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Analyzing the Surface Chemistry of Ni-Fe Hydroxide Alloy Nanoparticles as Catalysts for the Oxygen Evolution Reaction by X-ray Photoelectron Spectroscopy Analysis

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Analyzing the Surface Chemistry of Ni-Fe Hydroxide Alloy Nanoparticles as Catalysts for the Oxygen Evolution Reaction by X-ray Photoelectron Spectroscopy Analysis

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Abstract:

Water electrolysis has been proposed as a renewable source of hydrogen, a possible replacement to harmful fossil fuels. This process can be broken down into two half reactions, the hydrogen evolution reaction and the oxygen evolution reaction. Because the oxygen evolution reaction has slow kinetics and a high overpotential to overcome, a catalyst is needed to speed up the kinetics and ensure faster and more efficient production of molecular hydrogen. The use of Ni-Fe hydroxide alloy nanoparticles as a catalyst has been shown to significantly improve the efficiency of the reaction by decreasing the overpotential, making the process more energy efficient [1]. Although most catalysts for electrochemical reactions degrade over time, past research conducted in the Greenlee Lab at the University of Arkansas has shown that the Ni-Fe catalysts tend to have low degradation and, in some cases, even improvement in the overall activity [1]. This change in overall activity, however, indicates there may be a significant change in the surface chemistry of the nanoparticle during electrocatalysis. In this research, the atomic level changes on the surface of the Ni-Fe catalyst were analyzed by using x-ray photoelectron spectroscopy (XPS) after the potential was cycled. Ultra-high vacuum (UHV)-XPS and near ambient pressure (NAP)-XPS revealed that metallic forms of nickel and iron are present at the surface of the synthesized nanocatalyst but are quickly gone after electrocatalysis, with only more oxidized forms present on the surface after use in the oxygen evolution reaction (OER). The XPS characterization also revealed that the ratio of nickel to iron significantly increases after catalytic use, showing an increase from 1:1 nickel to iron to 7:2 after just one cyclic voltammetry cycle. Overall, the results of this research enable a better understanding of the origins of the durability and increased performance of the catalyst after use in OER.

Keywords: *bimetallic nanoparticles, surface chemistry, oxygen evolution reaction, x-ray photoelectron spectroscopy, oxidation*

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I. Introduction

One of the most challenging issues facing humanity today is the search for a clean energy source with near zero emissions to support our growing economy. As the economy has become more and more reliant on the burning of fossil fuels, such as coal and oil, the amount of carbon in the atmosphere has dramatically increased, leading to the growing crisis of climate change, which has been most dramatically seen within the melting of glaciers in arctic environments. Because of its near zero emissions, hydrogen has been proposed as a possible clean energy source. The most sustainable way of producing this hydrogen is through water electrolysis, or water splitting, which is composed of two half reactions, the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) [1,2,4,8,11,12]. Without the presence of a catalyst, the oxygen evolution reaction has slow kinetics and a high overpotential, meaning the reaction requires a significant amount of energy to get the reaction to begin [1,2,4,8,11,12]. The inefficiency of the OER limits the amount of molecular hydrogen that can be produced, thus making the entire process infeasible for potential large-scale applications.

Most recently, Ni-Fe hydroxide alloy nanoparticles have been introduced as catalysts for the oxygen evolution reaction [1]. On its own, nickel oxyhydroxide (NiOOH) is a poor catalyst but the incorporation of iron into the NiOOH has been correlated to a reduced charge transfer resistance of the electrocatalyst, a higher ionic conductivity, and a faster electron transfer rate, even when present at low concentrations [8,11]. Results from past cyclic voltammetry (CV) experiments have indicated that the Ni-Fe hydroxide catalysts significantly reduce the overpotential and the Tafel slope of the curve, meaning more molecular oxygen, and thus hydrogen, was produced in the reaction [1,2,4,8,11,12]. As the potential was cycled, the electrocatalytic and nickel redox peak behaviors began to shift as the potential during CV testing was cycled [1]. Specifically, the overpotential, which correlates to the amount of energy required to begin the production of oxygen, did not increase significantly with continued catalytic use [1].

This trend in overpotential is quite strange when the data is compared to the long-term effects of electrochemical testing on other catalysts. The usual trend shows a steady decrease in the performance of the catalyst, especially when it comes to the overpotential of the CV, meaning the catalyst is degrading and the number of active sites is decreasing with use.

Because the Ni-Fe hydroxide nanoparticles have been shown to not break down over time, this catalyst is a promising material to potentially implement into the energy field. This promising performance drives the motivation to understand the mechanism behind the changes observed in the CVs and overpotential. The Ni-Fe hydroxide alloy nanoparticle's shift in catalytic ability of the material over time is a possible indication of a shift in the surface chemistry due to continual use for the OER. For the Ni-Fe bimetallic nanoparticles to become a feasible option for industry use in the energy field, it is important to understand the chemical makeup of the surface of the nanoparticle catalyst over time so the change in the effectiveness of the catalyst with use can be determined.

