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UNIVERSITY OF CALIFORNIA, SAN DIEGO

Study of Nickel Oxide Composites as an Efficient Electrocatalyst for
Photoanodic Water Splitting

A thesis submitted in partial satisfaction of the
requirements for the degree of Masters of Science

in

Electrical and Computer Engineering

by

Justin S. Cheung

Committee in charge:

Professor Deli Wang, Chair
Professor Jie Xiang
Professor Shadi Dayeh

2013

The Thesis of Justin S. Cheung is approved, and it is acceptable
In quality and form for publication on microfilm and electronically

Chair

University of California, San Diego

2013

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List of Abbreviations

PV	Photovoltaic
PEC	Photoelectrochemistry
NiO_x	Nickel Oxide
MEA	Monoethanolamine
FTO	Fluorine doped Tin Oxide
EC	Electrochemical
CV	Cyclic Voltammogram
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscopy
XPS	X-ray Photoelectron Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy

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Abstract of the Thesis

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by

Justin S. Cheung

Masters of Science

University of California, San Diego 2013

Professor Deli Wang, Chair

The discovery of a new viable renewable energy source is of significant importance for our generation. One approach scientists are addressing this problem is to use sun for solar power. There has been a lot of success in converting solar energy into electricity using solar panels. Now, scientists are trying to take it one step further and use this same idea to split water and

make hydrogen. This process is called Photoelectrochemistry (PEC). PEC is more complicated as there are many more issues to address such as the electrolyte to solar panel interface, having sufficient band-gap to split water, and the use of electrocatalysts to help aid in splitting water. This work here contributes to helping solve one of the problems, which is the development of an electrocatalyst to help photoanodic water splitting. These tests were done using electrodes with Nickel Oxide coated on them while running electrochemical tests to see their electrocatalyst performance. Here, we demonstrate that different preparation methods of a solution based Nickel Oxide precursor can affect its electrocatalytic performance, through potential shifting and current density increase, thereby enhancing its ability to aid in photoanodic water splitting.

1. Introduction

What happens when we run out of fossil fuels? What energy source will people turn too next? This energy source will be the sun or solar energy. One may think, does this provide enough energy? The amount of sunlight that reaches the earth's land surface equates to about 1924 pettawatthours¹ assuming there is 12 hours of sun in a day and a land surface area of 57.5 million square miles. This exceeds the amount of energy the world needs as, in 2008, the energy consumption was only 143.851 petawatthours². Currently, most of the solar energy is going into the biomass life or heating the earth, but a lot of it is still unused. This unused solar power could be converted into electricity or another form of energy that people could use.

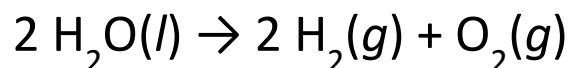
How does one manage to harness sunlight energy? This happens through photovoltaic (PV) cells. These PV cells work by turning photons(light) into electron/hole pairs(electricity). This works because of the photovoltaic effect³ which is described as sunlight hitting a material, usually semiconductors, and an electron in the valence band absorbs the energy moving it to the conduction band becoming a free electron. These electrons then diffuse and reach a built in potential junction that accelerates them into a different material generating an electromotive force, thus generating electric energy from solar energy. PV cells were initially developed in the 1950's and a lot of work has been done to improve their performance, which is beyond the

scope of this thesis. My work focuses on taking PV devices to the next level by using them for photoelectrochemistry (PEC), to generate hydrogen instead of electricity.

Hydrogen is an important energy source as it can be stored without losing energy, higher specific energy than fossil fuels, and no CO₂ emission as the product of using hydrogen is water.⁴ The advantage of storing hydrogen versus electricity is that storing in batteries will have leaks and loss of energy over time. With hydrogen, there is no leakage or loss of energy by storing it, considering the container is leak proof. The specific energy of Hydrogen is 123 MJ/kg while the specific energy of gasoline is 46 MJ/kg, so by weight Hydrogen has more energy.⁵ This makes Hydrogen a good candidate to replace gasoline in cars. This will also make cars more environmentally friendly as no harmful carbon will be released into the atmosphere as hydrogen will just turn into water. This is why scientists are so interested in PEC to get this hydrogen economy started.

The goal of PEC is to convert light energy into chemical energy, such as hydrogen, by splitting water and storing it.⁶ This is important, as hydrogen, is another source of energy people can use besides electricity.⁷ How PEC works can be shown in Figure 1 below. It works by having two different photoelectrodes which act similar to PV cells, but underwater. The two photoelectrodes shown are the photocathode(p-type) and photoanode(n-type). These photoelectrodes will absorb light and have electron hole pairs, but have

different electrons and holes movement into the electrolyte to cause oxidation (p-side) of water or reduction (n-side) of water. The overall chemical equations are beyond this thesis, but the basic chemical reaction is shown below:



These photoelectrodes supply the voltage and current needed to split water which starts splitting at 1.23 V.⁸ This comes from the potential needed for reduction of water to produce hydrogen, which is -0.41V, and the potential needed for oxidation of water to produce oxygen, which is +0.82V. These potentials should be supplied by the photoelectrodes at both ends by absorbing light. By changing the characteristics of the electrode such as using different semiconductors, changing the doping concentration, or changing the morphology can have changes on the potential. These are all internal to the electrode and are beyond this paper, what this work focuses on is the external force to help with lowering these potentials and increasing the current. This external force comes in the form of an electrocatalyst.

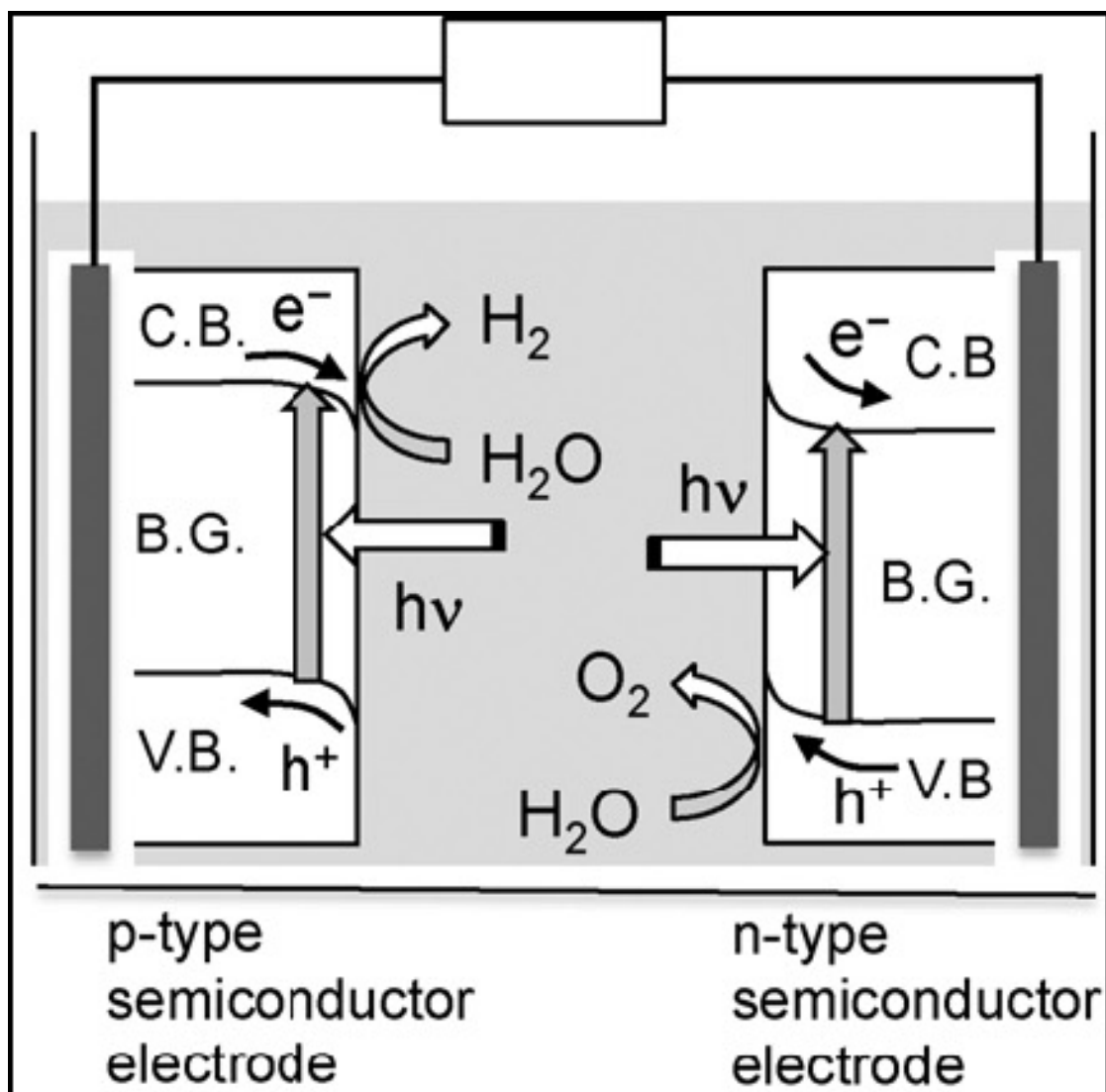


Figure 1. General PEC schematic showing oxidation and reduction of water.⁹

Electrocatalysts are located in between the photoelectrode and water/electrolyte interface. Electrocatalysts are important in PEC as it can help the photoelectrodes split more water by lowering the potential, needing a lower voltage to split, as well as achieving higher current densities, allowing for more rate of reaction.¹⁰ An example of how an electrocatalyst improves performance

is shown in Figure 2 below. Electrocatalysts can help reduce the potential by reducing the resistance loss between the electrolyte/water and photoelectrode interface. This would cause a shift in the potential to decrease as there is less loss between them requiring less voltage to get the same current, as shown on the left in Figure 2. It can also help increase the current density by increasing charge transport or being an active catalyst in speeding up the rate of reaction of splitting of water. This increase in rate of reaction would increase the overall efficiency of the water splitting device. Electrocatalysts can also be used as a barrier to prevent passivation¹¹, but this work is not on a photoelectrode and instead a conducting FTO glass was used, so this parameter wasn't considered.

