CHARACTERIZATION OF OXYGEN EVOLUTION REACTION CATALYSTS[SB1]

by

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A THESIS

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Dr. Shannon W. Boettcher

This thesis reports studies on the effects of electrolyte cations, different Fe species in Ni-Fe (oxy)hydroxide films, and varying transition metal compositions on the activity of OER catalysts. Among the studied electrolyte cations (K^+, Na^+, Mg^{2+}, and Ca^{2+}), it is reported that K^+ contributes to the lowest overpotentials on both Ni(Fe)OOH and NiOOH films due to its favorable acidity and size. In a study evaluating two methods of Fe incorporation into NiO_xH_y, two different Fe species are reported: one on edge/defect sites and one in the Ni bulk. The results of this project suggest that OER activity is influenced by the active Fe edge sites rather than the Fe in the bulk. By varying ratios of Ni-Co-Fe in OER films, it is reported that there is no ternary composition more active than Ni(Fe)OOH. Additionally, the results support the hypothesis that local structure has a larger role in catalysis than the bulk electronic structure.

Acknowledgements

I would like to thank Professor Shannon Boettcher for his mentorship over the years and for giving me the opportunity to conduct research in his lab during my first year at the University of Oregon through the Research Immersion class. I would also like to thank my primary lab mentor, Dr. Michaela Burke Stevens, whose guidance, encouragement, and enthusiasm I am incredibly grateful. I would like to thank GTF Lisa Enman, whose support and advice have guided me throughout my research projects and the thesis, and Professor Susanna Lim for serving as my Honors College Representative on my Thesis Committee. I would like to thank members of the Boettcher lab for their help and support over the years. Especially, I would like to express gratitude towards my family and my partner Alex for their love and support.

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Introduction

Motivation:

As global energy consumption continues to increase, prominent use of fossil fuels has caused lasting damage on the environment and human health.[1] Aside from its harmful effects, the accessibility of fossil fuels such as oil, coal, and natural gas are dependent on unpredictable international relations and finite availability.[1,2] Renewable resources such as solar energy provide a promising solution to meeting global demands as solar radiation strikes Earth's surface with more energy in one hour than worldwide energy consumption within an entire year.[1] In order for solar energy to be a viable solution, methods must be developed to efficiently harvest and store the energy.

Developments in solar energy conversion have principally focused on improving the efficiency of photovoltaic devices, materials that convert light directly into electricity. Due to the intermittence of sunlight exposure, it is necessary to develop cost-effective and efficient methods of energy storage to maximize solar energy usage. Energy harvested from solar radiation can be stored using batteries, however sustainability remains a challenge due to the high costs and limited shelf life.[1] Alternatively, energy can be stored chemically, which operates upon the absorption and release of energy through the breaking and formation of chemical bonds.[3] Hydrogen gas (H_2) is a chemical fuel that can be produced through water electrolysis, a reaction that splits water into hydrogen and oxygen:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

Water electrolysis results in the evolution of hydrogen for fuel consumption and oxygen as a byproduct, which can be released into the atmosphere. Recombination of the generated H_2 fuel with atmospheric O_2 would result in regeneration of water, thus creating a cycle for clean fuel.[1,3] The water splitting reaction is composed of two half reactions, the hydrogen evolution (HER) and oxygen evolution reactions (OER):

$$(\text{HER}): \quad 4H^+ + 4e^- \rightarrow 2H_2$$

$$(\text{OER}): \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Water electrolysis, which uses electricity to split water into hydrogen and oxygen, can take place in an electrolyzer.[1] Electrolyzers consist of an anode, a cathode, and electrolyte to facilitate the transport of ions. Water reacts at the anode to form oxygen and hydrogen is evolved at the cathode. [Office2]However, the production of H_2 fuel by water electrolysis i[SB3]s hindered by the slow kinetics of the OER, meaning there is a large energy barrier required to complete this reaction efficiently.[4] Therefore, OER catalysts constitute a wide area of research as optimization of this process would provide a pathway for large-scale applications of an economical and sustainable fuel source.[3–5]

In order to optimize this process and make it a viable substitution for fossil fuels, catalysts must be made from nontoxic earth-abundant materials, have high activities, and high stability. The development of new OER catalysts depends on a fundamental characterization of intrinsic catalyst activity. The goal of this research is to understand how the activity and stability of OER catalysts can be tuned through ternary compositions, interlayer cations, and through the location of Fe species in order to illustrate prospective design principles. This thesis reports the results of studies which

have been accomplished in three parts: (1) Studying the effects of varying ternary catalyst composition using Ni, Co, and Fe, (2) understanding the effect of varying electrolyte cations on activity, and (3) characterizing the impact of local geometric structure on active sites in Ni-Fe (oxy)hydroxides.

Background: Electrocatalysis

In principle, water electrolysis is a simple process to execute, requiring only a power supply, two metal electrodes, and an electrolyte.[6] In a conventional electrochemical cell, water molecules are reduced to H_2 at the cathode and converted to O_2 at the anode. The thermodynamic potential at which water splitting occurs is 1.23 V vs RHE under standard conditions.[6] Experimentally, the reaction requires a greater applied potential (overpotential, η) to overcome factors such as the activation barrier, concentration gradients in the solution, ohmic resistance and the kinetics of the HER and the OER.[6] As described above, the slow kinetics of the OER is one of the main contributions to the overpotential associated with water splitting due to its requirement of four electron transfer steps whereas the HER is a two electron process. While the precise mechanism of the OER is not clearly defined, catalysts have long been studied to increase the efficiency of the reaction. An ongoing challenge in the optimization of the OER is the production of novel and well-defined catalysts. In order to design better catalysts and improve mechanistic understanding of the OER, it is necessary to characterize the relationship between structure, composition, electronic features and observed activity trends.