X-ray photoelectron spectroscopy (XPS) is an optimal characterization method because XPS is a surface-sensitive technique and can distinguish element-specific changes to chemistry, such as oxidation state and speciation. UHV is the traditional method of XPS characterization, but it has some severe drawbacks, which has warranted further study of the materials in NAP-XPS [10]. The ultra-high vacuum condition dries out the sample, removing any absorbed, liquid molecules on the surface [10]. Because of this, UHV does not provide a realistic, accurate depiction of the surface chemistry [10]. NAP, on the other hand, is done at near ambient conditions, providing a more accurate surface chemistry of the material in a water environment [10].

Using XPS characterization, a past series of experiments showed that there is a transformation of metallic Fe and Ni to more oxidized states, suggesting an increase of hydroxides, which explains the decrease in overpotential after continual cycling in cyclic voltammetry [2,4]. The presence of hydroxyl groups has been shown to make the material more

hydrophilic and aid in the transportation of oxygen to the catalyst active sites [8]. However, these experiments were conducted with Ni-Fe hydroxide films instead of nanoparticles. The effects due to the cycling of potential during OER may yield different surface chemistry changes for Ni-Fe hydroxide alloy nanoparticles than what was observed with the films, thus motivating this research. The findings of this research will yield a greater understanding of these Ni-Fe nanoparticle catalysts, thus supporting a scalable catalyst material that may eventually be implemented for hydrogen production via water electrolysis.

II. Experimental Methods

Synthesis of Ni-Fe hydroxide Alloy Nanoparticles. As previously described, a synthesis procedure, which is outlined in Figure 1, had already been developed through previous research conducted within the Greenlee Lab [1]. This procedure was replicated and then used to produce the Ni-Fe hydroxide alloy nanoparticles with a 1:1 nickel to iron ratio.
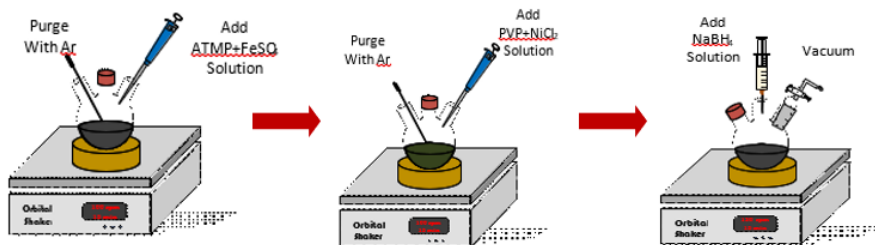

Figure 1. Schematic showing the synthesis procedure of the Ni-Fe bimetallic nanoparticles, created by the Greenlee Research Group.

To produce 20 mL of 1 g/L 50% Fe-Ni bimetallic nanoparticles, a solution of 99.64 mg $FeSO_4 \cdot 7H_2O$ and 0.2 mL of 203.6 g/L amino tri(methylene phosphate) in 3.8 mL of water was added to a three-necked flask. The flask was then shaken on an orbital shaker and bubbled with argon for 15 minutes at 100 rpm. A nickel solution composed of 85 mg $NiCl_2 \cdot 6H_2O$, 72 mg of 107.5 g/L poly(vinyl pyrrolidone) (PVP) and 10 mL water was added to the flask next and then bubbled and shaken again for 10 minutes at 100 rpm. Following this step, 65 mg of $NaBH_4$ was added to 6 mL of water and then added to the flask dropwise over a 2-minute time interval using

a syringe while the flask rested on a shaker at 120 rpm. The final solution was shaken under

vacuum for 15 minutes and finally washed with water and methanol, respectively.

Cyclic Voltammetry. For the cyclic voltammetry tests, a three-electrode system, seen in

Figure 2, was used with a reference electrode, an Ag/AgCl counter electrode, and a gold wafer

electrode on which a small amount of the catalyst ink was drop-casted. The catalyst ink was

prepared by mixing 500 μL of the nanoparticle solution with 167 μL of ionomer. 100 μL of the

catalyst ink was drop-casted onto the gold wafer.

Three gold wafer electrodes were prepared, and cyclic voltammetry was performed to

determine the materials catalytic performance in OER in a 1 M potassium hydroxide solution.

For one gold wafer electrode, no cyclic voltammetry testing was done. For the second, the

potential was cycled once during the cyclic voltammetry testing to determine any surface

chemistry changes that occur in the material with initial catalytic use. Finally, for the third

electrode, the potential was cycled ten times. Figure 3 shows the three gold wafer, catalyst