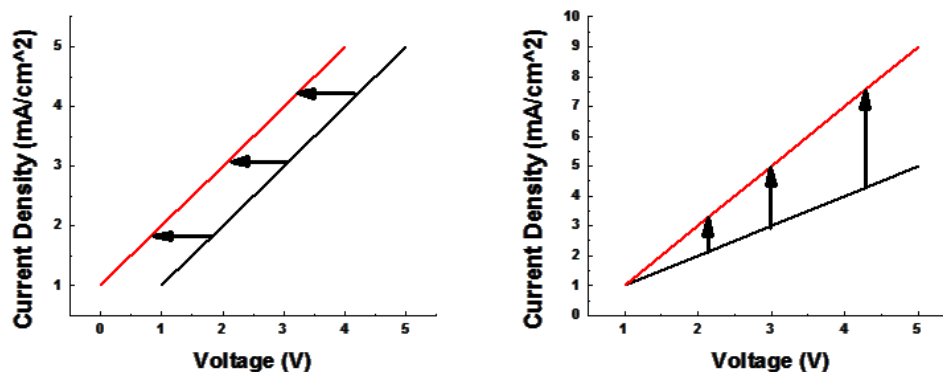


Figure 2. Examples of Potential Shift (left) and Current Density Increase (right) of electrocatalysts.

There are a variety of electrocatalysts to choose from to help in aiding the water splitting process. The best known electrocatalysts are Pt¹², Ir¹³, and Ru¹⁴ for both oxidation and reduction of water. For this work, we focused only

on the oxidation of water or photoanodic electrocatalysts. With this in mind, we wanted to look for a different electrocatalyst as the best known catalysts also happen to be some of the rarest metals on earth. These materials would not be suited for commercial use for hydrogen production PEC. Therefore, we decided to choose a new electrocatalyst.

The electrocatalyst I have chosen is Nickel Oxide (NiOx). The reason I chose NiOx is because it is less expensive than rare metals, more abundant than rare metals, and is known as a good catalyst.¹⁵ The performance of the NiOx catalyst can depend on a variety of factors such as the method used to fabricate NiOx¹⁶, the structure or morphology of NiOx¹⁷, or the phase or crystal structure of NiOx¹⁷. The crystal structure can be controlled with temperature and morphology change is limited by the fabrication method so we decided to investigate which fabrication method would suite us best. NiOx can be made from a variety of methods such as sol-gel¹⁸, sputtering¹⁹, and atomic layer deposition²⁰. These are just a few of the methods to develop NiOx. Out of these methods, I chose to do a sol-gel/solution approach to making NiOx.

The reason we chose to do a solution growth method is because it is a fast method to prepare and make NiOx, more cost efficient as there is no need for an expensive machine, easier to fabricate as spin coating and dip coating is more straight forward, and we get more control of how NiOx can turn out after annealing by adding different chemicals, like surfactants, to change the precursor solution. There are disadvantages to using this solution method,

such as residues being left over from the precursor if not carefully burned off and having to have extra chemical processing steps to ensure quality precursor solutions which can decrease the performance of NiOx. Also, in this solution method we are hoping to minimize the amount of energy put into making the nickel oxide, such as precursor heating/mixing, stability of the precursor so that it made be stored and used over long durations, low cost and use of large machines, annealing at as low temperature and low amount of time as possible, and low amount of energy to active the NiOx catalyst, as some NiOx catalyst need activation energy. The reason we want to minimize the energy is to see if highly active and stable NiOx can be made to produce hydrogen without using an enormous amount of energy to create NiOx itself.⁷

Therefore, I will be demonstrating the use of a solution method that does not require any heat to mix the solution as well as a low annealing temperature, resulting in a highly active NiOx by changing the chemical composition of the precursor solution. By changing the precursor solution, by adding surfactants, I am able to achieve better performance than the original solution, with no surfactant, and show how different surfactants can have a positive or negative effect on the end product of NiOx, causing a potential shift and/or current density increase.

2. Methods

Nickel (II) Acetate Tetrahydrate, $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich), Ethanol 99% (Sigma-Aldrich), Triton X-100, $\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$ ($n = 9-10$) (Sigma Aldrich), and Monoethanolamine, $\text{C}_2\text{H}_7\text{NO}$ (Sigma Aldrich) were all used as received from supplier. All reactions were performed under ambient conditions.

2.1 Solutions

The NiOx precursor solution is made from Nickel (II) Acetate Tetrahydrate and Ethanol 99%. The ratio of Nickel used in this experiment was gathered from a literature paper²¹ using a ratio of 0.05M and instead of using Nickel Nitrate, this study was done with Nickel (II) Acetate. The reason we chose to follow this paper is because of its initial mixing step. There is no external heat added as they simply stir the solvent, metal salt, and surfactant together until fully dissolved. In this study, I used 10mL of ethanol and added 0.124g of Nickel salt. This solution was made in either a plastic or glass bottle and was shown to be unstable as the solution. After one week the precursor would stick to the side of both containers and no longer be a homogeneous dissolved solution, but instead have flakes and is no longer viable to use as shown in Figure 3(a).

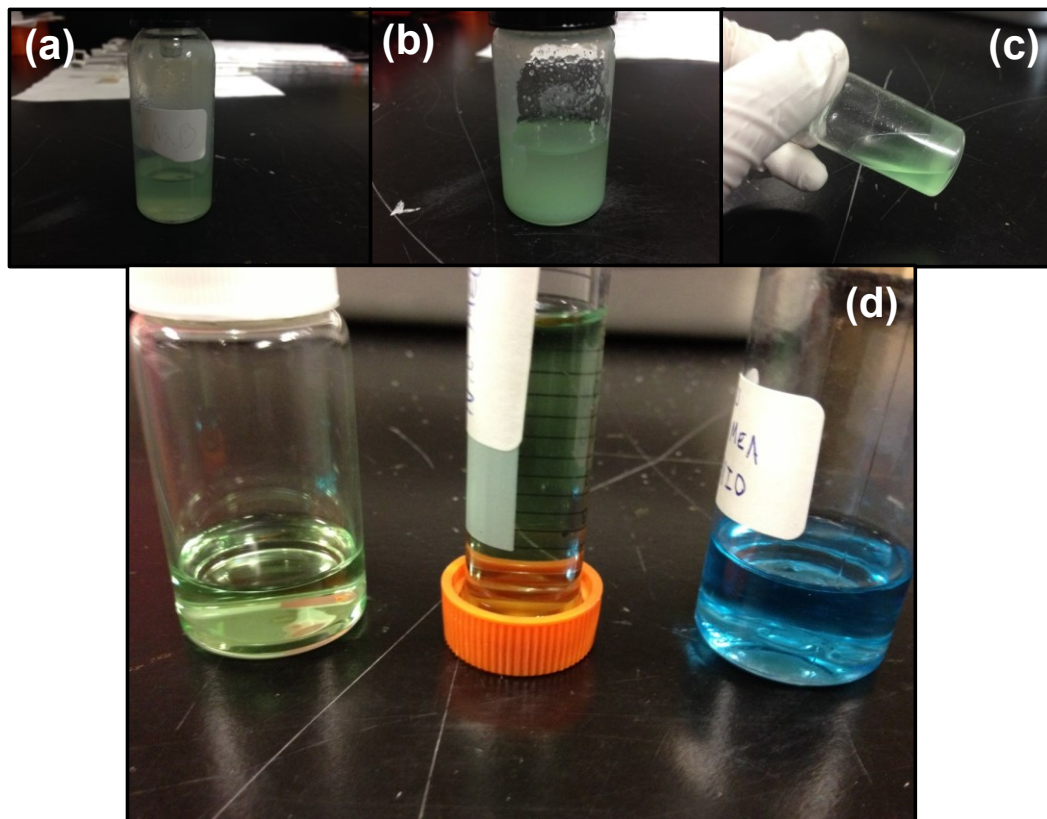


Figure 3. Nickel Acetate with Ethanol a.) in plastic, b.) in glass, c.) with Triton X 100, d.) with MEA 1x in glass (left) MEA 1x (center) and MEA 10x (right)

From ref [20], they also used a surfactant called Triton X-100. The amount used is 0.012M or about 0.15g per mmol of salt. Surfactants, like Triton X, have been used to help create a colloidal network making it a sol-gel which would yield more surface area of NiOx sticking to the surface of the substrate before annealing.²² The additive is an important part of the solution process because if this chemical is changed for another, it can yield a different precursor solution that can change the morphology of the NiO.²³ This is studied here as I tried using different additives for the same process above

that have been used in other methods. The precursor is still unstable and will stick as before shown in Figure 3c.

Their work has gone up to here with a different salt using Nickel Nitrate instead of Nickel Acetate. From here they were able to make their own Nickel Oxide thin film of about 5 nm in thickness from annealing at 300C for 1 hour on a hot plate. They have shown by pumping in 1 hour of 10 mA/cm² they can activate their NiOx and have significant current density increase. This work goes beyond that by trying to reduce the extra energy put into activating the Nickel Oxide by changing the recipe in terms of surfactant and lowering the annealing temperature or time in order to see if we can improve the overpotential and current density without this enormous activation energy.

The other surfactant and most studied one is Monoethanolamine (MEA). This was used in other papers as a stabilizer¹⁸. In this case I have found that the concentration of MEA is very critical to this recipe and shows that the type of surfactant used is very important in producing different results. The molar ratios of MEA were varied and studied at 1x, 5x, 10x, and 20x concentration, with 1x being the same molar ratio as the Triton X 100, as to compare the catalyst activity and potential shift of NiOx. This stabilizer also yielded a precursor solution that did not stick and continued to be a homogeneous solution for up to nine months and is still currently stable as shown in Figure 3d. This is an important factor for viable solution grown NiOx

electrocatalysts as this will ensure stability and long term duration of use of the precursor.

2.2 Spin Coating

All samples were prepared on Fluorine doped Tin Oxide (FTO) glass unless stated otherwise. The substrates were prepared by cleaning the surface with 5 minutes ultrasonic in acetone and then another 5 minutes in IPA. Substrates were then rinsed off with DI water and dried with a Nitrogen gun in a clean room. One edge of the sample was tapped off to allow for electrical contact later. Each sample was loaded with 100 microliters of solution and spun at a speed of 5000 rpm at 90 seconds. After spin coating was completed, the tape was removed immediately. Then, it was directly transferred to a hot plate to anneal at 300°C in air for 1 minute. After heating, it was set to cool on a glass slide before use into making an electrode.

