Investigation of Electronic Structure Effects of Transition Metal Oxides toward Water Oxidation and CO₂ Reduction Catalysis

THESIS

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By

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Abstract

Energy conversion and storage technologies are often limited by the stability and selectivity of catalysts. One reaction of great importance in the energy conversion process is CO\textsubscript{2} reduction. For CO\textsubscript{2} reduction, selectivity is often influenced by the structure of the catalyst material. Also, catalysts need to be selective for CO\textsubscript{2} reduction over the hydrogen evolution reaction. Recent studies have shown that the selectivity of catalysts to high energy dense products is dependent on the band gap of the catalyst materials. This approach has also shown potential to be used to outcompete the hydrogen evolution process. Earth abundant metal oxides have narrow band gaps that would be energetically favorable for this process. These materials such as CuFeO\textsubscript{2} and Cu\textsubscript{2}O have narrow band gaps (E\textsubscript{g}) and Fermi levels (E\textsubscript{F}) that are suitable for reducing CO\textsubscript{2} as well as the oxidation of water. By investigating the electronic structure of these catalysts, we can better understand how electron transfer impacts the selectivity of different products. To this end, catalysts that are selective to high energy density products can be produced. Thus by investigating metal oxides of varying electronic structure, we can elucidate trends in product selectivity. We have produced Fe\textsubscript{2}O\textsubscript{3}, CuO, and CuFeO\textsubscript{2} catalysts by electrodeposition to investigate the photoelectrocatalysis of CO\textsubscript{2} reduction. Only the CuFeO\textsubscript{2} mixed phase catalyst produced selective photocurrent under CO\textsubscript{2} reduction conditions. Our CuFeO\textsubscript{2} was able to produce acetate at approximately 70\% faradaic efficiency as confirmed by standard addition method using Ion Chromatography and Nuclear Magnetic Resonance Spectroscopy. By looking at the structure using X-ray
Photoelectron Spectroscopy, we conclude that our catalyst has an iron rich surface that we believe to be responsible for this high selectivity under CO\textsubscript{2} reduction conditions. We believe there is a metal to metal charge transfer from the Fe to the Cu where the hole is localized to Cu 3d orbitals in the valence band and the electron is localized to Fe 3d orbitals in the conduction band. This state results in a long-lived Fe\textsuperscript{2+} excited state that we hypothesize is responsible for the reduction of CO\textsubscript{2}. In the near future, we plan to probe charge transfer dynamics of this material via soft X-ray transient absorption spectroscopy, which is oxidation state and element specific. Additionally, we have produced NiO\textsubscript{x}, CoO\textsubscript{x}, and MnO\textsubscript{x} catalysts. Cyclic voltammetry was used to investigate trends in the overpotential for the water oxidation reaction at pH 7 and pH 13. Both NiO\textsubscript{x} and CoO\textsubscript{x} have significantly lower overpotentials than any of the other oxides with the overpotential corresponding to 3d orbital occupancy. Additionally, nickel doping of Fe\textsubscript{2}O\textsubscript{3} lowers the overpotential significantly, with a 10% nickel molar ratio in the electrolyte being optimal. By investigating the ground and excited state x-ray spectra of these oxides, we can determine how electronic structure and the band gap of these materials correlate with the overpotential for water oxidation.
Dedication

This document is dedicated to my family and friends.
Acknowledgments

I would first like to thank my advisor Dr. L. Robert Baker for the support and funding of my work. I would also like to thank the Baker group for their support throughout the experimentation and writing process. Specifically, I would like to thank Xin Yang for help with the CO$_2$ reduction data, Jakub Husek for the X-ray absorption spectroscopy data, and Kyle Mincheff for help with the collection of data for the water oxidation project. Beyond this I would like to thank my fellow graduate students for their moral support throughout this process. I would like to express an abundance of gratitude to my family for teaching me how to learn and giving me support. I would especially like to thank my grandfather, Larry W. Gooch, for teaching me the importance of learning and discovery. I would also like to thank the Ohio State University department of Chemistry and Biochemistry as well as the Air Force Office of Research for funding the CO$_2$ reduction work and the Department of Energy for funding the water oxidation work.
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Fields of Study