Background: Oxyhydroxide Catalysts[Office4]

While various compositions of metals have been synthesized as catalysts for the OER, the materials used in this particular study are earth abundant first-row transition-metal oxyhydroxide catalysts. An issue with other structures such as selenides, phosphides, and sulfides is their instability under OER conditions.[7] Under oxidizing conditions, most of the above-mentioned materials will convert to oxyhydroxide and hydrated oxide phases.[7] Among the various materials used to optimize OER catalysts, nickel oxyhydroxide (NiOOH) has been shown to be one of the most efficient under alkaline conditions when doped with Fe.[8] The porous layered structure of NiOOH, composed of weakly interacting hydroxide layers, allows for better intercalation of water and anions than shown in dense nickel oxide (NiO) layers.[8] Additionally, the NiO based catalysts are typically unstable in basic media and will convert to NiOOH under prolonged OER conditions.[8] The abundance, high activity, and stability of Ni, Co, and Fe oxyhydroxides thus makes them ideal catalysts to study in optimizing the efficiency of the OER.

Background: Activity metrics[SB5]

In order to discuss the relationship between structure, composition, and activity, a common metric for catalyst performance must be established. The turnover frequency (TOF) is a commonly used activity metric for OER catalysts and is defined as:

$$\text{TOF} = \frac{\text{mol } O_2/\text{s}}{(\text{mol active sites})}$$

The TOF is normalized with respect to the amount of active material (i.e. the amount of the catalyst that is participating in the reduction/oxidation reactions).[7]

Catalysts with high activity will drive higher current densities, increasing the amount of O_2 produced per unit time. A second way to evaluate the efficiency of a catalyst is by measurement of its overpotential η. A low overpotential is ideal as it would require a smaller amount of applied voltage to drive the water oxidation reaction. The overpotential η *is* calculated using the equation $\eta = E_{measured} - E_{rev} - iR_u$ where $E_{measured}$ is the measured potential, E_{rev} is the reversible potential calibrated against a reference electrode, i is the measured current, and R_u is the uncompensated series resistance.

Electrochemical methods of analysis used to measure these quantities are conducted through use of a potentiostat, an instrument used to apply a controlled voltage at an electrode and measuring the resulting current.[9] Cyclic voltammetry (CV) is a common experiment conducted with a potentiostat as it can be used to evaluate the redox (reduction/oxidation) of a species, reaction reversibility, and a qualitative evaluation of the overpotential. [7,9]A characteristic NiOOH CV is shown in Figure 1. The peaks correspond to the reduction (bottom) and oxidation (top) of the catalyst material, while the sharp exponential increase in current corresponds to the region of water oxidation (OER).

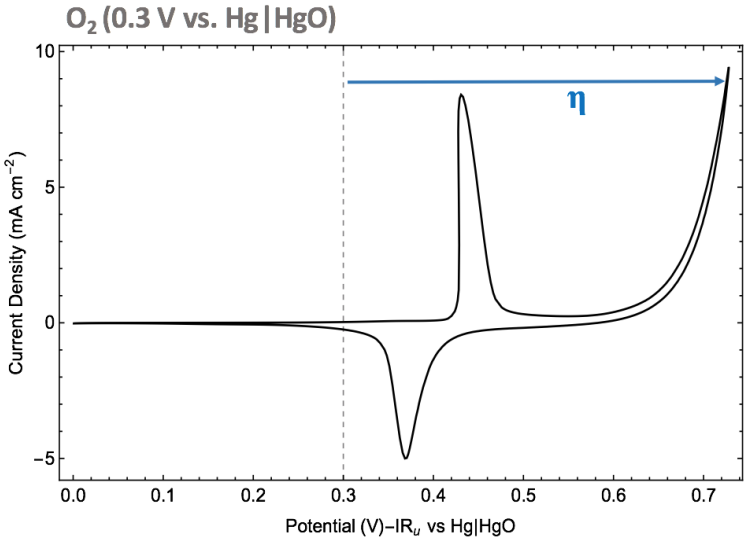

Figure 1. A schematic of CV showing a typical NiO_xH_y redox peak. The peaks correspond to a change in oxidation of Ni: oxidation from Ni^{2+} to Ni^{3+} (top) and reduction of Ni3+ (bottom). The exponential current corresponds to O_2 gas being evolved at the anode.