2.3 Electrochemical Setup

The electrodes were made using copper wire, silver paste (Pad Tella), and epoxy (Loctite). The exposed wire was laid on top of the FTO glass where no NiOx is present to ensure ohmic contact. Silver paste was used to adhere the wire to FTO also making an ohmic contact as tested with a multimeter. After letting the silver paste dry a layer of epoxy was made and put over the sample covering it all except for the sample surface. All edges were covered

as leaving exposed glass to the Sodium Hydroxide (NaOH) solution could etch the glass²⁴, contaminating the electrolyte solution.

We used a three electrode configuration to do all of our CV scans. A schematic of the setup is shown in Figure 4 below. The three electrode configuration consists of a working, counter, and reference electrode. The whole point of the three electrode system is to have the reference hold a steady potential while the current runs between the counter and working electrode. Normally, with two electrodes this is very difficult because it is difficult to pass current through an electrode and keep the voltage constant.

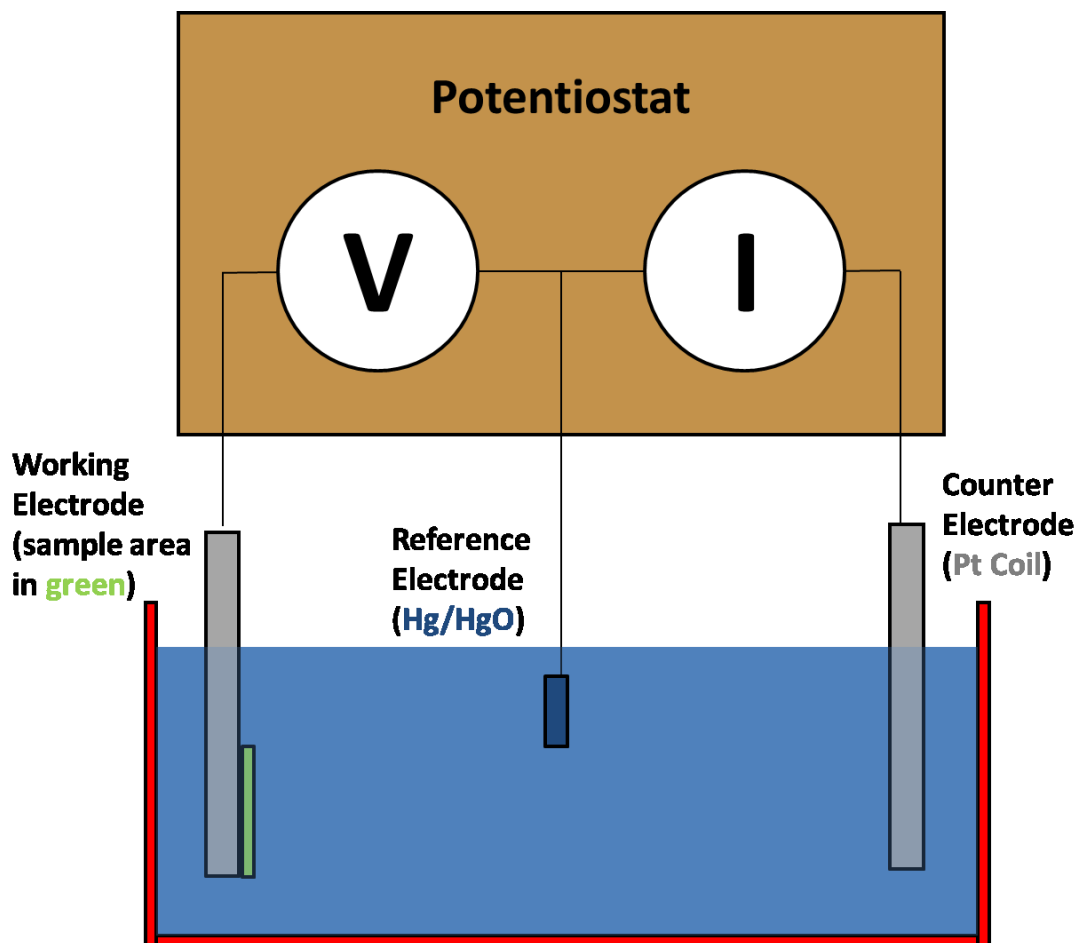


Figure 4. Schematic diagram of three electrode EC setup.

The solution used for Electrochemical (EC) testing was 1 M NaOH, which has a pH of 14. Basic solution was used to measure the results because it is the optimal parameter for testing photoanodic current or oxidation of water.^{25,26} A cylindrical Teflon container was used to hold the solution. Nitrogen gas was flown into solution constantly to purge the solution of excess oxygen. The counter electrode used was a Platinum coil. The reference electrode used was a Teflon Hg/HgO electrode. The solution was stirred with a magnetic stirrer and the working electrode was 3 centimeters away from the

Platinum electrode as shown in Figure 5. The Cyclic Voltammetry scans were done using a two-channel potentiostat (Digi-Ivy DY2300).

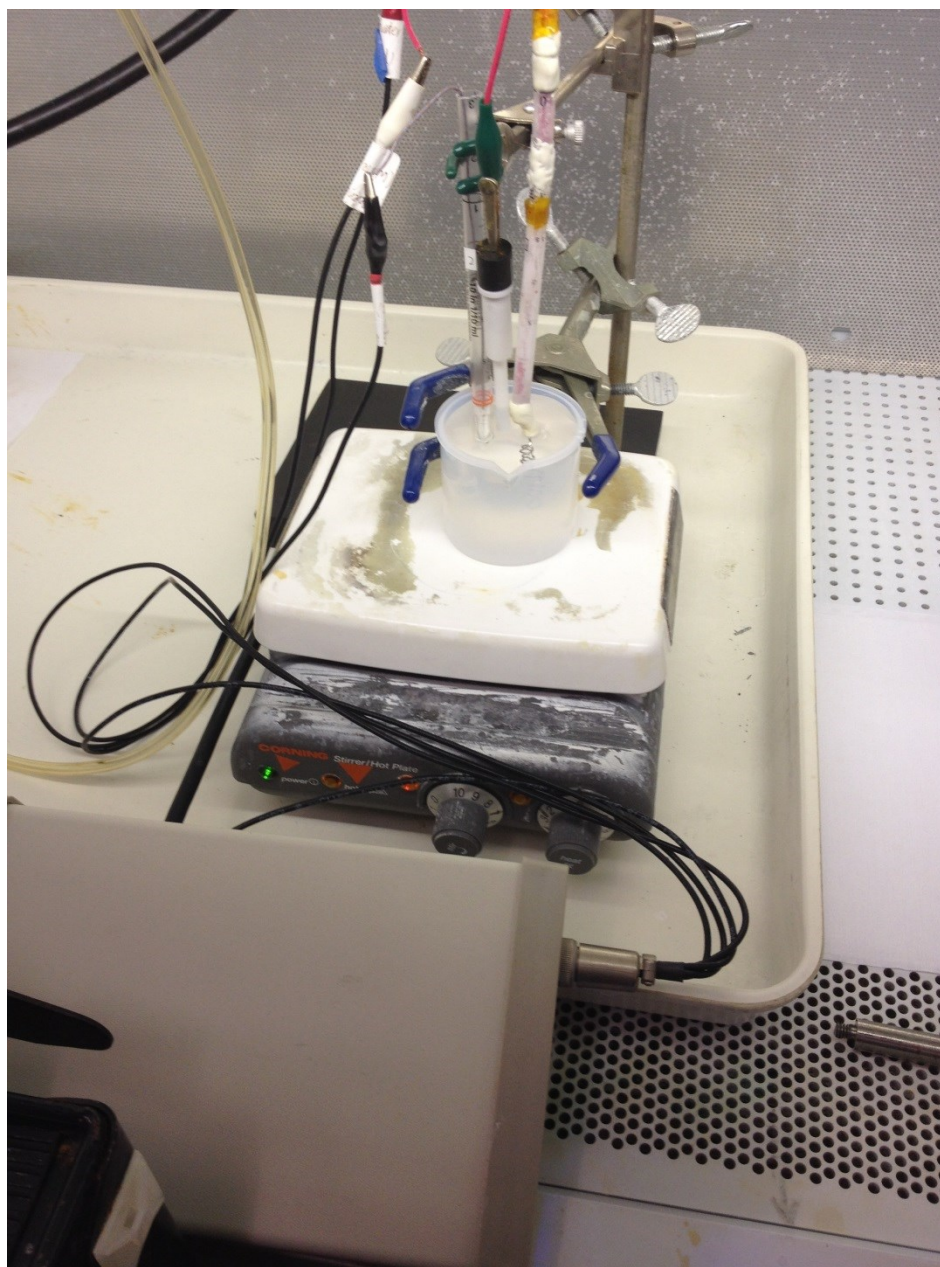


Figure 5. The three electrode potentiostat setup with a platinum counter electrode, a Hg/HgO reference electrode and a working electrode with Nickel Oxide.

3. Results and Discussion

We use Cyclic Voltammetry(CV) scans to show us potential versus current of a working electrode in respect to a reference. Depending on the different type of reference used will give different results. For comparison purposes most have been left at the reference of Hg/HgO, which is the reference electrode used. The comparison between Triton X 100 and MEA was converted to RHE (reverse hydrogen electrode) which is a standard people use to compare their data to others. This was done to make an accurate comparison with other works, but there is no need to convert if comparing works under the same reference. The potential is ramped linearly versus time until it reaches the desired potential, for NiOx on FTO this is usually about positive 0.8 volts, then ramps back down to the starting voltage, usually the open circuit voltage of the device. At each of these intervals the current is measured giving a voltage versus current plot at the end. We then transform the current to current density by dividing by the area of our sample surface to effectively compare each sample. Also, you can input a parameter of scan rate which can dictate the sampling speed. Using a slower scan speed is seen as more accurate data as fast changes can lead to fast current spikes in data. For this reason we used 10mv/sec scan rate to show accurate and comparable data.

The purpose of these CV scans is to see the reduction and oxidation peaks as well as see the onset potential, the potential in which the current starts to go through the electrolyte and splitting of water.²⁷ For NiOx, we are hoping to see both these peaks, but are most interested in the onset potential as this is where water splitting can start to occur. With a shift to a lower onset potential we can decrease the amount of energy needed to start splitting water for the PEC devices. We can also see increase in current density by taking the area and dividing it into the current. Using these CV scans we can quickly compare the catalytic activity and potential shift of each of the different NiOx solutions.