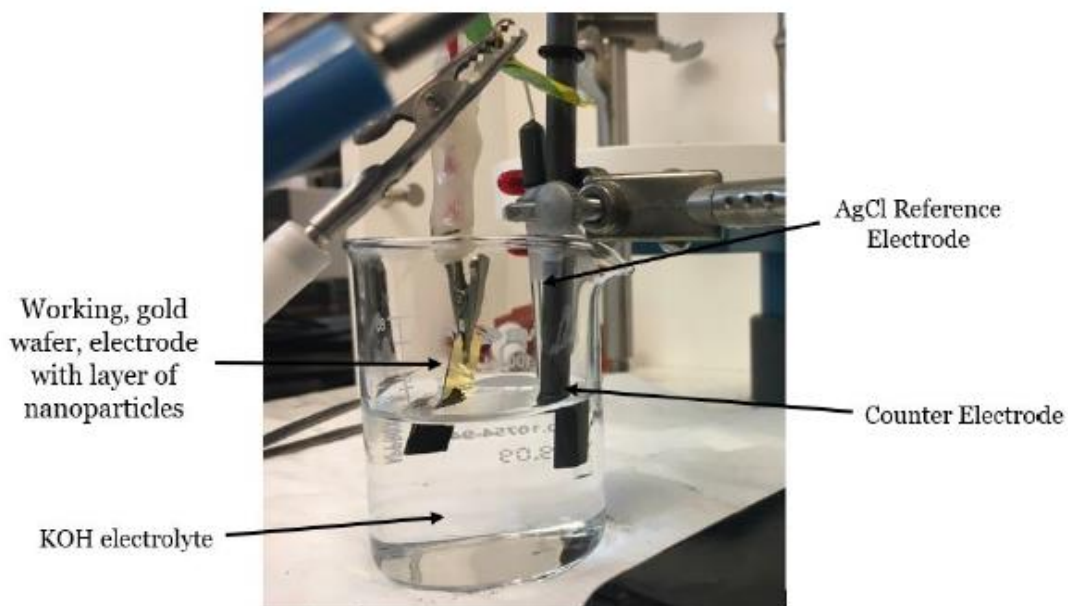deposited electrode samples that were used for XPS characterization.

Figure 2. Image of the electrochemical cell during the cyclic
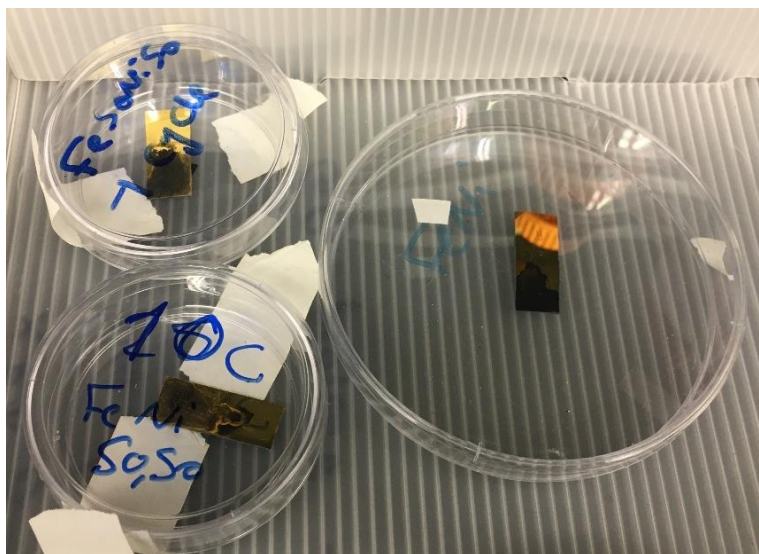voltammetry testing

Figure 3. Image of the catalyst samples after cyclic voltammetry testing; these three samples next underwent XPS characterization

X-ray Photoelectron Spectroscopy (XPS) Measurements. Two types of XPS data, survey and high-resolution spectra, were collected. The survey XPS data were used to determine the percent composition of each atom at the nanoparticle surface, and the high-resolution XPS data (e.g., of Ni 2p, Fe 2p, and O 1s binding energy regions) were used to detect changes in the oxidation state and chemical speciation of the element (from metallic to oxidized for example). Two different XPS methods were also used to analyze the samples: ultra-high vacuum XPS (UHV-XPS) and near ambient pressure XPS (NAP-XPS). The UHV-XPS measurements were conducted in a VersaProbe station from Physical Electronics (PHI) at the University of Arkansas, and the NAP-XPS data was collected by the SPECS Surface Nano Analysis GmbH, Enviro Analytical Instruments GmbH and SPECSGROUP (Germany). During the NAP-XPS data collection, the catalyst sample was surrounded by a 5 mbar water vapor environment. Figure 4 below shows an image of the gold wafer electrode with drop-casted catalyst ink undergoing NAP-XPS characterization.
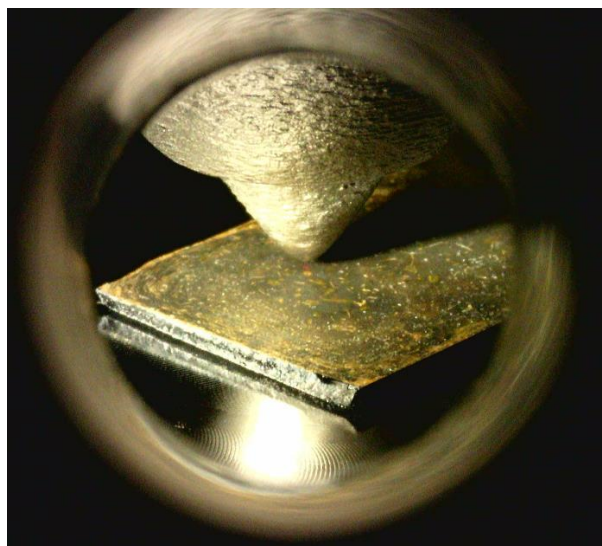
Figure 4. Image of sample during NAP-XPS characterization.