Major Field: Chemistry
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Chapter 1: Introduction

1.1 Global Energy Problems

Most of today’s energy sources are derived from fossil fuels. Unfortunately, our recoverable oil will fall greatly in the next 40 years.\textsuperscript{1} To combat this problem, an alternative source of energy needs to be found. To complicate the problem further, any source generating electricity from fossil fuels ultimately releases carbon dioxide into the atmosphere.\textsuperscript{2} In order that increasing demands are met for this process, we must develop clean energy sources that don’t rely on our dwindling fossil fuel supplies or have a large negative environmental impact. To this end, much development has been accomplished through solar and fuel cell technologies.

1.2 Electrocatalysis

In electrocatalysis, a potential bias is applied to overcome some thermodynamic barrier to make a reaction occur at a working electrode. The electrode can be either the cathode (where reduction occurs) or the anode (where oxidation occurs), but nonetheless, the reaction always occurs on the surface of the electrode.\textsuperscript{3} A potential is applied to the working electrode, which functions as the catalyst for the particular reaction of interest. The thermodynamic potential required to drive an electrochemical reaction is given below in equation 1, while overpotential is a way of quantifying the kinetic barrier to the reaction.
\[ \Delta G = -nF\Delta E_{eq} \quad (1) \]

In this equation \( \Delta G \) is the change in Gibbs’ free energy, \( n \) is the number of moles of electrons in the reaction, \( F \) is Faraday’s constant (96500 C/mole e\textsuperscript{-}), and \( \Delta E_{eq} \) is the difference in potential of the working electrode to the reference electrode at equilibrium.\textsuperscript{4} Most reactions don’t occur at the equilibrium potential though. More energy is almost always required to be put into the reaction than at the equilibrium potential. This is referred to as overpotential (\( \eta \)). The overpotential of a reaction can be related to electrochemical kinetics by the Tafel equation in equation 2:

\[ \Delta V \text{ or } \eta = A \times \ln\left(\frac{i}{i_0}\right) \quad (2) \]

Where \( \eta \) is the overpotential, \( A \) is referred to as the Tafel slope, \( i \) is the current density, and \( i_0 \) is the exchange current density. The exchange current density is the current density that occurs at equilibrium, and this describes the rate at which the reduced or oxidized species transfer electrons to the electrode. The Tafel equation is often used to describe activity of a catalyst.\textsuperscript{4} In addition to electrochemical methods, other means have also been utilized to lower overpotentials for reactions of interest.

1.3 Photoelectrocatalysis

Photo electrochemistry in the modern era is often referenced to have begun with a report of Honda and Fujishima in 1972 that a TiO\textsubscript{2} photoanode was able to split water into oxygen and hydrogen gas when illuminated.\textsuperscript{5} This means that photoelectrochemistry is one of the oldest techniques for solar energy conversion. Photoelectrochemical devices
(PEC devices) can be used to convert solar energy into fuels through the absorption of light. Unfortunately, several issues hinder the ability to make this route practical. In order to achieve the practicality that we need, catalysts should be simple, stable, and efficient for the reactions we would like to control. Semiconductors are typically used for this; in fact, one of the main differences between electrolysis and a PEC cell is that at least one of the electrodes needs to be a semiconductor.

A semiconductor is defined as a material that has an electronic band structure where there is a separation between the valence band (VB) and the conduction band (CB). The semiconductor will absorb the photons and convert them to an excited electronic state in the material. The electronic change within the material is composed of electrons and electron holes separated within the material. The separated electron-hole pair creates a potential that can be used to drive a reaction such as splitting water into H₂ and O₂ or reducing CO₂ into methanol. A diagram of this appears in Figure 1. As a photon is absorbed by the material, a core-hole is left in the valence band designated by a positive in the diagram. The band gap energy (E₉), is the energy needed to excite the electron to the conduction band. Any energy above this threshold can be used for this excitation, thus E should be a value greater than E₉. The electron is depicted by the negative charge. The electron can then be utilized to reduce A to A⁻ or the hole left can be used to oxidize D to D⁺.
One of the major challenges with PECs is selecting catalysts that absorb a large part of the ultraviolet-visible spectrum while still maintaining high efficiency. Additionally, not only should a catalyst absorb light across the visible range for a PEC application, but ideally it could convert these emissions into an energy source we can use. The ultimate goal would be to couple two reactions into a tandem solar fuel cell as shown in Figure 2. In this process, oxygen can be evolved at the anode and CO₂ reduction could occur to high energy dense products at the cathode.