3.1 Time and Temperature Dependence

The time and temperature of annealing NiOx was studied to see if there was a significant effect on the catalytic activity and onset potential of NiOx. The annealing time was chosen before in a previous study we have done on FTO with 1x concentration of Triton X, this time we changed the surfactant to MEA and conducted another time and temperature to see if it followed the same trend. The time samples were done at 300°C and times of 1 and 2 minutes. Our results are shown in Figure 6, which is similar to what we observed previously²⁸ that a longer annealing time after 1 minute would cause a shift in the voltage causing an increase in onset potential, making the NiOx need a higher voltage to turn on to drive a current. This time was said to be optimal for this temperature due to minimal heating to form enough NiOx to

have high catalytic activity without too much heating into a more crystalline state.²⁹ From here we got the optimal annealing time and all data presented afterwards will be taken to be 1 minute annealing unless otherwise stated.

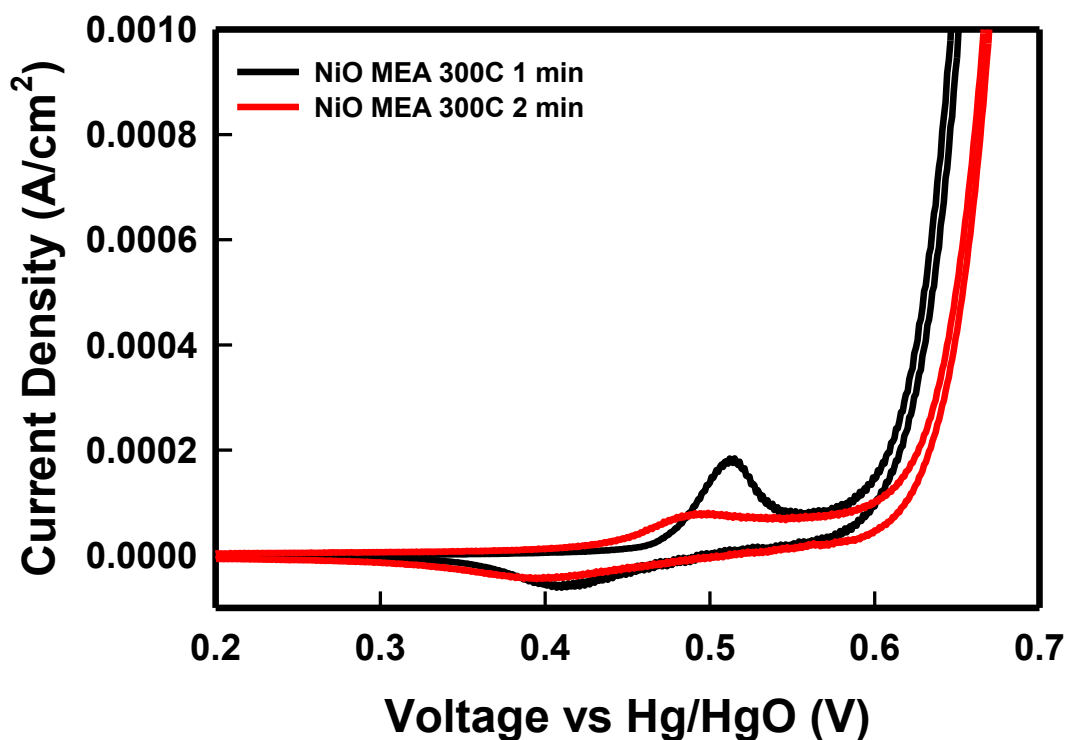


Figure 6. CV of annealing time effect on NiOx performance.

After seeing the time effect, we investigated the temperature effect as we varied the temperature around 300°C, choosing 250°C and 350°C for different annealing temperatures. The time was set to 1 minute to find the optimal point of annealing. The temperature needs to be sufficiently high enough to make sure no organics are left and that it is broken down as well as

sufficient heat to form NiOx.³⁰ The results of our study are shown in Figure 7 below. We can clearly see that the 250°C sample has the biggest potential shifting increasing the onset potential. We believe this decrease in performance is lack to significant NiOx formation as there is no bump visible in this CV scan for NiOx oxidation and reductions, as NiOx is said to be formed at 300°C.³⁰ The 350°C sample showed better performance than the 250°C sample, but still worse than the 300°C. The 350°C sample had increased onset potential compared to the 300°C and we believe this is due to the same reasoning in the time sample where NiOx may be receiving too much heating and losing catalytic activity and forming a more crystalline NiOx. Both must be optimized to ensure that this is the best parameter for this solution as it may have differed from our previous study²⁸, but was the same. The best condition is 300°C for 1 minute annealing on a hot plate to yield the best NiOx electrocatalyst.

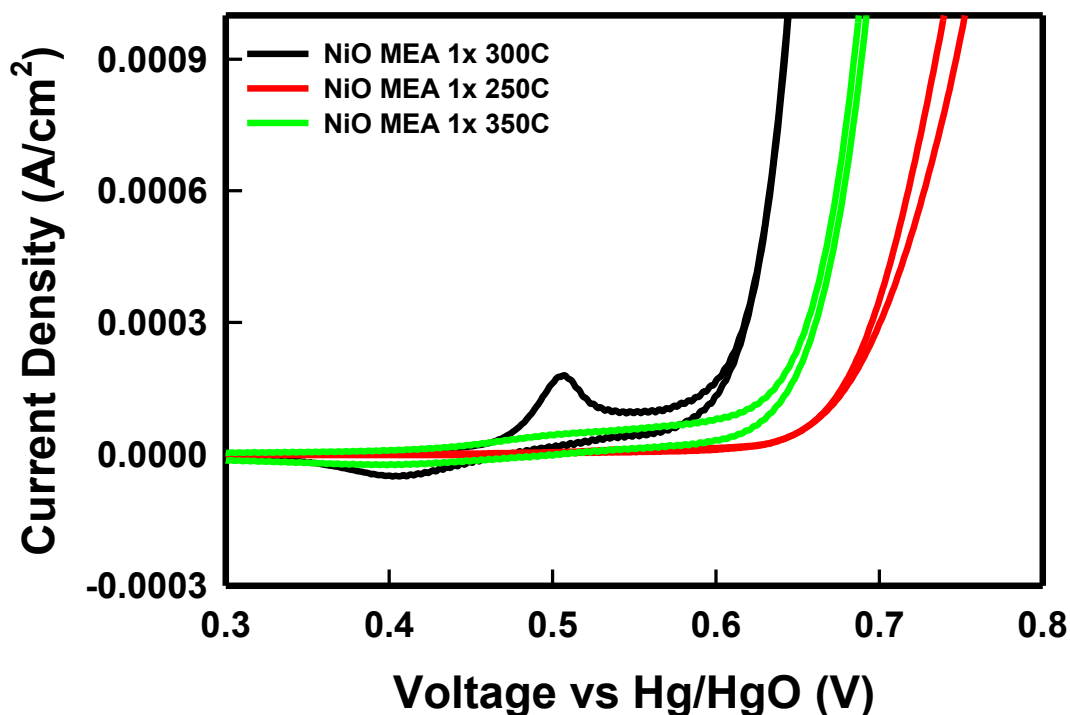


Figure 7. CV of NiOx with MEA at 250C, 300C, and 350C

3.2 Triton X and MEA surfactant CV comparison

The CV scans, shown in Figure 8, shows the potential, in volts, versus the current density, in A/cm^2 , of all the different NiOx with different surfactants and without. The bare sample of FTO only shows no significant current at this range and does not contribute to the NiOx current. This also shows that no significant current exchange happens with the ions in the electrolyte at this range as well. The NiOx only sample acts as our base and already shows good activation, just a couple CV scans to reach peak performance, as well as an onset potential of 1.63V vs. RHE to get a current

density of $5 \times 10^{-4} \text{ A/cm}^2$. With the addition of 1x concentration of Triton X 100 the potential did not change, but the slope of the current density changed which will affect the Tafel slope which will be discussed later in the paper. With the addition of 1x concentration of MEA the potential shifted to 1.61V vs. RHE as well as a slight current density increase. With these improvements due to the addition of a small amount of the surfactant we wanted to try higher concentrations to see if we would continue to see improved performance. The 10x concentration of Triton X 100 showed significantly decrease in performance as it was almost comparable to the bare FTO sample showing very little catalytic activity and no onset potential in this range. The reasons behind this will be looked into further detail in the analysis portion. The 10x concentration of MEA though, showed increased performance compared to the 1x concentration shifting the onset potential even lower to 1.59V with similar current density to the 1x concentration of MEA. With these results in mind, we decided to look into varying the concentrations of MEA to find the optimal condition and cease any further investigation of Triton X 100 as further addition of it caused decreased performance and adding a smaller amount would yield it closer to NiOx only.

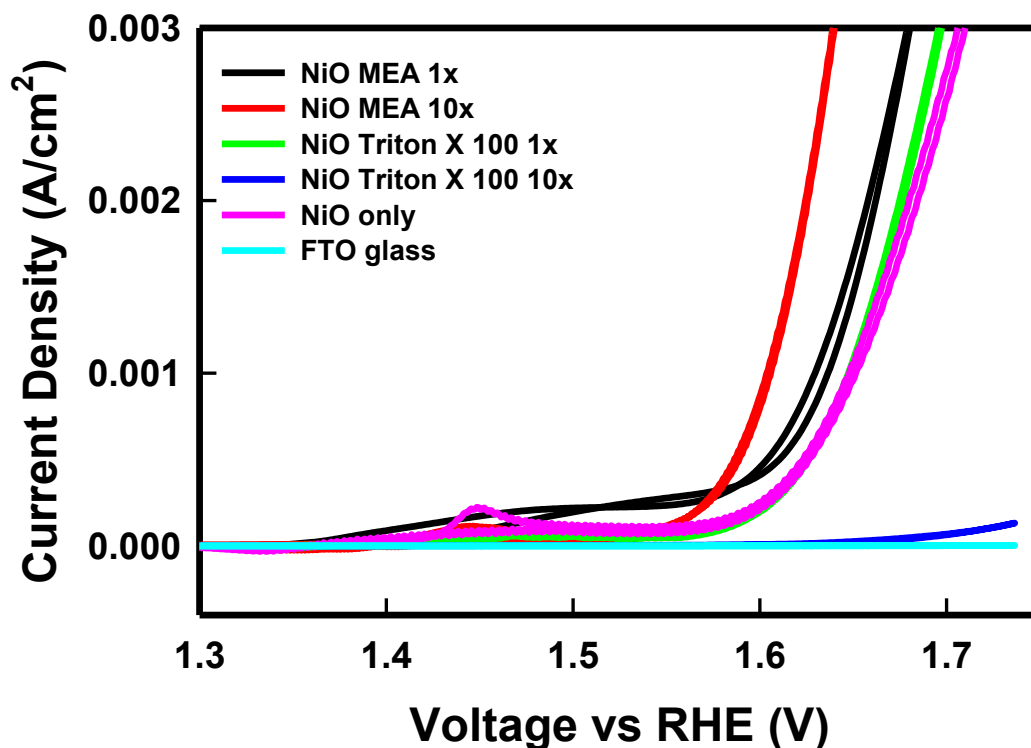


Figure 8. CV scans of 1x and 10x concentrations of Triton X and MEA compared with NiOx.