Experimental Methods

Film Preparation:

Ni, Fe, and Co- (oxyhydroxide) films were cathodically[SB6] deposited onto Au/Ti coated 5 MHz quartz crystal microbalance (QCM) crystals. Deposition solutions were prepared from $Ni(NO_3)_2$•$6H_2O$ (Sigma-Aldrich, 99.999%), $Co(NO_3)_2$• $6H_2O$, and $FeCl_2$•$4H_2O$ (Sigma-Aldrich, 98%) varying molar ratios and dissolved with 18.2 MΩ cm water. Upon application of a cathodic current, the nitrates in solution are reduced to ammonium ions. Production of ammonium ions raises the pH and causes the Ni^{2+} ions in solution to react with hydroxide ions to precipitate $Ni(OH)_2$ at the surface of the working electrode.[10] This process is described by the two equations below:

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10\,OH^-$$

$$Ni^{2+} + 2\,OH^- \rightarrow Ni(OH)_2$$

[0ffice7] Quartz crystals allow for quantification of loading mass in situ, which then allows for the calculation of TOF based on the amount of material deposited. To prevent the oxidation of $FeCl_2$ into insoluble FeOOH, the solution is covered in parafilm and purged with N_2 for ten minutes prior to and between depositions. Prior to film deposition, the QCM crystals were cycled in 1 M H_2SO_4 and cycled twice in 0.1 M electrolyte to ensure a clean electrode surface.[7]

For the project involving two different methods of Fe incorporation, as-deposited $Ni(Fe)O_xH_y$ thin films were electrodeposited from 0.1 M aqueous single or mixed metal nitrate and/or chloride solutions made from 18.2 MΩ cm water.

Film compositions were varied by mixing ratios of Ni and Fe. Fe-free films were prepared using ultra-high purity metal nitrate salts, $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich, 99.999% trace metal basis). Fe was added via co-deposition by adding $FeCl_2 \cdot 6H_2O$ to the deposition solution (Sigma Aldrich, > 98%). A concentration of 1 mM Fe was added for Fe-spiked experiments by adding $Fe(NO_3)_3$ (Sigma Aldrich, 98 %) to the electrochemical cell. Fe from spiked experiments partially precipitated, but sufficiently saturated the electrochemical cell electrolyte with Fe. All NiO_xH_y films were tested with Fe-spiking via the following steps in different electrochemical cells: 1) 4 cycles (0 – 0.85 V vs. Hg/HgO) in 1 M Fe-free KOH (semiconductor grade), 2) variable number of cycles (0.2 – 0.7 V vs. Hg/HgO) with 1 mM Fe(NO3)3 in 1 M KOH (semiconductor grade), 3) 3 cycles (0 – 0.7 V vs. Hg/HgO) in 1 M KOH (semiconductor grade). The films were rinsed briefly with 18 MΩ cm water between each step. Impedance measurements at 0.6 V vs. Hg/HgO were taken after each step. Films were removed from the spiked solution after a different number of cycles, i.e. 2, 10, 30, and 100 cycles. [11]

Electrolyte Preparation:

Solutions of 0.1 M KOH (Sigma Aldrich Semiconductor grade, 99.99 % trace metals) and NaOH (Alfa Aesar, 99.99 % trace metals) were prepared from salts with 18.2 MΩ cm water. The 1 mM $Ca(OH)_2$ and $Mg(OH)_2$ were made by spiking a 0.1 M KOH solution with $Ca(NO_3)_2 \bullet H_2O$ (Sigma Aldrich, 99.997 % trace metals) and $Mg(NO_3)_2 \bullet 6H_2O$ (Sigma Aldrich, 99.999 % trace metals), respectively. [12]

Electrochemical Measurements:

All electrochemical measurements were made (using Biologic SP-200 potentiostat) in a plastic cell cleaned between use with 1 M H_2SO_4 and ultrapure water. The three-electrode configuration consists of a QCM working electrode, Pt wire counter electrode (contained within a plastic fritted tube), and Hg/HgO reference electrode all within 0.1 M or 1 M electrolyte. The solutions are continuously bubbled with O_2 and magnetically stirred to limit bubble aggregation on the electrode surface. Cyclic voltammetry (CV) was corrected for uncompensated series resistance (R_u) by analysis of the Bode impedance to where the phase angle was closest to zero. Steady-state Tafel studies were conducted using chronopotentiometry (CP) measurements with current densities normalized to active electrode surfaces. Metal content was measured using X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) and film morphology analyzed by scanning electron microscopy (SEM). A schematic for a typical three-electrode cell is shown in Figure 2 where a working electrode (WE), Hg|HgO reference electrode (RE), and Pt counter electrode (CE) allow for measurement of the working electrode potential relative to a fixed reference potential.[7] The CE is enclosed within a plastic frit to minimize bubble aggregation, while the stir bar is also used to dislodge bubbles at the RE and WE.

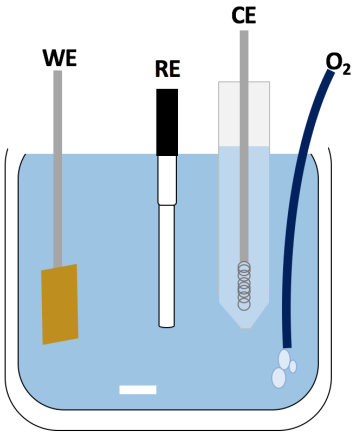

Figure 2. A schematic of three-electrode cell configuration[SB8] containing a working electrode (WE), Pt counter electrode (CE) enclosed in a plastic frit, Hg|HgO reference electrode (RE), stir bar, and O_2 bubbling.

Results and Discussion

Results and Discussion: Influence of Electrolyte Cations

Portions of this section were previously published as Zaffran, J.; Stevens, M. B.; Trang, C. D. M.; Nagli, M.; Shehadeh, M.; Boettcher, S. W.; Caspary Toroker, M. Influence of Electrolyte Cations on Ni(Fe)OOH Catalyzed Oxygen Evolution Reaction. *Chem. Mater.* **2017**, *29* (11), 4761–4767. Under the direction of M.B.S., C.T. performed the experimental work.

