated above ambient air compositions during the electrolysis, as seen in Figures 5.5, but also the gas chromatography data reveals the production of  $CO_2$ .



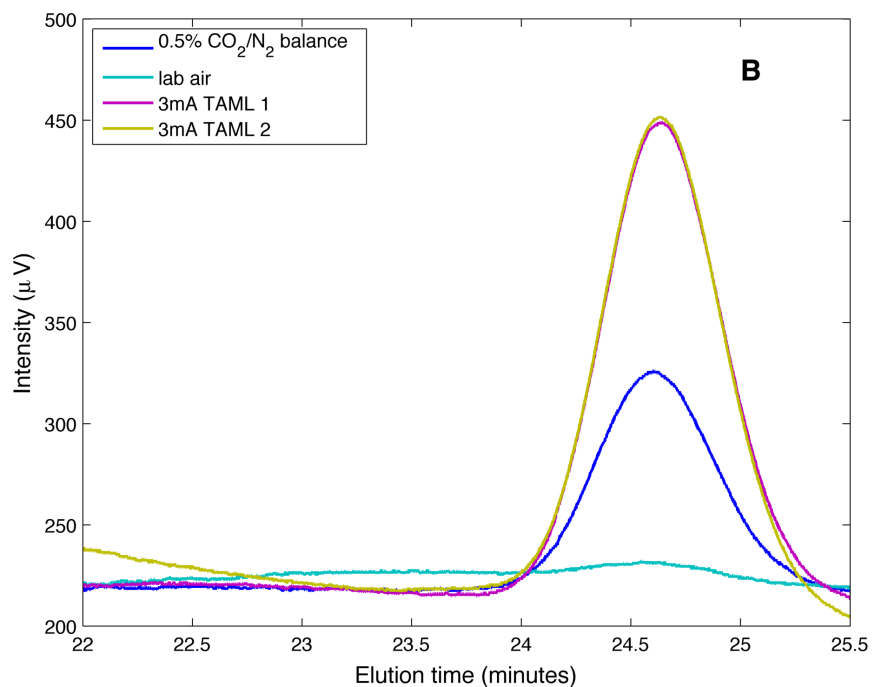


Figure 5.6. Characteristic gas chromatograms taken at the conclusion of a two hour constant current electrolysis experiment. Samples taken with 0.5% CO<sub>2</sub> calibration gas along with lab air are also plotted for comparison. (A) is zoomed to the region of O<sub>2</sub> and N<sub>2</sub> elution times, while (B) is the region for CO<sub>2</sub> elution.

Experiments were repeated multiple times with different catalyst loadings and currents applied. In Figure 5.7 we show that the selectivity of the current towards oxygen production is significantly higher with the supported TAML catalyst than without it, but we do not see 100% selectivity to O<sub>2</sub> production. However, the selectivity of the immobilized TAML catalyst still represents an over 3-fold improvement compared to the electrodes with no catalyst present.

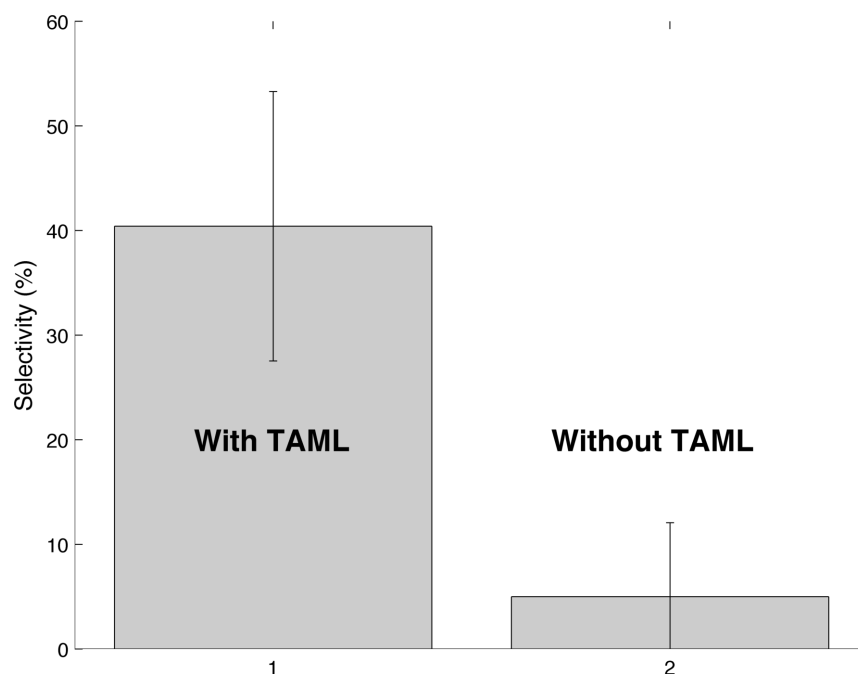


Figure 5.7. Comparison of the selectivity to O<sub>2</sub> evolution over electrodes with and without TAML present.