3.3 CV measurements and comparison of 1,5,10,20x MEA

After finding the optimal temperature and time conditions for NiOx, we decided to find the optimal amount of MEA needed for NiOx. We show the CV scans of concentrations of 1,5,10,20x of MEA in Figure 9 below. From the data shown we can see that the 10x concentration performs the best in terms of onset potential shift as it has the lowest onset potential. The current density slopes did not increase between concentrations, but stayed constant after adding in 1x concentration of MEA. The data showed decrease in

overpotential with increasing concentration up to a certain concentration. This concentration saturated after 10x as the 20x concentration of MEA showed decrease performance of MEA by increasing the onset potential. This showed that with increasing concentrations of MEA you expect to see increase in performance, a decrease in onset potential, until saturation is reached at 10x. After this saturation any additional MEA will decrease the performance of NiOx by having increased onset potential.

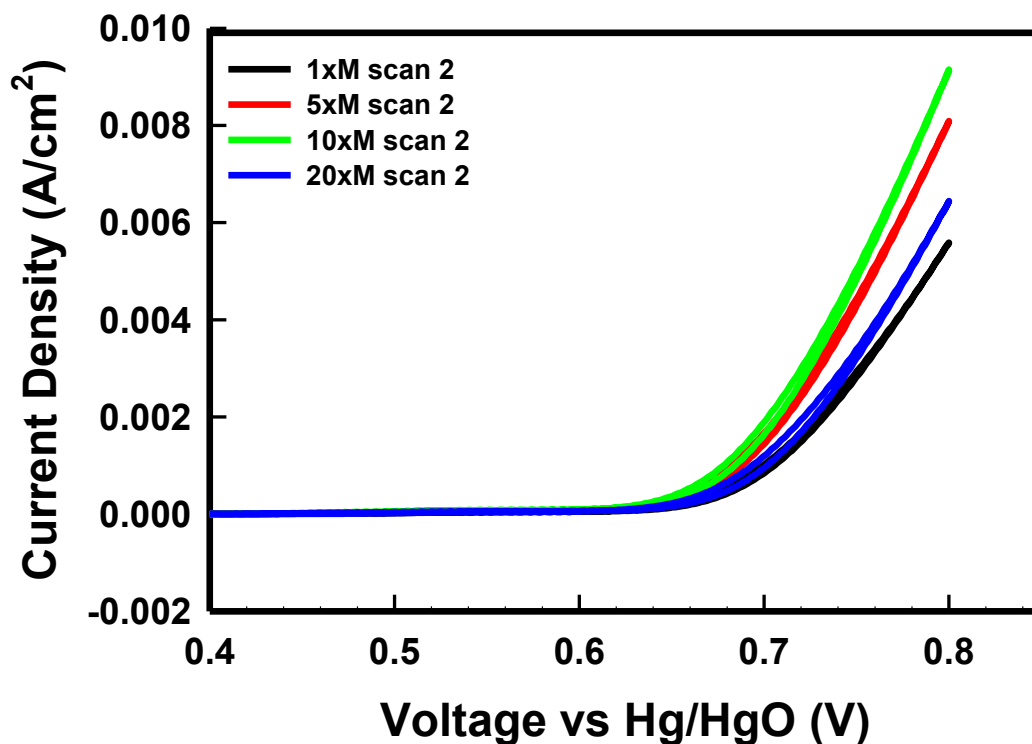


Figure 9. CV of NiOx with different varying concentrations of MEA. The 20x here shows decreased performance due to the fact that 20x may have less NiOx.

3.4 Stability and Performance of MEA

This overpotential shift was a vital step forward for the NiOx electrocatalyst as just by changing the chemical additive and optimizing its concentration, we were able to increase its performance. We also tested the stability to see if the different concentrations of MEA would also affect this as well.

The stability tests were done by multiple CV scans done at a high scan rate of 100mV/sec. These scans are not an accurate depiction of its performance in terms of potential shift or current density because of the high scan rate, but can show us the trend in its stability.³¹ We determine the stability of NiOx as the point before it starts degrading or loss of current density. This can results from NiOx particles disintegrating³² or losing activity by changing phase³³. From the results in Figure 10 below, we can see the degradation of the current density at 0.8V over different cycles. For the 1x concentration, the current density starts decreasing with more cycles showing the degradation of the NiOx catalyst after 40 cycles. For the 5x concentration, the NiOx starts degrading at around 80 cycles showing a slightly slower decay in current density. With the 10x concentration, the current density is actually still stable and is slightly increasing even after 160 cycles showing a much longer and more stable NiOx than the previous two. The 20x concentration starts degrading around 140 cycles which is higher than the 5x concentration even though it had a higher onset potential earlier. Table 1 shows a summary

of the ranges that the different concentrations of MEA have on the stability of NiOx. This shows that the MEA is also acting as a stabilizing agent, increasing the stability of the NiOx with increase concentration of MEA up to saturation at 10x concentration.

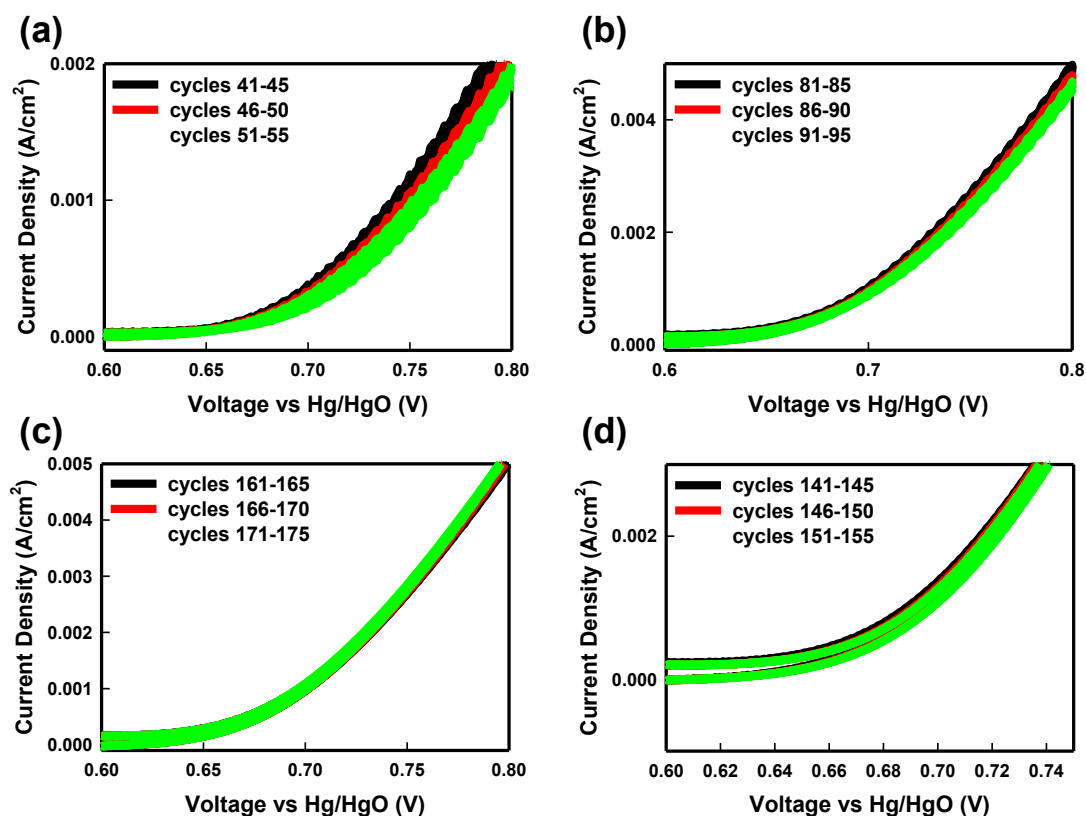


Figure 10. Multiple CV scans showing the stability of each concentration of MEA in NiOx: a.)1x, b.)5x, c.)10x, d.)20x

Table 1. Average cycle stability of varying concentrations of MEA

Solution	Cycles stable
1x MEA	40-60
5x MEA	80-100
10x MEA	160-200
20x MEA	120-140

3.5 Tafel Slope Analysis

The Tafel slope is an indication of the performance of a catalyst is in terms of how much voltage supplied can change a decade of current at the region of activation.³⁴ A Tafel plot, of overpotential versus the log of the current density, is shown below in Figure 10. The change in the voltage values shown on the graph is due to the fact that we are now showing the overpotential. The overpotential is the difference between the thermodynamic potential of water oxidation, which is 0.41 Volts^{35,36}, and the potential under which our experiments were observed. The region in which we calculated the slope for the NiOx catalysts are actually from the voltage values between 0.6 and 0.76 Volts from Figure 9, for the MEA portion.

From the plot we can see that NiOx only has the highest slope, meaning it takes more voltage to change a decade of current leading to a decrease in catalytic performance. The increase of surfactant had no change

on the Tafel slope after the initial amount added. This may be due to the fact that with the addition of these surfactants the chemical composition of the precursor changes to allow the formation of a NiOx with better electron transport as it cleans the surface of the FTO glass for better contact. This means that having a small amount in the solution, no matter what the concentration, is enough to clean the surface for better contact for charge transfer increasing the current density.³⁷

From Table 2, we can see the exact numbers we calculated from the plot. Here, we also compared to other group's work on NiOx catalyst as well as other catalysts to compare just the Tafel slope performance. We can see that the rare metals, Pt³⁸ and RuO₂¹⁴, perform better than our NiOx, as expected, as they are known to be the best, but we had improvement in getting NiOx closer to the level of rare metals. For some other NiOx we see that doping had a huge effect in increasing the Tafel slope which we hope to do later after optimizing our NiOx by doping it with Iron and Cobalt, to get 40mV/dec.³⁹ The other pure NiOx²¹ with a 29 mV/dec looks like it should be amazing, but what the slope doesn't tell is how much energy they put into getting that slope. They ran their NiOx for 1 hour running 10mA/cm² of current to get this slope equating to a huge power input to get this huge improvement in slope which is not what we are looking to do. The last NiOx⁴⁰ was comparable as they had similar activation to our method of running a few CV scans. As we can see, our NiOx had a decrease of about 35 mV/dec in the

Tafel slope. This concludes that our NiOx would need 35 mV less to change a decade of current leading to a better overall electrocatalyst.