Although electrolyte cations have long been considered as spectator ions during electrocatalysis, studies have shown that some may play a major role in the process.[12,13] A study conducted by the Kitchin group showed that varying the electrolyte has an influence on catalytic properties of NiOOH with increasing activity from left to right: Li^+, Na^+, K^+, and Cs^+ under Fe free conditions.[13] While this study showed that the activity can be tuned by electrolyte variation, the mechanism leading this trend is still unclear. In a joint experimental and theoretical study, we measured the electrochemical activity of NiOOH and Ni(Fe)OOH catalyst films using Na^+, K^+, Ca^{2+}, and Mg^{2+} based solutions while the electronic, energetic, and structural changes were investigated by collaborators using density functional theory (DFT). Improving understanding of the effects of electrolyte cations on OER activity could inform better selection of electrolytes in studies characterizing OER catalysts.

According to experimental results and computations, monovalent cations performed better than divalent ones[SB9] in both for NiO_xH_y and $Ni(Fe)O_xH_y$ catalysts for the OER reaction.[12] It was hypothesized that the cation acidity and its size are among

the main parameters influencing surface reactivity and affecting the stability of reaction intermediates with larger cations correlating to reduced activity.[12] Figure 3 shows the observed activity trends with different cations for NiO_xH_y and $Ni(Fe)O_xH_y$ films. As expected for catalysts containing Fe, the $Ni(Fe)O_xH_y$ films have lower overpotentials relative to the NiO_xH_y films at TOF = 0.1 s^{-1}. When comparing the different electrolytes, K^+ exhibits lower overpotentials for both catalyst types, followed closely by Na^+. While Mg^{2+} is shown to contribute to a lower overpotential for the Ni-Fe catalyst, this is attributed as an anomaly since $Mg(OH)_2$ precipitated out of solution in the experiments due to low molar solubility.

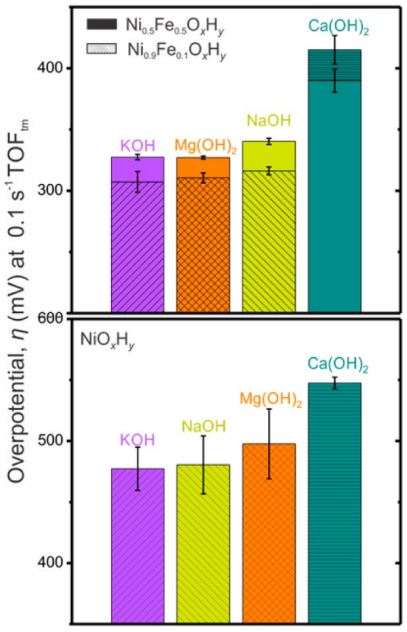

Figure 3. Trends for TOF of $Ni(Fe)O_xH_y$ (top) and NiO_xH_y (bottom) catalysts as electrolyte species are varied. Two compositions of $Ni(Fe)O_xH_y$ are shown in the top figure, one with 50% Fe (solid) and the second with 10% Fe (dashed). Figure is copyright of the American Chemical Society.[12]

To examine why the divalent cations contributed to higher overpotentials, Figure 4a and 4b show cyclic voltammograms of the Ni-Fe and NiO_xH_y films with and without the addition of $Ca(OH)_2$ to the KOH solution. Figure 6a shows addition of Ca^{2+} to the NiO_xH_y film, which immediately decreases the activity of the catalyst upon cycling. This is demonstrated by the increase in overpotential, a cathodic shift in the peak potential, and decreased OER current density. Figures 4b show the effect of Ca^{2+} addition to the Ni-Fe films, for concentrations of Fe at 10% and 50% Fe. The composition containing 10% Fe shows similar results to the cyclic voltammogram of a Ni film. However, the film with a higher ratio of Fe to Ni shows a significant broadening of the oxidation peak along with the expected increase in overpotential. Despite the change in peak shape, integration of the peak showed that the charge did not change.

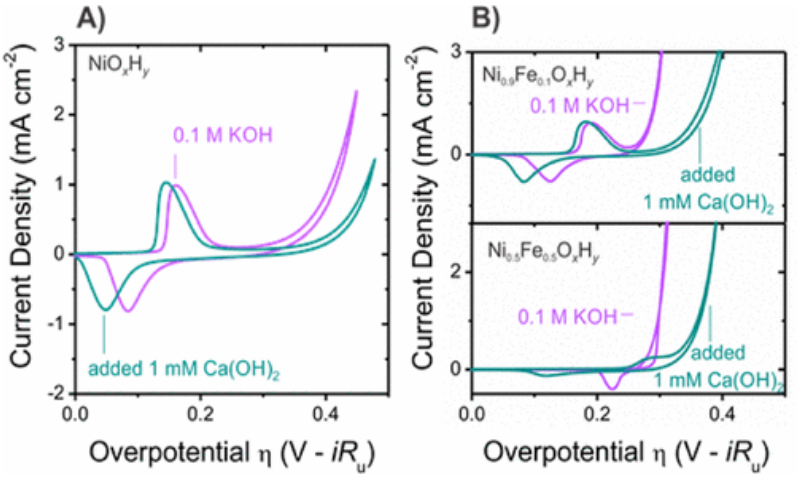

Figure 4. (A) NiO_xH_y, and (B) $Ni_{z-1}Fe_zO_xH_y$ at approximately $z = 0.1$ (top) and $z = 0.5$ (bottom) in 0.1 M KOH before and after the addition of 1 mM $Ca(OH)_2$. Figure is copyright of the American Chemical Society.[12]