Figure 1. Production of an electron-hole pair under illumination in a semiconductor. Nguyen, C. C.; Vu, N. N.; Do, T.-O. J Mater Chem A 2015, 3 (36), 18345–18359. Reproduced from reference 7 with permission of The Royal Society of Chemistry.
1.4 Metal oxides as fuel cell catalysts

In order for fuel cell catalysis to be a practical pathway to future energy technologies, the catalysts used must be affordable and stable under reaction conditions. Metal oxides are often used in these processes because they are inexpensive semiconductors and readily available. Often metal oxides are stable under conditions for specific reactions such as the water oxidation reaction. Figure 3 shows a diagram of various metal oxides used for energy applications along with the relative placement of their orbitals and their band gaps. The figure also shows the electronic structures of various catalytic metal oxides. For mixed metal oxides, the placement of metal 3d orbitals contribute to the band structure and thus the band gap of the different semi-conductors. These band gaps can then be utilized for
tuning specific products for water splitting or other reactions. This is due to the impact of electronic structure on hole thermalization as well as electron transfer.

Metal oxides have been utilized for numerous types of catalysis over the years not just for energy applications. They have long been used for supporting catalysts in gas phase reactions\(^9\) along with other types of catalysis such as the conversion of fatty acids to alcohols\(^10\), the evolution of hydrogen and oxygen\(^{11}\), CO\(_2\) reduction\(^{12}\), and even as catalysts for the electrochemical treatment of organics in wastewater.\(^{13}\) By investigating the mechanism of electron transfer and hole thermalization, we can understand how charge is transferred in various metal oxides. Understanding the role of charge transfer in single and mixed metal oxides provides an opportunity to impact many different fields of energy research.

1.5 Importance of CO₂ Reduction

CO₂ is widely known as a greenhouse gas, which means it has a significant impact on the environment. One way to reduce this impact and eventually completely eliminate fossil fuel usage would be to reduce CO₂ into a variety of energy dense products. Carbon dioxide could then be utilized as a feedstock. This energy could then be stored for later use. There are strategies to select for specific products.
Different products formed from CO$_2$ reduction require different amounts of energy to thermodynamically drive the reaction, and thus have different reductions potentials in aqueous solution. The formal potential describes how the potential can be affected by solvent choice.\textsuperscript{4} Table 1 shows equations 3-10, which describe the reduction of CO$_2$ to various diverse products at pH 7 in aqueous solution. The potentials were calculated from the potentials vs. the standard hydrogen electrode (SHE) given in references\textsuperscript{5,15} As can be seen in the table, all of the reduction potentials are negative vs. the Ag/AgCl electrode. This is an indication that energy must be added to drive the reaction, and the more negative the potential, the more energy will need to be added to drive the reaction. However, the energetics of this reaction are complicated by the kinetics of the breaking and formation of various bonds in this process. Direct formation of the CO$_2^\text{-}$ would be ideal, but this requires a lot of energy to accomplish, more than is currently practical. This intermediate would allow for the formation of energy dense carbon products from the reduction of CO$_2$. Energy dense products would contain many carbons and could potentially act as a gasoline replacement.

The potentials appearing in the table don’t provide a complete picture as to what is actually occurring in solution, however. As can be seen, the formation of acetate energetically doesn’t have as high a requirement as the CO$_2^\text{-}$\textsuperscript{5} However, other factors such as competition from the hydrogen evolution as well as kinetic barriers likely make the carbon-carbon bond coupling process required to make two carbon and higher products difficult to selectively produce in any sort of quantifiable amount\textsuperscript{10,16}
Table 1. Common formal reduction potentials for reduction of carbon dioxide to various productions at pH 7 in aqueous solution vs. the 3M (NaCl) Ag/AgCl reference electrode. Values are calculated from data in references 5 and 15.