All of this complex XPS data was analyzed using a software called CasaXPS, which has

an embedded library of peak locations and parameters for many metals for use during analysis

[6]. A Shirley background was applied to the data and the carbon 1s peak was used for

reference to account for peak shifting due to charge on the surface of the material. Analysis of

high resolution spectra for transition metals is challenging because of the peak asymmetries,

multiplet peak splitting into the Fe/Ni 2p 1/2 and Fe/Ni 2p 3/2 peaks, and uncertain and

overlapping peak binding energy positions, so published literature and XPS manuals, including

peak position and geometry were used for qualitative analysis across samples [3,5,8]. Figure 5

below shows the binding energies for various oxidation states of Fe 2p 3/2 and Ni 2p 3/2 in XPS

analysis from the "Handbook of X-ray Photoelectron Spectroscopy" that was helpful in

determining the oxidation states of the nickel and iron atoms at the surface of the Ni-Fe

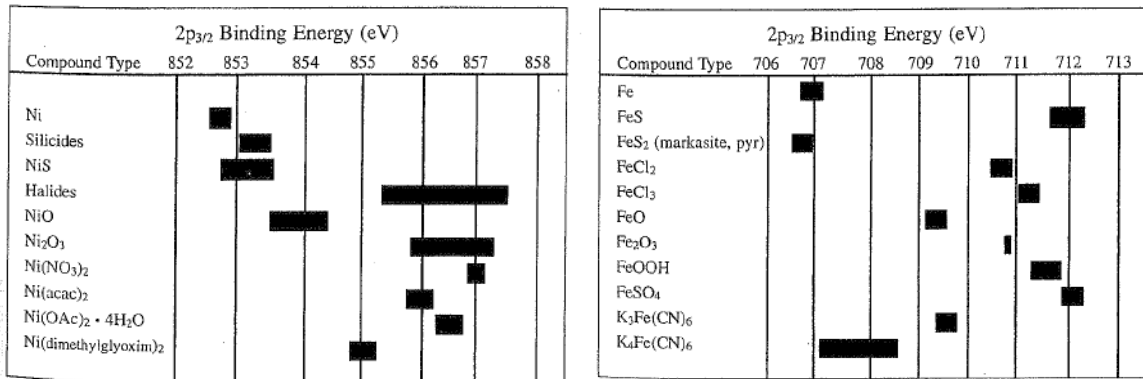hydroxide alloy nanoparticle samples [5].

2p$_{3/2}$ Binding Energy (eV)								2p$_{3/2}$ Binding Energy (eV)							
Compound Type	852	853	854	855	856	857	858	Compound Type	706	707	708	709	710	711	712	713
Ni								Fe								
Silicides								FeS								
NiS								FeS$_2$ (markasite, pyr)								
Halides								FeCl$_2$								
NiO								FeCl$_3$								
Ni$_2$O$_3$								FeO								
Ni(NO$_3$)$_2$								Fe$_2$O$_3$								
Ni(acac)$_2$								FeOOH								
Ni(OAc)$_2$ · 4H$_2$O								FeSO$_4$								
Ni(dimethylglyoxim)$_2$								K$_3$Fe(CN)$_6$								
								K$_4$Fe(CN)$_6$								

Figure 5. Binding energy peak locations to distinguish oxidation states of Fe 2p and Ni 2p in XPS characterization [5].

III. Results and Discussion

Cyclic Voltammetry Data. Figure 6 below is the CV linear sweep data collected over ten cycles of the potential. When analyzing CV data, the most important feature of the data to look for is the onset potential, which is the overpotential at which a current density of 10 mA/cm^2 is obtained. Visually, the onset potential corresponds to the overpotential (x-axis) at which the current density begins to slope upward. As stated earlier, the lower the onset potential of the material, the less energy that is required to begin the production of oxygen, and thus hydrogen. For this research, the CV data was used to qualitatively ensure that the same catalytic trends seen in previous research was replicated in the catalyst samples that were studied in further XPS surface chemistry analysis.
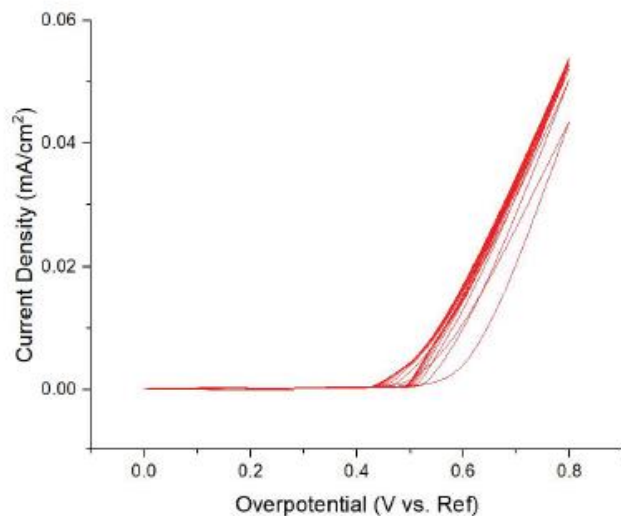
Figure 6. Cyclic voltammetry data collected after the voltage was cycled ten times.