Tafel Plot

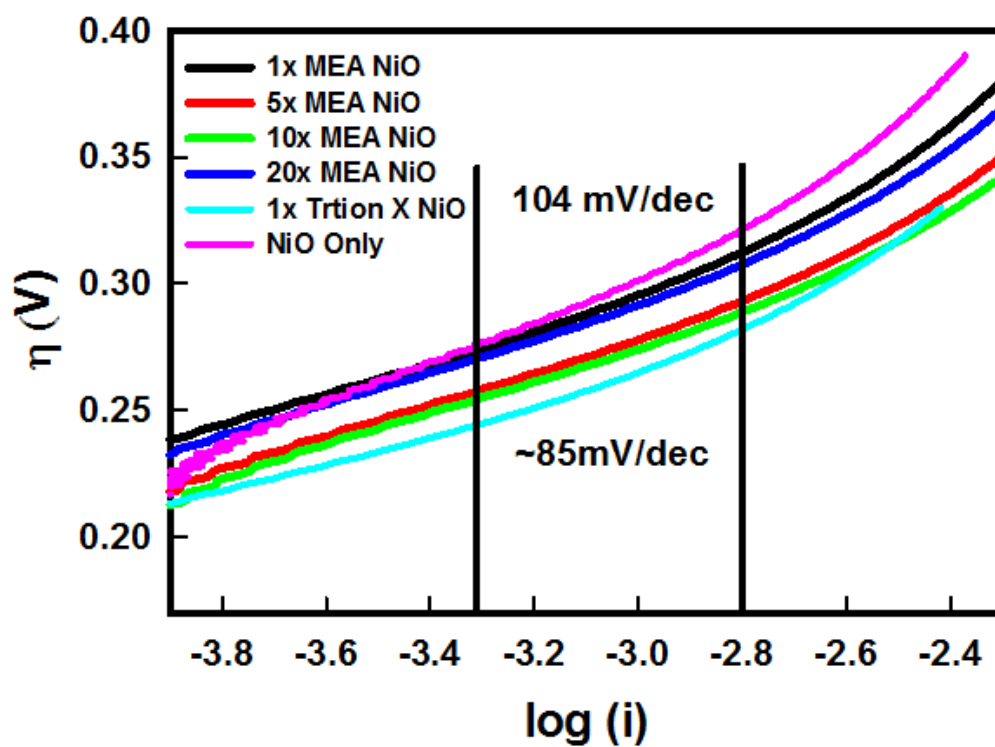


Figure 11. Tafel Plot of log current versus the potential (V)

Table 2. Tafel slope of catalysts,

Catalyst	Tafel Slope (mV/dec)	Catalyst (other work)	Tafel Slope (mV/dec)
NiO only	104	$\text{Fe}_{40}\text{CO}_{40}\text{Ni}_{20}\text{Ox}$	40
Tirton X 1x	87	NiO	29
MEA 1x	83	NiO	120
MEA 5x	86	Pt	50
MEA 10x	84	RuO_2	55
MEA 20x	85		

3.6 MEA and Triton X 100 Analysis

In order to gain a better understanding of the mechanism behind MEA in NiOx we conducted a series of tests to gain some insight. We started by identifying the morphology to see if there is any change from the addition of a surfactant. We decided to take Scanning Electron Microscope (SEM) images , shown in Figure 12. It is unclear to see any type of morphology change on FTO glass due to its surface roughness. There is some difference between each sample taken on FTO, but nothing definitive to show the structure of the NiOx. We speculate that our NiOx has a thickness of about 5 nm as we use similar conditions to those in ref 20. With a thickness this small, SEM didn't seem like a wise choice to see small differences between them and instead moved on to different analytical device.

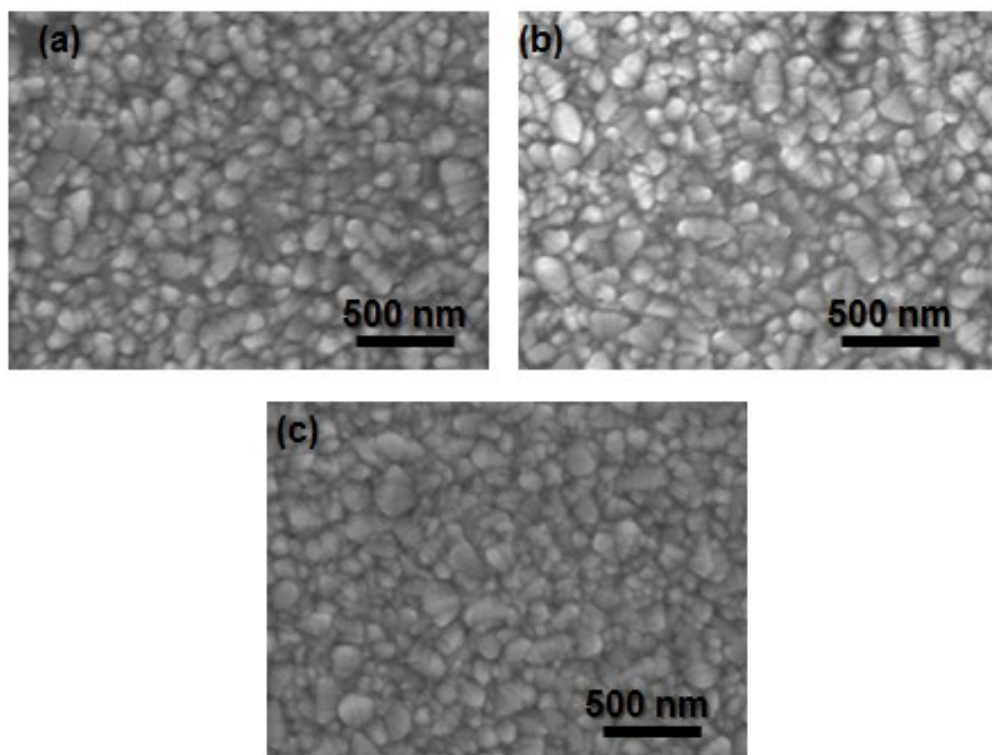


Figure 12. SEM pictures of: a.) NiOx 10x MEA, b.) NiOx 10x Triton X, c.) FTO glass.

Since SEM wasn't a good choice to see the morphology the next step was to try Atomic Force Microscopy (AFM) on atomically flat 001 Silicon substrate. The annealing condition for this substrate was reduced to 30 seconds as this was equivalent to 1 minute on FTO from a previous study²⁸ we performed. The results of the AFM images show that with the addition of Triton X 100 there is a morphology change on the surface of the Si compared to that of NiOx shown in Figure 11 below. We can see that there are a lot of small particles and a lot higher distribution of these small particles for the Triton X 100 sample. It is hard to say if that is all NiOx or some organic

residues that may have been left over which will be discussed in the XPS results. The MEA, on the other hand, has no morphology change on the NiOx as we can see that even in the 10x concentration of MEA that the particle sizes are still roughly the same with a radius of about 80nm. It does not increase the area or number of particles even with increasing concentration of MEA added to the solution. This gives conclusive evidence that the MEA surfactant does not affect the surface area and morphology of the NiOx. This concludes that the increase in performance due to the MEA doesn't not come from a physical change in the NiOx particles or increase coverage on the substrate.

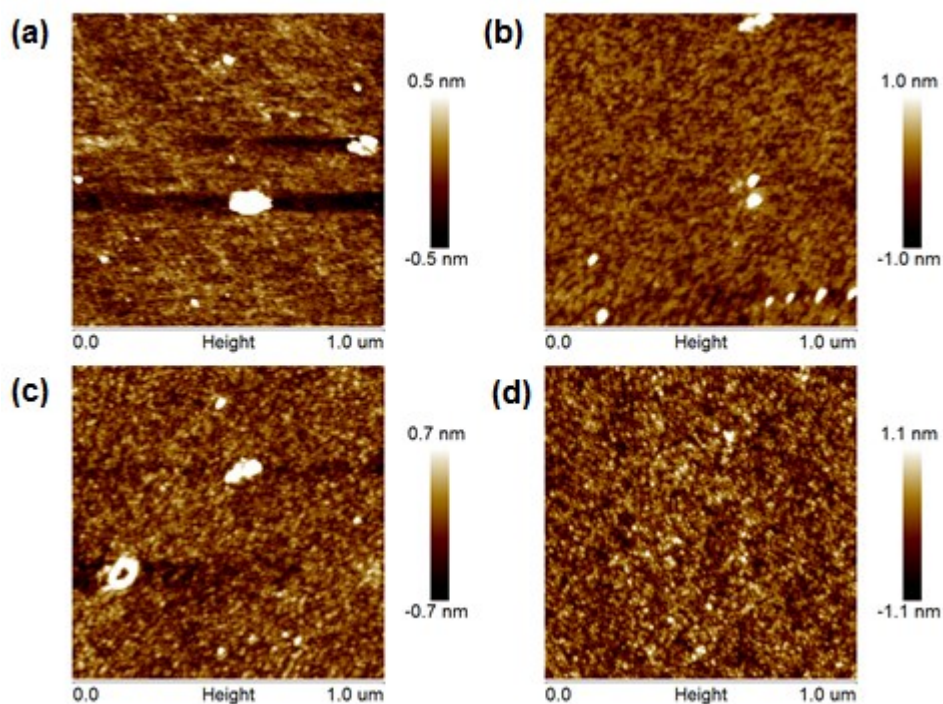


Figure 13. AFM images of: a.) NiOx only, b.) NiOx 10x MEA, c.) NiOx 1x MEA, d.) NiOx 1x Triton X.

Since, there is no sign of a morphology change we decided to examine any sign of chemical change in the NiOx. To do so, we decided to use X-ray Photoelectron Spectroscopy (XPS) to determine the chemical composition after annealing shown in Figure 14. XPS would help us is to determine the elements that could be contaminating the surface as well as the Nickel states that will appear. In Figure 14 a, we can see the Nickel 2p $3/2$ peaks corresponding to the binding energy from 850 eV to 860 eV and the Nickel 2p $1/2$ peaks corresponding to the binding energy from 870 eV to 880 eV, with the second smaller peak being a satellite peak. These satellite peaks are due to the X-ray source emitting X-rays of higher photon energy causing ionization of the Nickel, thus resulting in the small peak afterwards. The Nickel also has a doublet state indicating we have Nickel in both of those states as shown. These Nickel 2p peaks could originate from Ni^{2+} species, such as partially decomposed nickel acetate-surfactant complexes, $\text{Ni}(\text{OH})_2$ or NiOx.