The activity trends of Ni and Ni-Fe catalysts with varying electrolyte show that K^+ contributes to lower overpotentials than Na^+ due to its low acidity and on average, longer bond lengths. The experimental activity trend for NiO_xH_y is KOH ≈ NaOH ≈ $Mg(OH)_2$ > $Ca(OH)_2$ and for $Ni(Fe)O_xH_y$ with both 10% and 50% Fe, the activity trend is: KOH ≈ Mg(OH) ≥ NaOH >> Ca(OH[SB10]).

Calculations [Office11]using density functional theory indicate that differences between the average bond lengths of the cations and Lewis acidity are responsible for the observed trends. According to DFT calculations, the trend for increasing overpotential for $Ni(Fe)O_xH_y$ and NiO_xH_y are NaOH ≈ KOH >> Ca(OH) > Mg(OH) and KOH > NaOH >> Ca(OH) > Mg(OH), respectively. Due to the layered NiOOH structure, the electrolyte cations are coordinated to oxygen atoms within the layers of the catalyst and to water molecules. The distance between the cation and the oxygen atom depends on the acidity, bond length, and electronegativity of the cation. On average, the bond length for K^+ is 2.85 Å, followed by ~2.40 Å for Na^+ and Ca^{2+}, and 1.98 Å for Mg^{2+}. The higher overpotentials caused by addition of Ca^{2+} to electrolyte is correlated to its high electronegativity and shorter bond lengths, which causes it to bind stronger to water than K^+ and Na^+ cations. Due to the lower electronegativity and "looser" bonding of K^+ and Na^+ to surrounding O atoms, the interlayer water molecules are able to interact with intermediate OER species and better facilitate the reaction.

Results and Discussion: Methods of Fe Incorporation

Portions of this section were previously published as Stevens, M. B.; Trang, C. D. M.; Enman, L. J.; Deng, J.; Boettcher, S. W. Reactive Fe-Sites in Ni/Fe (Oxy)Hydroxide Are Responsible for Exceptional Oxygen Electrocatalysis Activity. *J. Am. Chem. Soc.* **2017**, *139* (33), 11361–11364. Under the direction of M.B.S., C.T. performed the experimental work.

While it is known that Fe incorporation increases OER activity, the mechanism by which it increases the activity of Ni and Co (oxy)hydroxides is unclear. [11] It has been demonstrated that varying compositions and methods of Fe incorporation yields changes in the electrochemical profile (redox potential, peak size, and shape) of a catalyst, but the relationship between these structural changes and catalytic activity have not been fully explored.[11] To examine the role of Fe on the relationship between structure and activity of Ni-Fe catalysts, two methods of Fe incorporation were used to compare the electronic properties and activities of Ni-Fe (oxy)hydroxide materials. An additional goal was to evaluate how these factors play into the role of Fe as a potential active site and to study how structure might affect the activity in two compositionally similar films.

To elucidate the role of Fe in Ni oxyhydroxide OER catalysts, two Fe species are reported in this study: one rapidly incorporated into the NiOOH from Fe cations in solution and the second incorporated into the bulk NiOOH structure, showing differences in electrochemical properties.[11] The first method incorporates Fe cations by spiking them into solution as a NiOOH film is cycled in alkaline electrolyte.

When 1 mM Fe is spiked into solution, there is an immediate decrease in overpotential, which demonstrates an increase in activity (Fig. 5). There is 125 mV decrease in overpotential by cycle 5 and ~20 mV decrease between cycle 5 and 100. Following 100 cycles, the anodic peak (E_{pa}) shifts a maximum of 30 mV and steadily decreases in size with increased cycling.[11] The Fe content after variable cycling is determined by ICP-OES analysis, showing a range of Fe uptake of up to 24% from cycle 5-105 in Figure 5b. As Figure 5c shows, there are minimal changes in activity but steady changes in peak position and e^- per Ni as cycling increases. When Fe is initially incorporated upon five cycles, the increase in activity is immediate however the peak position and shape do not change significantly. The small change in activity compared to the changes in the redox features as a function of Fe incorporation suggests that catalysis is influenced by Fe incorporation at edge/defect sites rather than Fe in the bulk NiO_xH_y structure.[11][SB12] When Fe is initially [Office13]spiked into the electrolyte, Fe species on the edge or defect sites of the NiOOH structure modulate the activity but do not affect overall bulk NiOOH structure. However, as cycling continues, Fe becomes increasingly incorporated in the NiOOH bulk, which leads to the changes in electrochemical profile as seen by cycle 105 (Fig 5a inset). [Office14]