The presence of CO<sub>2</sub> as observed in the GC data, confirms the occurrence of parasitic carbon oxidation. The source of carbon oxidation is a crucial metric in determining the viability of TAML as a water oxidation catalyst. Due to the low solubility of CO<sub>2</sub> in acid(31), the electrolyte can be ruled out as a possible source. The three most likely sources are then the ligand structure of the catalyst, the polymer backbone of the Nafion binder, and the carbon black support material. In order to determine the source of carbon oxidation, immobilized TAML electrodes were examined before and after a set of electrolysis experiments using X-ray photoelectron spectroscopy (XPS).

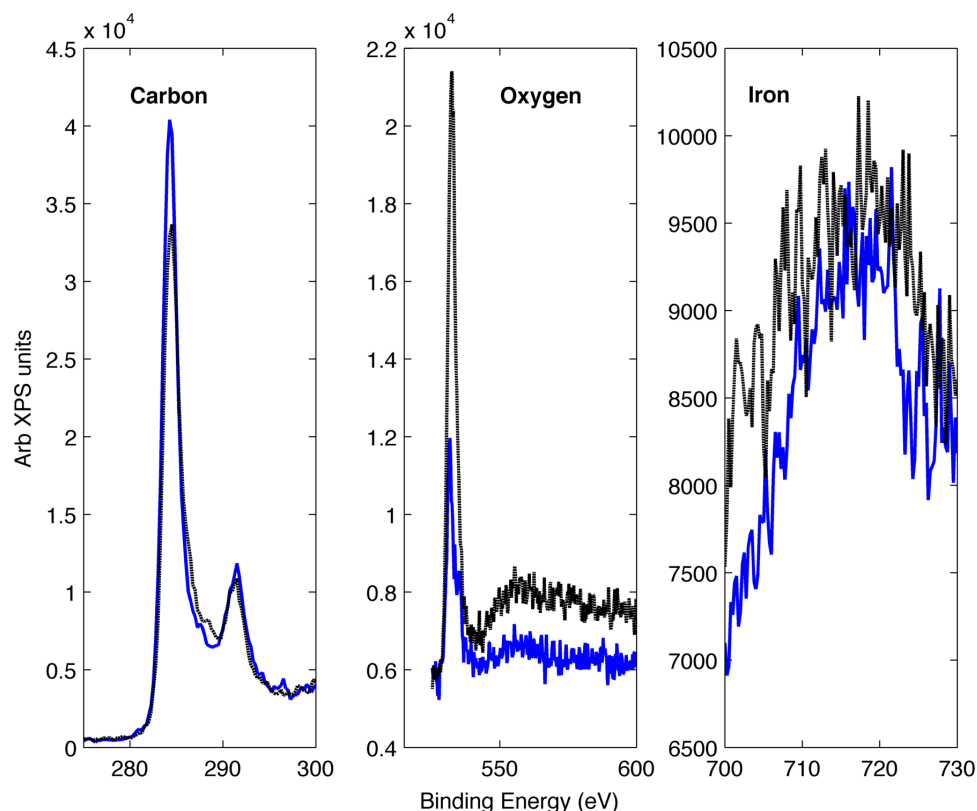


Figure 5.8. XPS data of TAML-modified electrodes pre (solid blue) and post (dashed black) electrolysis experiments.

The results from these experiments are shown in Figure 5.7 and the major differences between before and after are seen in the oxygen and carbon spectra. There are two carbon peaks present in the spectra, with the higher binding energy peak,  $\sim 291$  eV being the result of carbon near a strong electron-withdrawing element, i.e. the carbons in Nafion. The decrease in the lower energy peak indicates that these are the carbon atoms being oxidized and released as  $\text{CO}_2$  while the lack of a change in the 291 eV peak eliminates the possibility of Nafion oxidation as the mechanism of  $\text{CO}_2$  formation. The oxygen spectra show a large increase in intensity after the electrolysis experiments, which indicate the release of  $\text{CO}_2$  is a multi-stepped process of surface carbon oxidation. Also from XPS, there is a broad peak for iron observed in the 700-730 eV energy range that is



present in both the fresh and used electrode, which suggests that it is the carbon black support that is oxidizing rather than the catalyst material.