<table>
<thead>
<tr>
<th>Eq</th>
<th>Reaction</th>
<th>$E^0^\text{ vs. 3M NaCl Ag/AgCl (V)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$\text{CO}_2 + e^- \rightarrow \text{CO}_2^-\cdot$</td>
<td>-1.644</td>
</tr>
<tr>
<td>4</td>
<td>$\text{CO}_2(g) + \text{H}_2\text{O (l)} + 2e^- \rightarrow \text{HCOO}^-(\text{aq}) + \text{OH}^-\cdot(\text{aq})$</td>
<td>-0.459</td>
</tr>
<tr>
<td>5</td>
<td>$\text{CO}_2(g) + \text{H}_2\text{O (l)} + 2e^- \rightarrow \text{CO}_2(g) + 2\text{OH}^-\cdot(\text{aq})$</td>
<td>-0.315</td>
</tr>
<tr>
<td>6</td>
<td>$\text{CO}_2(g) + 3\text{H}_2\text{O (l)} + 4e^- \rightarrow \text{HCOH}^-\cdot(\text{l}) + 4\text{OH}^-\cdot(\text{aq})$</td>
<td>-0.279</td>
</tr>
<tr>
<td>7</td>
<td>$\text{CO}_2(g) + 5\text{H}_2\text{O (l)} + 6e^- \rightarrow \text{CH}_3\text{OH}^-\cdot(\text{l}) + 6\text{OH}^-\cdot(\text{aq})$</td>
<td>-0.193</td>
</tr>
<tr>
<td>8</td>
<td>$\text{CO}_2(g) + 6\text{H}_2\text{O (l)} + 8e^- \rightarrow \text{CH}_4(g) + 8\text{OH}^-\cdot(\text{aq})$</td>
<td>-0.04</td>
</tr>
<tr>
<td>9</td>
<td>$\text{CO}_2(g) + 6\text{H}_2\text{O (l)} + 8e^- \rightarrow \text{CH}_3\text{COO}^-\cdot(\text{aq})$</td>
<td>-0.084</td>
</tr>
<tr>
<td>10</td>
<td>$2\text{H}_2\text{O (l)} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-\cdot(\text{aq})$</td>
<td>-0.208</td>
</tr>
</tbody>
</table>

Copper metal has been used in recent years as a catalyst for this reaction, converting $\text{CO}_2$ to ethylene and methane with high efficiency.\textsuperscript{16} Unfortunately, a high overpotential is required for this reaction due to thermodynamic barriers. The reaction also doesn’t proceed with high selectivity to the desired products. The challenge then is to find inexpensive catalysts like copper metal that allow for lower overpotentials.
The larger the overpotential, the more unfavored the reaction, meaning that extra energy input is required to reduce carbon dioxide to products. Because these potentials are very close in numerical value, it is also challenging to have high selectivity to a specific product. For CO$_2$ reduction to be of practical value, high selectivity at low overpotentials must be achieved. These are likely due to improper adsorption energies of key intermediates in this process.$^{17}$ For example, the CO$_2^-$ intermediate, which is formed by an electron transfer to a molecule of CO$_2$ occurs as the first step of this reaction at highly negative potentials.$^{16}$ Figure 4 demonstrates the complexity of this process for the electrochemical reduction of CO$_2$ on a Cu (111) surface just for the formation of simple products such as methanol and methane. The process becomes even more complex for products involving carbon-carbon bond coupling.
1.5.1 Competition with Hydrogen Evolution Reaction

Another barrier to the practical application of CO$_2$ reduction lies in its overlap with the hydrogen evolution reaction shown below in equation 11:

\[
\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 \quad (11)
\]

In this process protons gain electrons to form hydrogen gas. The main issue is that this reaction is slightly exothermic, meaning it can occur at any negative potential. Because of this, the hydrogen evolution reaction can easily outcompete CO$_2$ reduction. The challenge then is to develop catalysts that specifically bind molecules of carbon dioxide to the surface over hydrogen molecules. By controlling the amount of time carbon dioxide intermediates bind to the surface of the catalyst, intermediates can react with each other.
forming high energy dense products. Unfortunately, an intermediate binding energy is required to form products with many carbon atoms.\textsuperscript{5}