We can also see this from the Oxygen 1s, Figure 14c, that the NiOx only sample has a broad range of oxygen that could be present. As we increase the concentration of surfactant though, we observed that the Oxygen peaks and Nickel peaks both became sharper. These peaks indicated a trend toward the formation of NiOx, instead of other Nickel complexes.

From the Carbon 1s data shown in Figure 14b, we can see there was also a slight change in the carbon peaks as with low concentration of surfactant we see a small carbon peak, at 288.3 eV, which we believed were

due to acetate capping^{41,42} of the NiOx, from the interaction of small amount of surfactant with Nickel Acetate from our previous study. The 10 x concentrations of the surfactant changed completely as the MEA showed fully decomposed Acetate with no extra carbon peaks leading to no carbon contamination. On the other hand, we can see that the Triton X 100 has a significant carbon peak, at 286.4 eV, which corresponds to an undecomposed Triton X 100 surfactant⁴³ which would explain why the CV results, mentioned earlier, showed poor performance as even in the presence of NiOx, these Carbon contaminations are inhibiting its performance.

Together, this data shows that the 10x MEA has a good NiOx formation with The Nickel peak at 856.2 eV and the oxygen peak as 532.1 eV indicating an increase in a single nickel state and an increase in a single oxygen state leading to a NiOx state. Also, that MEA has no carbon contamination with higher concentration with one possibility that the MEA interacts with the Nickel more removing the acetate groups and thereby stopping the acetate capping as it gets removed from the Nickel complex. Even though the Nickel concentration is less, we can see that by having a cleaner NiOx formation has led to a better electrocatalyst performance.

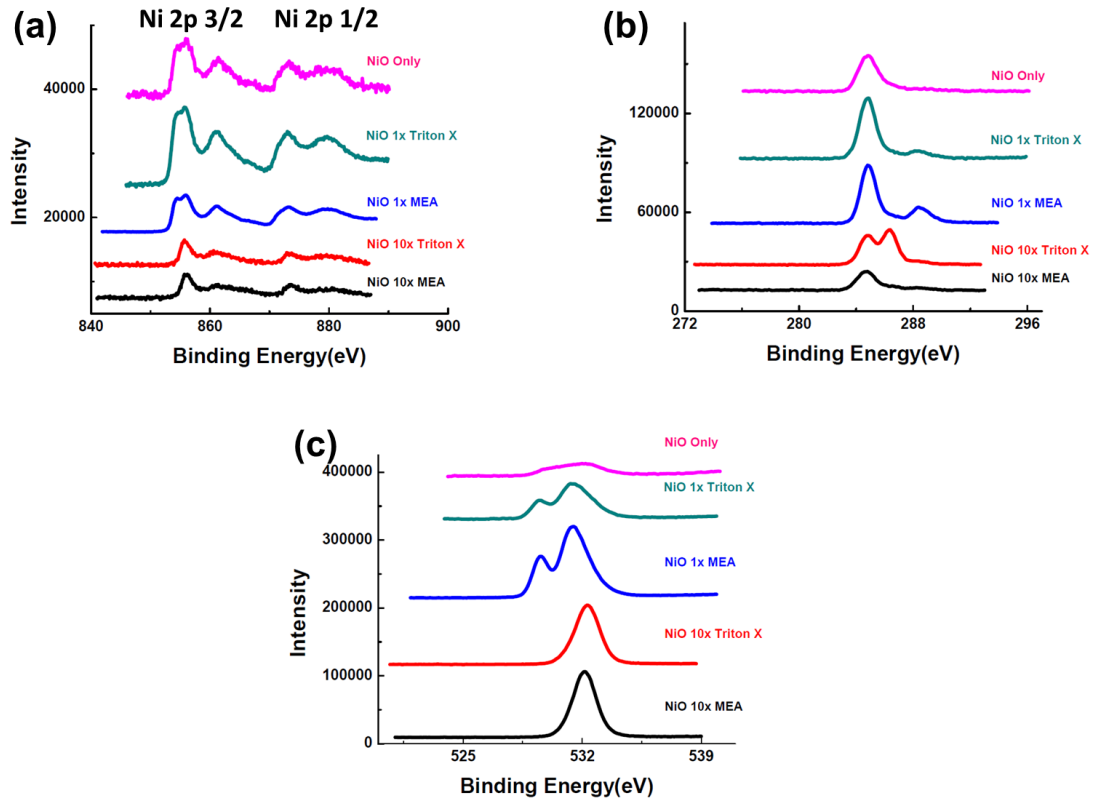


Figure 14. XPS peaks of the: a.) Nickel, b.) Carbon, c.) Oxygen.

XPS was fairly convincing to see that there was a chemical composition change due to the different surfactants after annealing. It does help to identify some type of mechanism between the MEA with the Nickel Acetate complex post annealing. Unfortunately, it doesn't tell us anything about the chemical composition in the precursor solution state. In order to see any change, we did a Fourier Transform Infrared Spectroscopy (FTIR) to determine the bonds and see if any type of covalent bonding occurred between the MEA and Nickel Acetate precursor. From Figure 15, we can see the different FTIR peaks and in Table 3 the corresponding bonds associated with those peaks. All the peaks

were measured with an ethanol background to help see the smaller differences in chemical bonds and compared using this reference⁴⁴. Not all the peaks perfectly align to match the indicated values in table 3. For instance, the 1400 peak can correspond to a shift in the C=O from 1600 to the 1400 as we can see from the Nickel Powder there is a strong peak here relating to the Acetate group. The 1574 peak corresponds to the C-O bond in the Acetate group, the 1656 peak corresponds to the C-C bonding in MEA, the 3154 peak corresponds to the O-H bonding in MEA, and the 3416 peak corresponds to the N-H bonding in MEA. These FTIR results were done running an ethanol background except for the powder. Not all the peaks are accounted for as below 1400 the peaks become less unique and become harder to distinguish losing some of the bonds that are weaker in energy or having a lower wavenumber. Judging by the position and growth of the peaks, we can clearly see that the ones increasing are the three peaks corresponding to the addition of more MEA. Therefore, we have no indication of any different bonding as the peaks that increase directly correlates to each of the peak in the MEA + Ethanol solution. This goes to tell us that there is no visible covalent bonding in this region, but some other mechanism driving the MEA to help shift the overpotential of FTO glass.

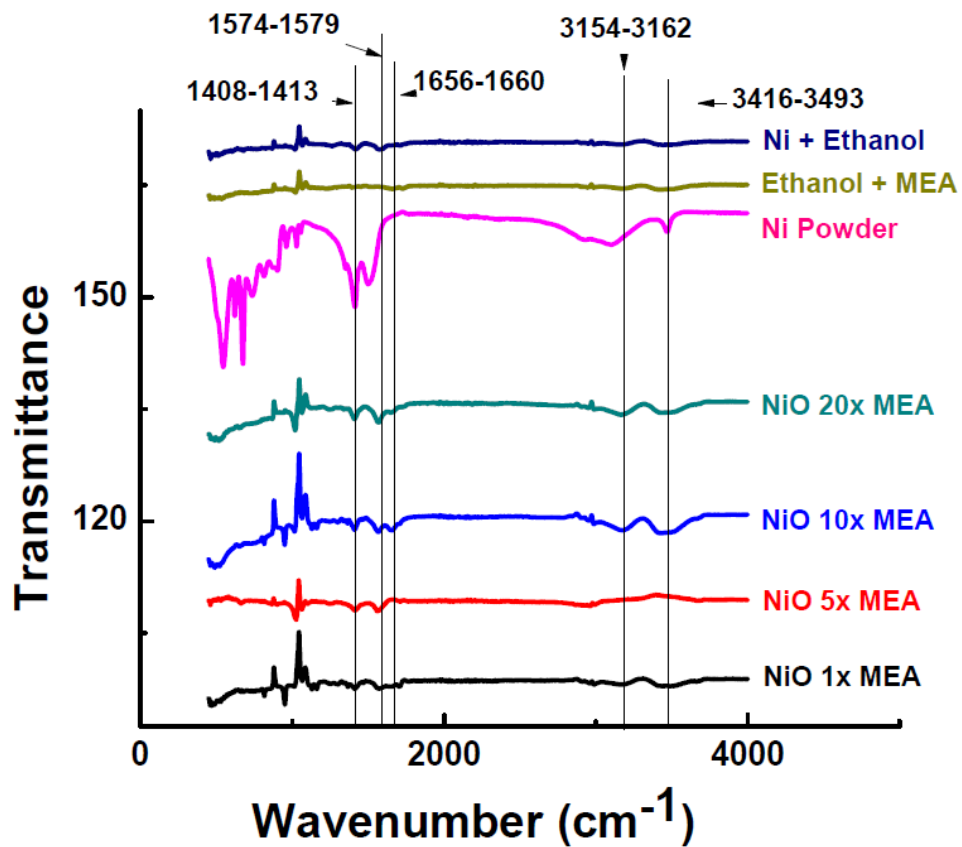


Figure 15. FTIR results with peaks mapped out at what wavenumber position.

Table 3. Corresponding bond to wavenumber showing all possible bonds.