The linear sweep data in Figure 6 shows an initial drop in onset potential after the first cycle but then a relatively constant onset potential for the remaining potential cycles. This trend in CV data collected on the catalyst samples for this research agree with the CV data previously collected by the Greenlee Research Group in Figure 7 below.
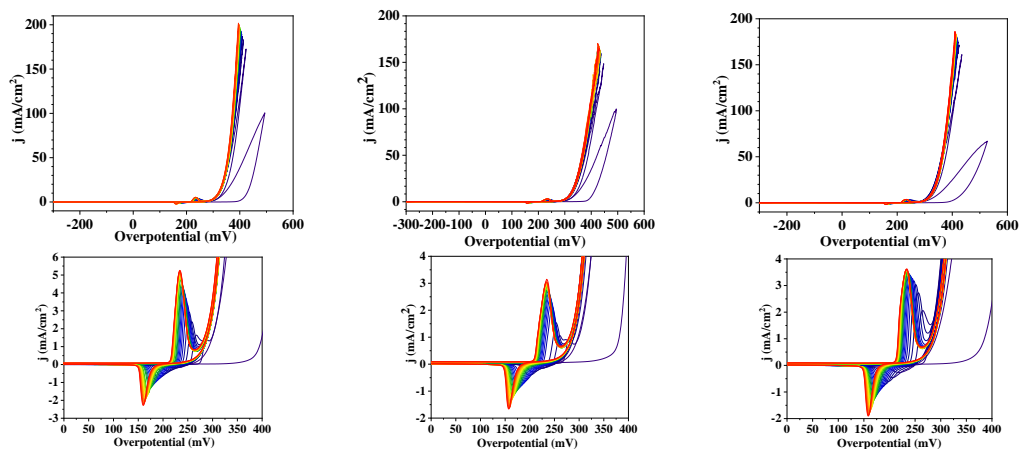

Figure 7. Results of cyclic voltammetry using 25% Fe-Ni bimetallic nanoparticles showing the cycling of potential; each test was run on different days using the same batch of nanoparticles, created by the Greenlee Research Group.

Ultra-High Vacuum XPS Data. The first surface chemistry characterization technique used to study the nanoparticle surface was UHV-XPS at the University of Arkansas. As previously stated, UHV-XPS does not provide the most accurate depiction of the true surface chemistry of the nanoparticle due to the harsh, dry conditions at which the measurements are taken, but UHV-XPS does provide an initial, qualitative understanding of the surface chemistry, which can be compared to the more accurate NAP-XPS technique [9]. Figure 8 below shows the survey and high resolution spectra for the catalyst surface before electrochemistry testing, after one cycle of potential in CV testing, and after ten cycles of potential in CV testing. For the UHV-XPS data, the high resolution nickel 2p and iron 2p peaks after 10 potential cycles in electrochemical testing were not able to be analyzed due to intensity issues, leading to spectra with too much noise to be analyzed accurately.

In the survey spectra, which shows the atomic composition at the surface of the nanocatalyst, an initial 1:1 ratio of Fe 2p to Ni 2p before electrochemistry was calculated, verifying that the synthesis procedure successfully produced the desired atomic composition of the catalyst. After only one cycle of electrochemistry, the ratio of the area of the nickel 2p peak to the area of the iron 2p peak had increased to 7:2. This indicates that the concentration of iron at the surface of the nanoparticle is significantly affected with initial catalytic use in OER. This result also suggests the difference between the first cycle in the CVs of Figure 6 and 7 and subsequent cycles is likely an indication of the change in surface chemistry that is occurring. From the data collected in this research, the reason as to why the iron concentration at the surface of the bimetallic nanocatalyst cannot be concretely determined is due to the technique used. XPS is a technique that just probes the surface of the material before and after electrocatalysis, not during electrocatalysis. Some theories can be proposed, however. One theory for the loss of iron at the surface is that the iron is being lost to the electrolyte during catalysis, but further characterization is needed to support this theory. Recent computational