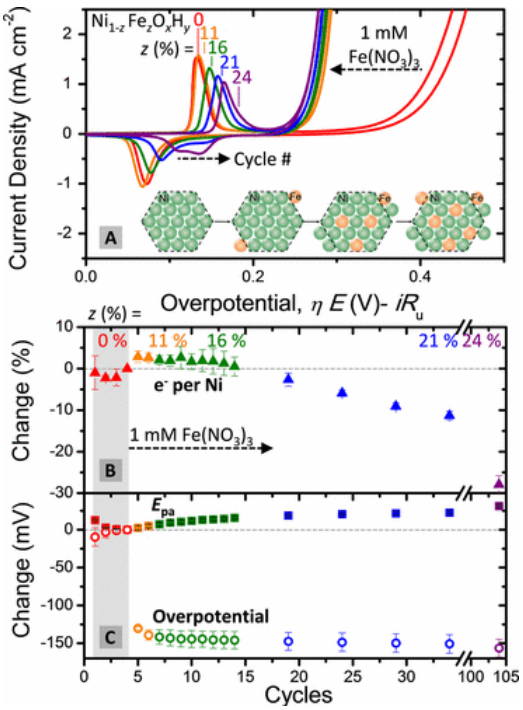

Figure 5. As 1 mM Fe is spiked into solution, the overpotential decreases by ~130-150 mV (A); The size of the anodic peak showing charge per Ni decrease as cycling increases (B); The anodic peak position (E_{pa}) shifts by approximately 30 mV with increased cycling, whereas the overpotential changes most within the first 5-15 cycles. Figure is copyright of the American Chemical Society.[11]

For the second method, we compare the activity and electrochemical properties of a co-deposited Ni(Fe)O_xH_y film to the spiked Fe-NiO_xH_y film. Figure 6 compares the cyclic voltammetry and activity of a spiked Fe film and a co-deposited film of similar compositions. As expected, the reduction potentials of both Ni(Fe)O_xH_y films are shifted anodic of the Fe-free film. While the spiked and co-deposited films have similar activities, the main differences between them appear in the shape of the redox curve and the peak potentials (E_{pa}). Comparing the peak potentials of the co-deposited and spiked films with low Fe content (Fig 6a), there is a ~10 mV anodic shift in E_{pa} for the spiked film and a ~26 mV anodic shift for the co-deposited film. In the films with higher Fe

content (Fig 6b), E_{pa} of the spiked film shifts ~20 mV anodic of the NiO_xH_y and ~65 mV shift in E_{pa} for the co-deposited sample.

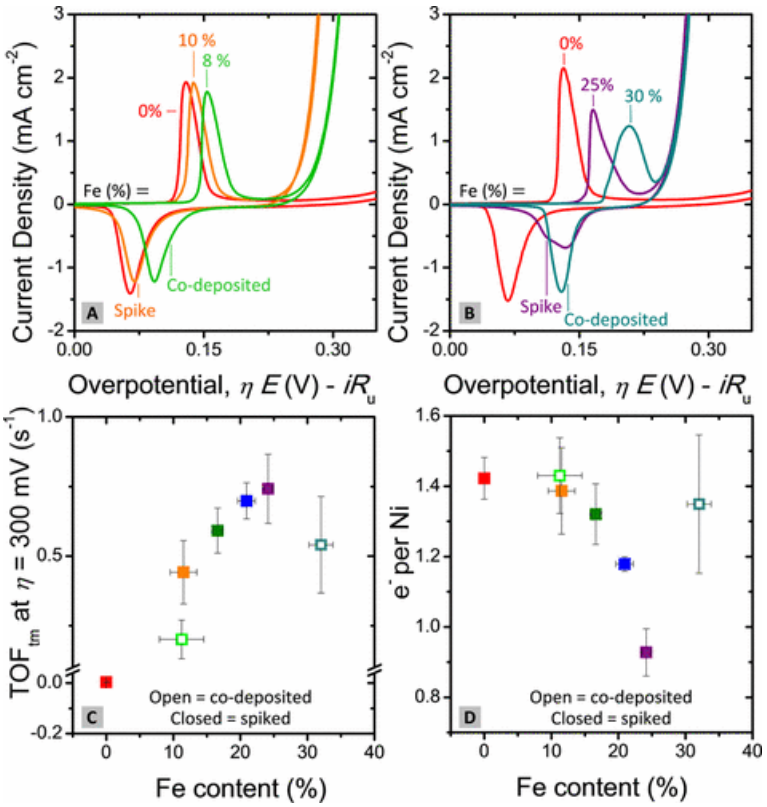

Figure 6. Cyclic voltammetry of Fe-free NiO_xH_y film (red) compared to (A) spiked $Ni(Fe)O_xH_y$ cycled 2 (orange, 10% Fe) and (B) 100 (violet, 25% Fe) times in 1 mM $Fe(NO_3)_3$ and codeposited $Ni(Fe)O_xH_y$ films with similar Fe content (green 8% Fe and teal 30% Fe, obtained by integration of the oxidation wave. Metal content and ratios were determined after electrochemical analyses using ICP-OES. Open and closed symbols are for codeposited and Fe-spiked samples, respectively. Figure is copyright of the American Chemical Society.[11]