1.5.2 CO\textsubscript{2} Reduction Photoelectrocatalysis

To this end, the photocatalysts process has been used to select for specific CO\textsubscript{2} products. By modifying the band gap of metal oxides, visible light along with a bias can be utilized to select for specific products over the hydrogen evolution reaction. For the purposes of CO\textsubscript{2} reduction, light would be absorbed by a metal oxide catalyst to reduce CO\textsubscript{2}. As light with more energy than the band gap of the material is absorbed, electrons from the catalyst can flow to CO\textsubscript{2} to reduce it.\textsuperscript{18} Typically, p- type semiconductors are used in this process because of the appropriate band bending to allow electrons to flow across the interface.

In an effort to investigate catalysts of particular importance for CO\textsubscript{2} reduction, we looked at specific band gaps of metal oxides whose conduction and valence bands were properly spaced to absorb visible light. From comparing the band gaps of various oxides, we decided to begin our investigations with copper and iron oxide. We were interested in electronic structure of the metal oxides and exploring how electronic structure trends influence catalytic selectivity. An ideal catalyst would have a conduction band higher than the energy needed to transform CO\textsubscript{2} into CO\textsubscript{2}\textsuperscript{-} intermediate.\textsuperscript{19} However, for catalysts where this is not the case, the combination of external bias and light can be used to drive the electrochemical reduction of CO\textsubscript{2}. As with the electrocatalysis discussed above, competition with H\textsubscript{2} evolution is a major challenge.
1.6 Water Oxidation

1.6.1 High Overpotentials Due to Slow Kinetics

Efficient splitting water into hydrogen and oxygen gases would lead to large progress in energy storage technologies. However, the slow kinetics of this reaction limit its efficiency for both electrocatalytic and photoelectrocatalytic processes.\(^{20}\) The water oxidation reaction is also known as the oxygen evolution reaction (OER). This reaction is often coupled with the HER, with the OER occurring at the anode or photoanode and HER occurring at the cathode or photocathode. The overall reaction that occurs in a fuel cell appears below in equation 12:

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2
\]  

(12)

In recent years, much research focus has been dedicated to the oxygen evolution reaction at the anode because of the high overpotential of this half of the reaction along with major energy loses due to inefficiencies.\(^{21}\) Due to large differences in activity in catalysts because of different preparation methods, the active site for the OER is still hotly debated. Because of all this, designing a stable first row transition metal oxide catalyst continues to be an important challenge.

Traditionally, for photoelectrocatalysis of the OER TiO\(_2\) has been used as a photoabsorber. TiO\(_2\) is readily made in different structures and investigations have been performed on the different facets of this material.\(^{22}\) TiO\(_2\) has also been used in conjunction with other catalysts to investigate the role of TiO\(_2\) overlayers.

The late transition metal oxides (Fe, Co, Mn, Ni) have been used to catalyze the OER, but for electrocatalysis rather than photocatalysis.\(^{21}\) Nickel in particular has been
found to show lower overpotentials than some of the other metal oxides. When nickel is combined in some form with iron oxides, the overpotential has been shown to be lower than nickel or iron oxides alone. These effects raise even more questions about the active site or active sites for the evolution of oxygen.

To complicate matters, the oxygen evolution reaction is dependent on proton concentration, which is a function of pH. Below in equations 13 and 14 the reactions occurring at both the cathode and anode appear under acidic conditions:

\[
\text{Anode: } 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (13)
\]

\[
\text{Cathode: } 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (14)
\]

This reaction occurs at 1.23 V vs. the standard hydrogen electrode (SHE) at pH 0. A large overpotential is one where more than 400 mV past the equilibrium potential is needed to drive a reaction. The high overpotential for OER comes from multiple intermediates that must couple two oxygen atoms together while at the same time releasing 4 protons and 4 electrons. So far, the best catalysts to accomplish this are RuO\(_2\) along with IrO\(_2\) in acidic conditions.