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work, utilizing Ab Initio Molecular Dynamics, Molecular Dynamics with Monte Carlo simulations and Density Functional Theory, has provided the basis for another theory to understand the changes in the nickel to iron ratio at the surface of the bimetallic catalyst. These computational studies show that iron has a core-preference because it has a higher cohesive energy and smaller Wigner-Seitz cell radius than nickel; overall, this would indicate that iron would prefer to be intercalated into the core of the nanoparticle leaving a higher concentration of nickel at the surface of the catalyst [6,12].
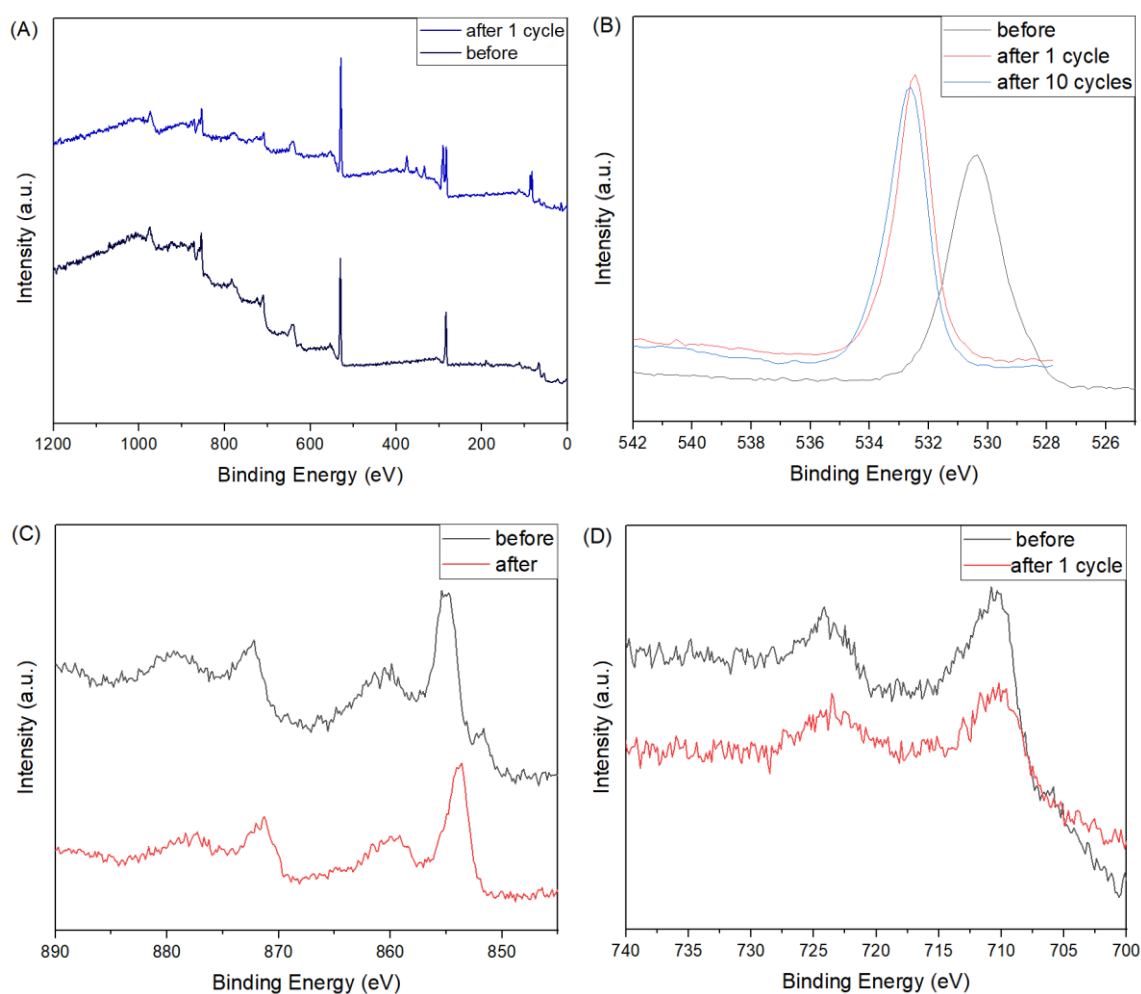

Figure 8. Results from UHV-XPS data analysis at the University of Arkansas for the Ni-Fe hydroxide alloy nanoparticles: (A) survey data and high resolution data for (B) oxygen 1s, (C) Ni 2p and (D) Fe 2p.

Analysis of the high resolution spectra was used to determine the oxidation states of the iron and nickel atoms on the surface of the nanocatalyst; the high resolution spectra for nickel 2p, iron 2p, and oxygen 1s are in Figure 8 above. For both the iron 2p peaks and the nickel 2p peaks, a metallic peak was observed before electrochemistry and this metallic component mostly disappears after just one potential cycle of cyclic voltammetry testing. After the initial CV potential cycle, the only forms of iron and nickel that are present are the more oxidized oxide and hydroxide forms.