## 5.4 Conclusions

We have demonstrated the use of Fe-TAML as an electrocatalyst for the OER. Experiments with TAML used as a homogeneous catalyst did not result in any appreciable benefit relative to the control experiment, but there was evidence of TAML oxidation/reduction chemistry. Immobilized TAML on carbon black was then used as a heterogeneous electrocatalyst. The results from these experiments showed that a much larger amount of TAML was undergoing redox chemistry, and higher currents relative to the control experiments were observed indicating catalysis. Gas quantification using the fluorescent O<sub>2</sub> sensor along with gas chromatography both indicated the production of O<sub>2</sub> during constant current electrolysis experiments. Lower than 100% Faradaic efficiency was indicated in the FOXY data, which was corroborated by the presence of CO<sub>2</sub> elution peaks in the gas chromatograms. While selectivity to O<sub>2</sub> evolution is limited by parasitic C oxidation, the high turnover numbers along with evidence from XPS suggest that the catalyst material is stable despite the oxidation of the supporting materials. These results suggest that immobilization of Fe-TAML catalysts on electrically conducting supports could be an important new class of OER electrocatalysts.

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## 6. Conclusions

### 6.1 Introduction

The work contained within this thesis describes ways in which base metal catalysts can be promoted for the oxygen evolution reaction (OER). Two major obstacles to further utilization of electrolysis as an energy storage technology are coupled. One, there are large kinetic barriers that must be overcome through catalysis, and two, the best performing materials contain iridium or ruthenium, which are prohibitively expensive. Utilizing earth-abundant materials mitigates the problem of materials cost in exchange for higher energy costs associated with lower performing catalysts. This work demonstrated that the electrochemical OER activity could be enhanced for NiO materials through both the choice of electrolyte and the addition of small loadings of iron with NiO. The use of thin-film electrodeposition allowed for surface characterization of the electrode materials under reaction conditions, and through analysis of these data, we have shown a correlation between the presence of  $\gamma$ -NiOOH and electrochemical activity.

The last chapter in this work explored the use of Fe-TAML as a molecular electrocatalyst of the OER. While Fe-TAML had previously been demonstrated to homogeneously evolve  $O_2$  in the presence of chemical oxidants(*I*), this work represented the first demonstration of immobilized Fe-TAML as a heterogeneous  $O_2$  evolution catalyst.

## 6.2 Effect of Electrolyte Cation Choice on the Oxygen Evolution Reaction

We examined the role of cation choice in the series of alkali hydroxides ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) on the electrochemical OER activity over thin-film NiO electrodes deposited on a gold substrate. From these experiments, the activity was observed to increase going down the periodic table from LiOH to CsOH, with a 2-fold increase in observed activity in CsOH relative to LiOH. In situ electrochemical Raman spectroscopy was performed on the thin-film electrodes to probe any changes in surface chemistry that accompany changes in the electrochemical activity. The onset of Ni surface oxidation differed greatly ( $\sim 125$  mV) when comparing the spectra collected in CsOH to that in LiOH. Also, more subtle differences in the spectra suggest different phase behavior in the two electrolytes. We found that  $\gamma$ -NiOOH was formed in CsOH, while  $\beta$ -NiOOH was observed in LiOH. The two phases differ in their inter-layer spacing and more importantly, the overall oxidation state of the Ni atoms(2, 3). The  $\gamma$ -NiOOH phase has an overall oxidation state of  $\sim 3.7$ , which indicates a greater proportion of the Ni atoms are oxidized to the +4 state compared to  $\beta$ -NiOOH, with an oxidation state of  $\sim 3.1$ (4-6). Thus, we conclude that CsOH promotes the  $\gamma$ -NiOOH phase, which results in a greater number of high valence Ni atoms, in turn, promotes the oxygen evolution reaction.

## 6.3 Promotion of the Oxygen Evolution Reaction using mixed Ni-Fe Electrocatalysts

The promotion of the OER on mixed Ni-Fe systems was a known effect since its initial documentation by Corrigan in the 1980s(7). Much of the subsequent works in the literature focused on understanding the effect of the iron, but no consensus was achieved in elucidating the mechanism of OER promotion(4, 8-12). The early work in our group focused on electroless preparation of high surface area, crystalline powder materials that facilitated the use of ex situ characterization techniques in order to elucidate a possible structure-function explanation for the OER enhancement(13). The results of this work suggested surface Fe may be the cause of the enhancement. We subsequently examined the effect of depositing Fe onto the surface of NiO particles on OER activity. The activity of the as-prepared Ni@Fe core-shell catalyst materials showed no change in activity relative to the NiO core material. To further examine the nature of the active site and the role of iron in the activity promotion, thin-film Ni-Fe electrodes were prepared and examined using in situ Raman spectroscopy.