As shown in equations 15 and 16, the reactions are somewhat different in basic pH compared with acidic conditions:

\[
\text{Anode: } 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \quad (15)
\]

\[
\text{Cathode: } 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (16)
\]

This is critical for finding inexpensive metal oxide catalysts for the water oxidation reaction, because metal oxides aren't stable under acidic conditions.
Equations 13-16 also demonstrate another facet of this problem: the mechanism for oxygen evolution under basic conditions is likely very different than that under acidic conditions.

1.6.2 Stability of Catalysts in Photoelectrocatalysis

As previously mentioned, metal oxides are often stable at basic pH, but not in acidic conditions. One interesting way metal oxides are being utilized in photoelectrocatalysis of the OER is by combining a metal oxide electrocatalysts with a light absorber like TiO$_2$. The electrocatalysts influences the charge transfer on the photoanode.$^{25}$ Figure 7 shows what electron transfer might look like in a PEC cell for water splitting. Ion permeability and activity of electrocatalysts have been investigated by the Boettcher group who show that these parameters seem to affect the charge transfer to a photoabsorber.$^{26}$ This could potentially be controlled via different deposition methods.$^4$
Stability of catalysts is just one of many challenge areas of interest with regards to the OER. Our focus lies in studying the effect of electronic structure and active sites on the electrocatalysis. By utilizing mixed phase and mixed metal oxide materials, we can tune the electronic structure, and thus band gaps of materials to decrease the overpotential for the OER. Future work will involve the study of mixed metal oxide electrocatalysts and the charge transport effects compared to the single metal oxides.
Chapter 2: Materials and Methods

This section contains descriptions of the procedures used to produce the catalysts along with the theory and instrumentation used for characterization of them and the parameters used in the experiments.

2.1 Preparation of Catalysts by Electrodeposition

The process of electrodeposition allows for control of the morphology of the catalysts as well as control over their concentrations. This process has been well known for quite some time. In this process, the thickness of a catalyst can be controlled by sweeping a potential, continuous cycling, or a potential hold for a specific period of time. By integrating the current over a specific period of time for the deposition, and having a general idea of what the crystal structure might look like, the thickness of the catalyst film can be estimated by equation 17:

\[ m = \frac{QA}{nF} \]  

(17)

This is known as Faraday’s law, where \( m \) is the deposited metal mass in grams, \( A \) is the atomic weight of the metal, \( F \) is Faraday’s constant (96485 C/mol), and \( n \) is the moles of electrons transferred. \( Q \) is the net charge that passes through the circuit in coulombs. If the current is constant, then as shown in equation 18:

\[ Q = I*\tau \]  

(18)

If the current isn’t constant, then you can integrate to find the amount of charge as follows in equation 19:

\[ Q = \int I d\tau \]  

(19)
These equations were used to determine an approximate thickness of the deposited films. For the films deposited at a constant potential, a potential was applied until the amount of charge applied to the clean FTO pieces was equal to the amount needed for the desired thickness.

The setup utilized for deposition of all the catalysts appears in Figure 6. The temperature is controlled by an oil bath on a hotplate from Thermo-Fisher Scientific along with a thermometer. All of the catalysts were prepared by the electrodeposition technique using an Ag/AgCl (3 M NaCl) with a counter electrode produced by sputter coating 20 nm of titanium on a glass slide, followed by 20 nm of platinum. The working electrode in each case was clean 18 Ω/cm² Fluorine-doped tin oxide (FTO) obtained from Sigma-Aldrich.

Figure 6. Experimental setup for electrodeposition of non-aqueous CuFeO₂.
The FTO was cleaned by sonicating in deionized water with a resistivity of 18.2 MΩ with saturated detergent. The FTO was then rinsed with acetone and sonicated again for 5 minutes, followed by a final sonication of 5 minutes in ethanol. The FTO were used directly after cleaning. The potentials were applied using a Biologic® SP-50 potentiostat.