Near-Ambient Pressure XPS Data. Compared to UHV-XPS analysis, NAP-XPS provides a more accurate/realistic understanding of the surface chemistry of the nanoparticle material because data is collected in conditions closer to atmospheric pressure and in a water vapor environment. Figure 9 below shows the survey and nickel 2p, iron 2p, and oxygen 1s high resolution spectra results for the NAP-XPS analysis done in Germany.
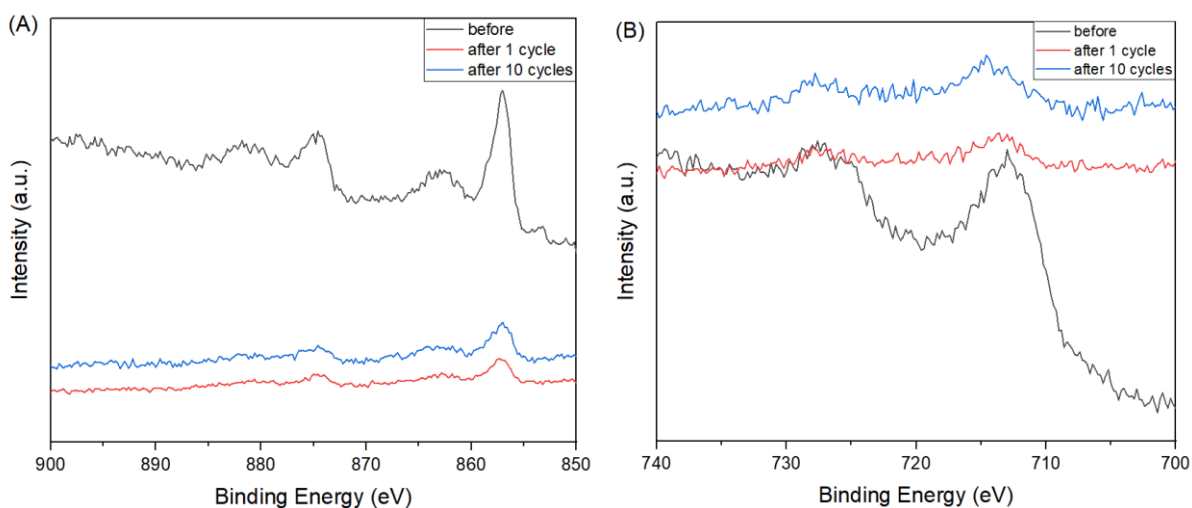

Figure 9. High resolution NAP-XPS spectra for (A) nickel 2p and (B) iron 2p with no manipulation of y-axis, showing loss in intensity after electrochemistry.

In the survey spectra, the compositions of iron and nickel on the surface of the material after catalytic use were not able to be determined since the concentrations of iron and nickel at the surface were not high enough, leading to loss in peak intensity during the NAP-XPS measurements. This loss of intensity is even seen in the high resolution spectra in Figure 10. All

graphs produced for high resolution spectra in this paper have independent y-axis between data

on the same graph to improve the visual analysis of the data for comparisons.
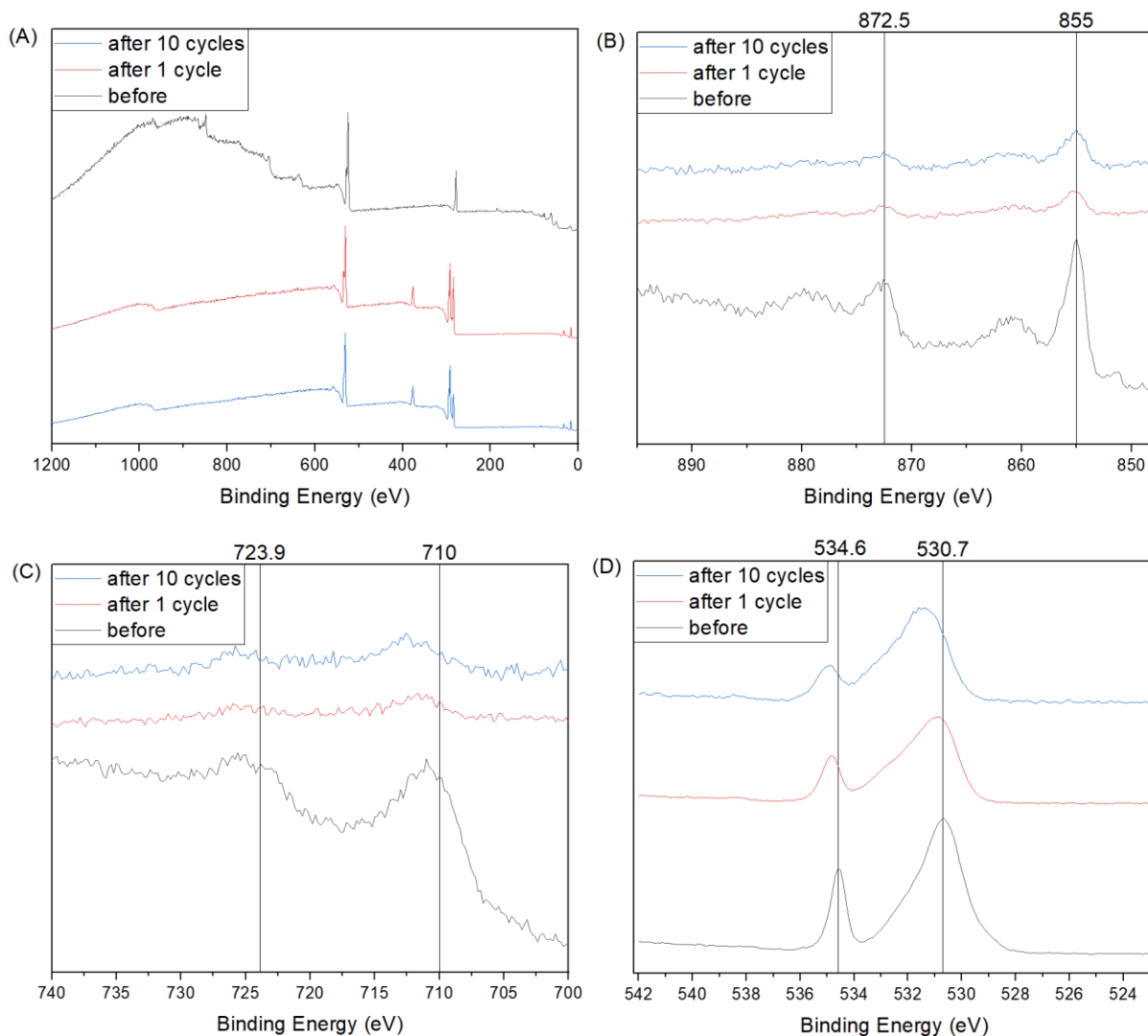

Figure 10. Results from NAP-XPS data characterization in Germany for Ni-Fe hydroxide alloy nanoparticles: (A) survey data and high resolution data for (B) Ni 2p, (C) Fe 2p, and (D) oxygen 1s.