Fig 6d compares the e^- per Ni for each film, [SB15]which is determined from integration of the oxidation wave and the total metal content from ICP-OES. Since the oxidation and reduction of Ni is expected to be a one electron process, the peak integration yielding a number greater or less than one is indicative of the

electrochemical accessibility of a catalyst. If the peak integration yields a number greater than one, it is hypothesized that Ni is oxidized to a higher oxidation state and if less than one, this indicates that the entire film is not being fully oxidized or reduced[Office16]. While the e^- per Ni is similar between the films of low Fe content, there is ~30% more e^- per Ni in the co-deposited than in the spiked film. The broader features of the redox peaks in the spiked 25% Fe sample suggest inhomogeneous incorporation of Fe in the sample, which also affects the position of the redox waves.[11] This could indicate a different mechanism by which Fe is incorporated into the layered structure of the catalyst, where it could be incorporating at the edges of the catalyst or onto the surface before moving into the bulk structure of the film. The similarities in activity between the co-deposited and spiked films seem unaffected by the differences in E_{pa}, which suggests that the peak position does not correlate with activity. While differences in deposition method and electrochemical conditioning lead to two Fe-sites in different local environments, the overall activities of two compositionally similar films are not affected by different peak positions or e^- per Ni in the redox waves. Although the e^- per Ni decreases as more Fe is incorporated into the bulk of the NiO_xH_y, the activity of the films remain high. This supports hypotheses on Fe being the active site in OER catalysis since the activity is not strongly influenced by changes in the Ni bulk electronic structure, but instead by Fe incorporation at accessible edge sites.

Results and Discussion: NiCoFe

This section contains unpublished work: Stevens, M. B.; Enman, L. J.; Trang, C. D. M.; Asbury, J.; Kast, M. G.; Toroker, M. C.; Boettcher, S. W. *In preparation*. Under the direction of M.B.S., C.T. performed the experimental work.

One of the most active materials in OER catalysis are Ni-Fe (oxy)hydroxides in alkaline conditions.[8] Co-Fe oxide/oxyhydroxide catalysts have also been well-studied in literature and have been shown to be stabilizing and electrically conductive when combined with other first-row transition metals. [14,15] Binary compositions including Fe have shown higher activities than single-component catalysts of the same elements.[8,16] The effect of Fe on OER activity has also pervaded previous studies where impurities present in glass materials and electrolyte have led to convoluted activity trends.[16,17] The result of incidental and intentional Fe incorporation is shown in Fig 7, showing an anodic shift of the redox waves, decreased overpotential, and increase in OER current.[16]

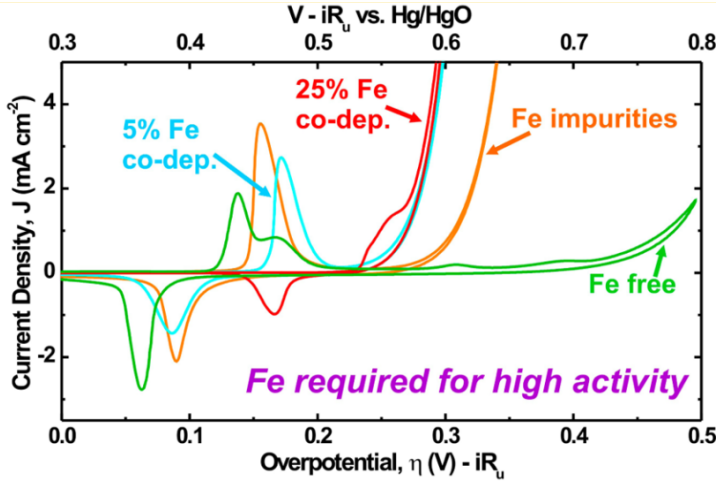

Figure 7. The effects of intentional Fe incorporation compared with trace Fe impurities present under certain experimental conditions (i.e., glass materials, electrolyte). Figure is copyright of the American Chemical Society (2014).[16]

Although Fe has been shown to enhance the activity of OER catalysts, it has been shown to be a poor catalyst on its own.[18] The reason for the poor activity of Fe based catalysts is hypothesized to be due to its low electrically conductivity and instability in OER conditions.[18] While Fe has been shown to increase the OER activity when incorporated into Ni or Co (oxy)hydroxides, ternary arrangements of these materials have not been thoroughly characterized. This motivates our study of varying ratios of Ni, Co, and Fe catalysts to explore whether activity can be tuned through composition.

While the activity trends of Ni-Fe and Co-Fe catalysts have been studied, the activity of mixed Ni-Co-Fe (oxy)hydroxide films have not been well defined in literature due to Fe contamination.[16,19] To evaluate the effects of composition on activity, we first examine varying ratios of Fe-free Ni-Co (oxy)hydroxide films (Fig. 8). Figure 8a shows that the peak potentials shift cathodically as Co concentration increases. In addition, the size of the peaks also change as the ratio of Co to Ni is varied, which indicates changes in the electronic structure of the film. The activities, reported as the total metal TOF, of the Ni-Co films are compared in Fig 8b at varying overpotentials. These results show that the activity is highest in the films with higher Co:Ni, however all binary compositions are more active than the NiO_xH_y alone. The kinetics of the reaction with changing composition are shown in Figure 9b (inset), where the change in Tafel slope as Ni content is increased indicates a change in the reaction mechanism.