Bond	Type of Bond	Specific	Absorption
C-O	alcohol	Primary	1040-1060 cm^{-1}
C-N	Aliphatic Amine	Any	1020-1220 cm^{-1}
C-O	Carboxylic Acids	Any	1250–1300 cm^{-1}
C=O	Carboxylic Acids	Carboxylates(salts) (Ni Acetate)	1550-1610 cm^{-1}
C-C	acyclic C—C	alkenes	1645-1670 cm^{-1}
C-H	alkyl	methyl	2960 cm^{-1} (med) 1380 cm^{-1} (weak)
O-H	Alcohols, phenols	high concentration	3200–3400 cm^{-1}
N-H	Primary Amines	Any	3400-3500 cm^{-1}

The type of mechanism that can be speculated from this analysis is that MEA has no morphological change, but some chemical change within the precursor solution. To look more into this, we decided to look into the molar ratio of the MEA to Nickel Acetate as it seems that 10x performs the best and any excess MEA doesn't help improve the NiOx. From table 4. we discovered that a molar ratio of 2:1 of MEA to Nickel Acetate for 10x MEA was the best ratio. The 10x though is over twice the molar ratio of Nickel Acetate, but we can already see it's near the saturation limit because the 20x gets worse with increasing concentration and the 5x is worse with less concentration. This ratio

is important because for each Nickel Acetate there is one Nickel atom surrounded by two acetate groups. This means with a 2:1 ratio of MEA to Nickel Acetate there is actually a 1:1 ratio of MEA to the acetate groups. This could lead to an interaction between MEA and Nickel Acetate in which the MEA could create an ionic bond with Nickel replacing the two acetate groups or binding to the outside of Nickel Acetate surrounding it. One exact possibility is that the MEA is binding to the Nickel during the annealing process as the acetate groups fall off and decompose. Then, MEA can help the Nickel bind to the surface easier when forming Nickel Oxide. Thereby, reducing the surface tension or helping the electron transport to reduce the overpotential causing a shift in the voltage to decrease.

Table 4. Concentration of elements.

Chemical	Concentration (M)
Nickel Acetate	0.05
MEA 1x	0.012
MEA 5x	0.06
MEA 10x	0.12
MEA 20x	0.24

Conclusion

Here we have demonstrated a deeper understanding of trying to improve NiOx electrocatalyst through chemical additives in the precursor solution. These additives play an important role in NiOx as they can change its morphology, overpotential shift, catalytic activity, and stability. With the introduction of MEA into the system we were able to see an increase in overpotential shift as well as an increase in the catalyst activity. The changes due to the increase of concentration of MEA shows that there is some chemical saturation limit in which MEA can help increase the NiOx performance. The best concentration of MEA turned out to be 10x which also had a molar ratio of almost 2:1 of MEA to Nickel Acetate. These changes are important to understand before doping as this can lead to an even better metal oxide catalyst. This work was unable to completely solve the mechanism behind the MEA and Nickel Acetate to improve the onset potential. However, by understanding how each additive can change the behavior of the NiOx catalyst, we can take advantage of the solution grown method by having many combinations of additives to achieve a perfect NiOx catalyst that can have increased surface area, high catalytic activity, and better onset potential.

References

1. How much Sunlight hits the Earth. 1 (2006). at <http://www.ecoworld.com/energy-fuels/how-much-solar-energy-hits-earth.html>
2. Eenergiläget in Sweden 2011 figure 49 and 53. in
3. Rappaport, B. P. The Photovoltaic Effect and its Utilization*. (1959).
4. Crabtree, G. W., Dresselhaus, M. S. & Buchanan, M. V. The Hydrogen Economy. *Phys. Today* **57**, 39 (2004).
5. Edwards, P. P., Kuznetsov, V. L., David, W. I. F. & Brandon, N. P. Hydrogen and fuel cells: Towards a sustainable energy future. *Energy Policy* **36**, 4356–4362 (2008).
6. Gr, M. Photoelectrochemical cells. **414**, (2001).
7. Johnston, B., Mayo, M. C. & Khare, A. Hydrogen: the energy source for the 21st century. *Technovation* **25**, 569–585 (2005).
8. Heller, A. Conversion of Sunlight into Electrical Power and Photoassisted Electrolysis of Water in Photoelectrochemical. 154–162 (1981).
9. Photocatalytic Water Splitting « 中国科学院物理研究所太阳能材料与器件研究组 . at http://solar.iphy.ac.cn/?page_id=1775&lang=en
10. Debe, M. K. Electrocatalyst approaches and challenges for automotive fuel cells. *Nature* **486**, 43–51 (2012).
11. Benea, L., Luigi, P., Borello, A. & Martelli, S. Wear corrosion properties of nano-structured SiC – nickel composite coatings obtained by electroplating. **249**, 995–1003 (2002).
12. Adzic, R. R. *et al.* Platinum Monolayer Fuel Cell Electrocatalysts. *Top. Catal.* **46**, 249–262 (2007).
13. Electrocatalytic oxygen evolution on iridium oxide films.pdf.
14. Lee, J.-W. & Popov, B. N. Ruthenium-based electrocatalysts for oxygen reduction reaction—a review. *J. Solid State Electrochem.* **11**, 1355–1364 (2007).

15. Du, P. & Eisenberg, R. Catalysts made of earth-abundant elements (Co, Ni, Fe) for water splitting: Recent progress and future challenges. *Energy Environ. Sci.* **5**, 6012 (2012).
16. Pang, S.-C., Anderson, M. a. & Chapman, T. W. Novel Electrode Materials for Thin-Film Ultracapacitors: Comparison of Electrochemical Properties of Sol-Gel-Derived and Electrodeposited Manganese Dioxide. *J. Electrochem. Soc.* **147**, 444 (2000).
17. Wang, X., Luo, H., Parkhutik, P. ., Millan, A.-C. & Matveeva, E. Studies of the performance of nanostructural multiphase nickel hydroxide. *J. Power Sources* **115**, 153–160 (2003).
18. Al-Ghamdi, a. a., Mahmoud, W. E., Yaghmour, S. J. & Al-Marzouki, F. M. Structure and optical properties of nanocrystalline NiO thin film synthesized by sol-gel spin-coating method. *J. Alloys Compd.* **486**, 9–13 (2009).
19. Miiier, E. L. & Rocheleau, R. E. Electrochemical and Electrochromic Behavior of Reactively Sputtered Nickel Oxide. **144**, (1997).
20. Leskelä, M. & Ritala, M. Atomic layer deposition (ALD): from precursors to thin film structures. *Thin Solid Films* **409**, 138–146 (2002).
21. Trotochaud, L., Ranney, J. K., Williams, K. N. & Boettcher, S. W. Solution-cast metal oxide thin film electrocatalysts for oxygen evolution. *J. Am. Chem. Soc.* **134**, 17253–61 (2012).
22. Kluson, P., Kacer, P., Cajthaml, T. & Kalaji, M. Preparation of titania mesoporous materials using a surfactant-mediated sol-gel method. *J. Mater. Chem.* **11**, 644–651 (2001).
23. Engineering, C. Ordered Micelle Structuring in Thin Films Formed from Anionic Surfactant Solutions I. Experimental. **133**, (1989).
24. Paz, Y., Heller, A. & Introduction, I. films on soda lime glass : The deleterious effect of sodium contamination and its prevention. 2759–2766 (1997).
25. Tryk, D. A., Hashimoto, K. & Fujishima, A. Electrochemical Behavior of Highly Conductive Boron-Doped Diamond Electrodes for Oxygen Reduction in Alkaline Solution. **145**, 4–6 (1998).
26. Surendranath, Y., Kanan, M. W. & Nocera, D. G. Mechanistic Studies of the Oxygen Evolution Reaction by a Cobalt-Phosphate Catalyst at Neutral pH. 16501–16509 (2010). doi:10.1021/ja908730h.(45)
27. Cited, L. Theory and Application of Cyclic Voltammetry f m Measurement of Electrode Reaction Kinetics. 1351–1355

28. Sun, K. Nanostructured Metal Oxide enabled Silicon based Solar Fuel Cell. *ProQuest Diss. Theses* 206 (2013). at <http://search.proquest.com/docview/1417988098?accountid=14524>
29. Carnes, C. L., Stipp, J., Klabunde, K. J. & Bonevich, J. Synthesis , Characterization , and Adsorption Studies of Nanocrystalline Copper Oxide and Nickel Oxide. **21**, 1352–1359 (2002).
30. Srinivasan, V. & Weidner, J. W. Studies on the Capacitance of Nickel Oxide Films: Effect of Heating Temperature and Electrolyte Concentration. *J. Electrochem. Soc.* **147**, 880 (2000).
31. Wipf, D. O., Kristensen, E. W., Deakin, M. R. & Wightman, R. M. Fast-scan cyclic voltammetry as a method to measure rapid heterogeneous electron-transfer kinetics. *Anal. Chem.* **60**, 306–310 (1988).
32. Schulze, M. & Gülzow, E. Degradation of nickel anodes in alkaline fuel cells. *J. Power Sources* **127**, 252–263 (2004).
33. Van der Ven, a., Morgan, D., Meng, Y. S. & Ceder, G. Phase Stability of Nickel Hydroxides and Oxyhydroxides. *J. Electrochem. Soc.* **153**, A210 (2006).
34. Gnanamuthu, D. S. & Petrocelli, J. V. A Generalized Expression for the Tafel Slope and the Kinetics of Oxygen Reduction on Noble Metals and Alloys. *J. Electrochem. Soc.* **114**, 1036 (1967).
35. Electrolysis in Aqueous Solutions. **2**, 61–67
36. Surendranath, Y., Dinca, M. & Nocera, D. G. Electrolyte-dependent electrosynthesis and activity of cobalt-based water oxidation catalysts. *J. Am. Chem. Soc.* **131**, 2615–20 (2009).
37. Ohmi, T. Total Room Temperature Wet Cleaning for Si Substrate Surface. *J. Electrochem. Soc.* **143**, 2957 (1996).
38. Walter, M. G. *et al.* Solar water splitting cells. *Chem. Rev.* **110**, 6446–73 (2010).
39. Smith, R. D. L., Prévot, M. S., Fagan, R. D., Trudel, S. & Berlinguette, C. P. Water oxidation catalysis: electrocatalytic response to metal stoichiometry in amorphous metal oxide films containing iron, cobalt, and nickel. *J. Am. Chem. Soc.* **135**, 11580–6 (2013).
40. Sadiq, I. M., Mohammad, A. M., El-Shakre, M. E. & El-Deab, M. S. Electrocatalytic activity of nickel oxide nanoparticles-modified electrodes: Optimization of the loading level and operating pH towards the oxygen evolution reaction. *Int. J. Hydrogen Energy* **37**, 68–77 (2012).

41. Chakroune, N. *et al.* Nanoparticles : XPS , XAS , and HRTEM Studies. 6788–6796 (2005).
42. Comparelli, R. *et al.* UV-induced photocatalytic degradation of azo dyes by organic-capped ZnO nanocrystals immobilized onto substrates. *Appl. Catal. B Environ.* **60**, 1–11 (2005).
43. Sertchook, H. & Avnir, D. Submicron Silica / Polystyrene Composite Particles Prepared by a One-Step Sol - Gel Process. 1690–1694 (2003).
44. Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*. (Wiley, 2004). at
<<http://books.google.com/books?id=LDoAAjMnwEIC>>