For the high resolution data, Table 1 includes peak positions and percent area values for

all components of nickel and iron found during data analysis in CasaXPS. In the high resolution

spectra for Fe 2p and Ni 2p, the presence of a metallic component of iron and nickel, seen in

the UHV-XPS, was supported, with the metallic peak gone after initial catalytic use. After the

initial cycle, the only components in the high resolution spectra are more oxidized oxide and

hydroxide forms of nickel and iron. In Figure 10, a slight shift in peak binding energy for the oxygen 1s spectra, indicating a shift to more oxidized states in the sample. In addition to the peak shift in the oxygen 1s spectra, two distinct peaks were found for the NAP-XPS oxygen 1s spectra, as opposed to only one in the UHV-XPS. To analyze the oxygen 1s spectra further, reported literature regarding oxygen 1s spectra was utilized. It was found that metal oxides and hydroxides are represented by peaks in the regions of 531 to 528 eV and 532 – 531 eV, respectively; these oxidation states are thus represented by the right peak in the NAP-XPS oxygen 1s spectra with the peak centered at approximately 530.7 eV [2,5]. In the oxygen 1s spectra, the peak at approximately 534.5 eV represents absorbed water vapor [2]. There are no significant peak position shifts seen in the high resolution Fe 2p and Ni 2p spectra (still the disappearance of metallic nickel peak). Overall, through the high resolution peak analysis, it can be concluded that the surface of the catalyst initially has a small concentration of metallic iron and nickel, which then oxidize to form oxide and hydroxide states.

Ni 2p	Position (eV)	% Area
Before electrochemistry		
2p 3/2	855.06	42.32
2p 1/2	872.64	21.66
metal	851.53	2.91
After 1 cycle		
2p 3/2	855.35	30.48
2p 1/2	872.74	19.25
After 10 cycles		
2p 3/2	855.17	32.99
2p 1/2	872.83	16.92

Fe 2p	Position (eV)	% Area
Before electrochemistry		
2p 3/2	710.08	71.54
2p 1/2	723.87	22.20
metal	703.99	6.26
After 1 cycle		
2p 3/2	711.37	67.88
2p 1/2	724.00	32.12
After 10 cycles		
2p 3/2	712.06	64.43
2p 1/2	724.06	35.57

Table 1. Summary of high resolution data collected for NAP-XPS, including peak position and % area for all samples

IV. Conclusions

With the growing economy and threat of climate change, an efficient source of clean energy is vital. Recently, hydrogen has been proposed as a clean energy source with near zero emissions. Water splitting is the most sustainable source of hydrogen and is composed of two half reactions: the oxygen evolution reaction and the hydrogen evolution reaction [1,2,4,8,11,12]. On its own, the oxygen evolution reaction is not efficient, requiring a catalyst [1,2,4,8,11,12]. Ni-Fe hydroxide alloy nanoparticles have recently been shown as good catalysts for the oxygen evolution reaction, and have shown to not degrade with use, which is what

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happens to most catalysts [1]. Because of its long term durability in catalytic use, this nanocatalyst has promising potential in clean energy applications, making it important to understand the surface evolution that leads to its enhanced catalytic performance. In this research, UHV-XPS and NAP-XPS were used to analyze the surface chemistry of the material before and after electrochemistry.

When analyzing the complex XPS data, changes within the data set are real and indicate real transitions in surface chemistry. In the UHV-XPS data, a change in the atomic composition of the nanocatalyst at the surface was detected, with an increase in the nickel to iron ratio from 1:1 to 7:2. Future work can use different characterization techniques to determine why this ratio is changing during the catalyst's use in the oxygen evolution reaction. The increase in nickel at the surface with time could possibly help the catalyst to not degrade over time. In the high resolution data, it was shown that there is a transformation of metallic Fe and Ni to more oxidized states, showing an increase in oxides and hydroxides, which is similar to what was seen in Ni-Fe hydroxide films [4]. This transformation could explain the decrease in overpotential initially after one voltage cycle. After the initial cycle of CV testing, the surface chemistry of the material does not change significantly, which might explain why the overpotential remains slightly constant after the first voltage cycle. Overall, the Ni-Fe Hydroxide Alloy nanoparticles have a promising future for use in clean energy because of their catalytic performance and this research studying the changes in surface chemistry of catalyst with use can be used to understand the mechanisms allowing the catalyst to perform well in the oxygen evolution reaction.

V. Acknowledgements

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