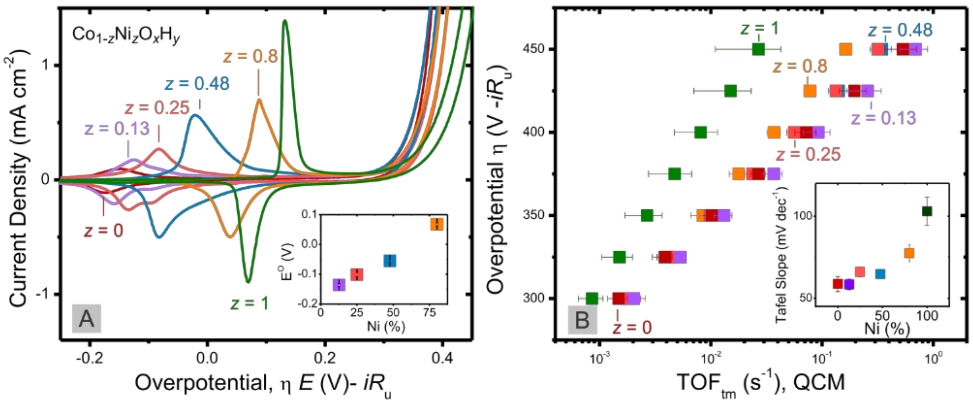

Figure 8. **(A)** Ni(Co)O_xH_y (10 mV s^{-1} in 1 M KOH, cycle 2) with inset of redox wave position (E^0) as function of Ni content. **(B)** The activity (TOF_{tm}) at varying overpotentials with the mass measured by QCM. The inset shows the Tafel slope as a function of Ni content.

Activity is greater for the ternary compositions containing a higher Ni: Co ratio which is expected since Ni(Fe)O_xH_y has been reported as one of the most active OER catalysts, with greater activity than Co(Fe)O_xH_y or CoO_xH_y alone (Fig 9a).[15,18] Fig. 9b shows the activity and peak positions of co-deposited Ni(Co)FeO_xH_y films. As the Ni:Co ratio is varied, the activities remain similar while the peak position shifts anodically as Ni content increases. These results suggest that there is likely no synergism between Ni and Co since 9b shows that varying Ni:Co affects electronic structure but does not significantly affect activity.[Office17] When the Ni-Co films are co-deposited with Fe, there are large increases in activity but minimal changes in peak position. This supports the hypothesis of Fe in edge/defect sites playing a bigger role in enhancing activity over the bulk electronic structure (as monitored by peak position in 10b[SB18][Office19]).

Among the ternary compositions, the most active composition is one containing ~70% Ni, 30% Fe, and minimal Co, which indicates that $NiFeO_xH_y$ remains the most active catalyst[SB20].

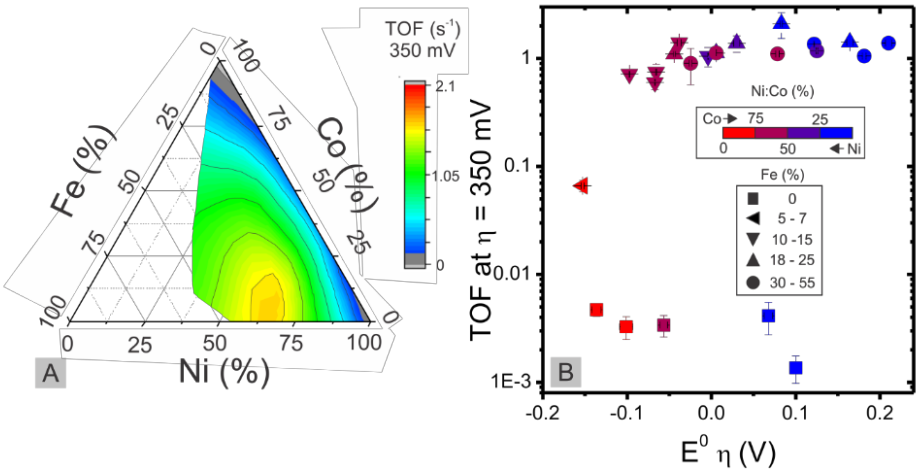

Figure 9. Activity of co-deposited Ni(Co)FeO_xH_y at η = 350 mV as (A) a function of Ni:Co:Fe ratio and (B) peak position (E^o). The activity of all ternary compositions are from ICP compositions.

Conclusion

The ability to rationally design OER catalysts for widespread energy storage and utilization depends on understanding intrinsic catalyst activities and specifically, how Fe affects the OER mechanism. The results of this thesis addresses how electrolyte cations, different catalyst compositions, and location of Fe species affects OER activity. The results of the first study on interlayer cation effects shows that activity of NiO_xH_y and $Ni(Fe)O_xH_y$ films is affected by the different size, acidity, and charge of cations, which challenges the belief that electrolyte cations are spectators during electrocatalysis.[12] It is shown that electrolytes containing K^+ yield the lowest overpotentials for both types of films, which also supports the results reported in the literature.[13] In addition, the role of Fe in enhancing OER activity is also explored. The results of this project show that there are two different ways Fe is incorporated into the structure of the film: rapidly from solution onto NiO_xH_y edge/defect sites and substitution into the bulk structure.[11] Their differing electrochemical redox features, but similar activities indicate that catalysis is mainly influenced by active Fe sites rather than the average electrochemical properties of NiO_xH_y or Fe located in the bulk.[11] In studying different ratios of Ni-Co-Fe films, the most active film remains the one that is closest to a $NiFeO_xH_y$ film. Upon addition of Fe to a Ni:Co film, the observed changes in activity and little to no shift in peak position is consistent with our results from the previous study, where Fe edge sites is responsible for activity enhancement. These results on the role of Fe in OER catalysis and the effect of different interlayer cations can be used to rationally compare structure/activity/composition trends reported in literature and improve overall understanding of common materials studies in literature.

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