2.1.1 CuO

Copper (II) oxide is readily produced by several different methods. For the purposes of our experiments, a procedure developed by the Choi group was followed closely. In this process, Cu$_2$O films were electrodedeposited in dimethyl sulfoxide (DMSO) solutions of 0.01M Cu(NO$_3$)$_2$•6H$_2$O onto clean Fluorine-doped tin oxide substrates (FTO) 18 Ω from Sigma-Aldrich. Before deposition, the solution was saturated with O$_2$ gas because this is known to lower the required overpotential for the reaction. For this deposition, an Ag/AgCl (4 M NaCl) reference electrode was used in conjunction with the titanium and platinum coated counter electrode previously described. The film was deposited at a temperature of 60 degrees Celsius with a potential of -0.2 V vs. Ag/AgCl (4 M NaCl). This potential was applied until a film of approximately 85 nm was produced for both the CO$_2$ reduction and water oxidation projects. This film appears bright yellow as deposited. To convert the film to CuO, the sample was annealed in a muffle furnace at a temperature of 300 degrees Celsius with a one-hour dwell time and a ramp rate of 4.5 degrees/min. The catalyst as deposited is a p-type semiconductor.

2.1.2 α-Fe$_2$O$_3$

For the purposes of our experiments, a procedure developed by the Choi group was followed closely for anodic deposition of this material. In this process, FeOOH films
were electrodeposited in aqueous solutions of 0.02M FeCl$_2$•5H$_2$O (Sigma Aldrich) onto clean Fluorine-doped tin oxide substrates (FTO) 18 $\Omega$ from Sigma-Aldrich. For this deposition, an Ag/AgCl (4 M NaCl) reference electrode was used in conjunction with the Titanium and Platinum coated counter electrode previously described. The film was deposited under anodic conditions at a temperature of 75 degrees Celsius with a potential of 1.2 V vs. Ag/AgCl (4 M NaCl). This potential was applied until a film of approximately 85 nm was produced for both the CO$_2$ reduction and water oxidation projects. This film appears as a yellow to red depending on thickness as deposited. To convert the film to hematite, the sample was annealed in the muffle furnace at a temperature of 520 degrees Celsius with a 30-minute dwell time and a ramp rate of 2 degrees Celsius per minute. This catalyst is an n-type semiconductor after annealing.

2.1.3 CuFeO$_2$

Copper Iron oxide catalysts have been produced by several different methods in recent years.$^{29}$ We have produced copper iron oxide mixed phase catalysts using several different modifications to the electrodeposition method. Our inspiration for making this catalyst primarily came from the Choi group.$^{30}$ In each case, the as-deposited catalyst is amorphous and appears as a dark brown color. The samples must be annealed to form crystalline delafossite structures. Our first catalysts were produced during cathodic deposition conditions on clean FTO using a 1 mM Cu(NO$_3$)$_2$•6H$_2$O, 3 mM Fe(ClO$_4$)$_3$, and 100 mM KClO$_4$ solution in DMSO. The deposition was performed at 70 degrees Celsius with an applied potential of -0.3 V vs. Ag/AgCl. These samples were annealed in an Argon-purged furnace at 650 degrees Celsius with a dwell time of one hour.
These initial p-type delafossite CuFeO$_2$ catalysts didn’t seem to be very photoactive for CO$_2$ reduction. In search of a better solution to a more photoactive catalyst, we turned to a deposition method developed by the Park group.$^{31}$ These catalysts were much more photoactive, and this is the eventual procedure we followed. This catalyst was believed to be a CuFeO$_2$ and CuO mixed phase. These catalysts were prepared using 1 mM Cu(NO$_3$)$_2$ $\cdot$6H$_2$O, 3 mM Fe(ClO$_4$)$_3$, and 100 mM KClO$_4$ solution in both aqueous and DMSO solution (referred to as aqueous and non-aqueous samples respectively). Both types of prepared catalysts were annealed for 3 hours in air furnaces at 650 degrees Celsius.