For the thin-film electrode materials, as with previous studies(7, 13), a maximum in OER activity was observed at a loading of ~10 mol% Fe. The results from in situ Raman experiments indicated the  $\gamma$ -NiOOH phase was formed at much lower potentials relative to the pure Ni(OH)<sub>2</sub> electrode. Iron was also detected in the Raman spectra, with the peaks corresponding to either  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or  $\alpha$ -FeOOH. These results suggest that the iron present is in the +3 oxidation state. Therefore, we propose Fe<sup>III</sup> stabilizes the +2/+4 oxidation of Ni to transition from

$\alpha$ -Ni(OH)<sub>2</sub> to  $\gamma$ -NiOOH, which has previously been suggested in the literature(11).

The Raman experiments, in conjunction with cyclic voltammetry also illustrated a mechanism for deactivation at higher loadings of iron. From the CV experiments at 25 mol% Fe loading, there is no longer evidence of Ni oxidation/reduction chemistry. However, the Raman spectra at this loading indicates small amounts of NiOOH present at elevated potentials, and the activity is higher than that of pure Ni(OH)<sub>2</sub>. Thus, we conclude that Ni oxidation still takes place at Fe loadings up to 25 mol%, and that these materials are more active than electrodes without Fe. This suggests that beyond 10 mol% Fe, the increased iron atoms begin to block access to the active sites for catalysis. By 50 mol% Fe, there is no evidence of Ni oxidation in either the CVs or the Raman spectra, and consequently, the activity of the electrode is no longer enhanced relative to Ni(OH)<sub>2</sub>.

This work has shown the influence of iron on increasing the OER activity for Ni(OH)<sub>2</sub> electrodes, and utilized a combination of synthesis and spectroscopic techniques to propose a mechanism for the enhancement.

## **6.4 Electrocatalysis of the Oxygen Evolution Reaction with Fe-TAML Molecular Catalyst**

Fe-TAML was examined for its use as an electrocatalyst for the OER. Molecular catalysts represent an area of potential growth, as the metal centers can be ligated in such a way to tune the reactivity for a given process. In this work, we have



demonstrated the use of a single Fe-TAML derivative as both a homogeneous and heterogeneous O<sub>2</sub> evolution electrocatalyst. The results from the homogeneous catalysis experiments showed Fe oxidation/ reduction chemistry; however, the currents observed at the potentials required for O<sub>2</sub> evolution were no higher than those of the control experiment. We proposed that the reason for the lack of catalysis was due to migration of the Fe-TAML molecules away from the electrode surface. To test this hypothesis and mitigate the migration, Fe-TAML was immobilized onto carbon black, and bound to the electrode surface using Nafion ionomer. The experiments on the immobilized Fe-TAML material showed not only more Fe oxidation/reduction, but also higher currents at the potentials required for OER. Gas quantification experiments confirmed that O<sub>2</sub> was being produced but also showed that CO<sub>2</sub> was concurrently being evolved; thus, decreasing the coulombic efficiency of the experiments to produce O<sub>2</sub>. Due to the sustained amount of time the experiments continued to evolve O<sub>2</sub>, oxidation of the carbon black support material was suspected. X-ray photoelectron spectroscopy measurements indicated that carbon black oxidation was likely the source of CO<sub>2</sub>.

Although CO<sub>2</sub> formation led to less than 100 % selectivity to O<sub>2</sub>, the selectivity with Fe-TAML was over 4-fold higher than the control experiments.

Immobilization on more oxidation-resistant materials could mitigate this issue.

This work has demonstrated the use of a single Fe-TAML derivative to electrochemically catalyze the OER. With this proof-of-concept, future research could be directed to examine the effects of changing the ligand chemistry to promote the catalysis.

## 6.5 Outlook

Electrochemistry is experiencing a boon in attention as society looks to alternative means to secure its future energy portfolio. Whether electrochemistry is ultimately utilized in energy storage or conversion or some mix of the two, the need for cheaper and better catalyst materials will be a necessity. This work has demonstrated one way in which advanced spectroscopic techniques can be paired with electrochemistry to more fully understand how oxygen evolution catalysis can be improved for a given catalyst system. Expansion of this philosophy to other catalysts and other electrochemical systems could ultimately lead to low enough costs to make the technology competitive for large scale applications.

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