2.1.4 NiO$_x$

Nickel (II) oxide catalysts were also prepared on FTO. These catalysts were prepared using an Ag/AgCl reference and the sample counter electrode. These catalysts were prepared using a pulsed potential deposition method developed by Koussi-Daoud et al.$^{32}$ In this procedure an aqueous deposition solution of 0.1 M Ni(NO$_3$)$_2$ $\cdot$6H$_2$O was prepared as the electrolyte. At a temperature of 80 degrees Celsius, the potential was stepped cathodically from -0.965 V vs. Ag/AgCl for 1 second followed by a potential hold for 4 seconds at 0.035 V vs. Ag/AgCl. This was repeated for 1500 cycles. The sample was then annealed in an air furnace for 1 hour at 300 degrees Celsius with a ramp rate of 4 degrees C per min. The as-deposited films appeared bright green, while the annealed films were black.

2.1.5 CoO$_x$

Cobalt oxide catalysts were prepared from a modified method recently described by Kuwabara et al.$^{33}$ and developed previously by Casella.$^{34}$ For the development of this
catalyst, citrate ligands needed to be used to control the solubility of cobalt in solution; the citrate ligands act to prevent the precipitation of Co(OH)$_2$ in basic solution. To prepare the deposition solution, 1.9x10$^{-4}$ mol CoCl$_2$•6H$_2$O and 1.9x10$^{-4}$ mol of sodium hydrogen citrate sesquihydrate were used to make 50 mL of solution. This solution was adjusted to pH 11.0 using 0.1 M NaOH solution. This solution was adjusted to 100 mL with deionized water after 0.1 M KNO$_3$ was added, and the pH of the solution was readjusted to pH 11.0. An Ag/AgCl reference and counter electrode produced as previously described were used for this deposition. For this deposition, a potential of 0.85 V vs. Ag/AgCl was used at a deposition temperature of 50 degrees Celsius.

2.1.6 MnO$_x$

Manganese oxide catalysts were produced from a procedure developed by Huynh et al.$^{35}$ For the preparation of these thin films, a solution of 0.5 mM MnCl$_2$•H$_2$O was prepared along with 0.9 M KNO$_3$ in aqueous solution. The same counter electrode as previously described was used along with an Ag/AgCl reference electrode. The potential was held at a constant 0.903 V vs. Ag/AgCl at room temperature for deposition. The solution was stirred using a stir bar with a stirring rate of 250 rpm. The catalyst forms on the surface of the FTO very quickly, with the deposition only taking 10 minutes or so to achieve a thickness of 85 nm.

2.1.7 Ni- doped Fe$_2$O$_3$

Ni-doped iron (III) oxide catalysts were produced in accordance with a procedure developed by Liu et al.$^{36}$ By using this procedure, we can vary the dopant level of the crystalline hematite after annealing. The deposition solution for this catalyst is prepared
by combining 5 mM FeCl₃, 5 mM NaF, 1.0 M H₂O₂ (made from 30% by volume) with 0.10 M KCl and the appropriate amount of Ni(NO₃)₂•6H₂O. The molar amount of Ni²⁺ needed for this deposition is found by calculating the molar ratio of Ni to Fe. The catalysts can be easily made with Ni molar percent from 0-15%. This is not directly correlated to the actual Ni incorporation, however, as previous studies conducted by Liu et al found using atomic absorption spectroscopy that there is a correlation to the incorporation ratio, but it’s not 1:1. This deposition was conducted using an Ag/AgCl reference electrode and the previously produced counter electrode by cycling the cell potential from -0.5V to 0.0V vs. Ag/AgCl at a sweep rate of 100 mV/s at a temperature of 50 degrees Celsius. The as-deposited sample is a yellow-orange color that turns to a scarlet after annealing. The as-deposited sample is then annealed at 500 degrees in a muffle furnace for 4 hours.

2.2 Electrochemical Characterization

2.2.1 Linear Sweep Voltammetry

In this technique, the potential of the working electrode vs. the reference is swept over a range and the current response is recorded as a function of time. The potential is swept from a lower to a higher potential as a function of time. The characteristics of the linear sweep voltammogram (LSV) is dependent on the voltage scan rate, the rate of electron transfer reactions, as well as the chemical reactivity of the electroactive species.³⁷ The Nerst equation (previously described) controls how the concentration affects the voltage in equation 20:

\[
E = E^\circ - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right)_{x=0}
\]

(20)
The formal potential (as discussed in chapter 1) is affected by the concentration of the reduced and oxidized species in the solution, and this is designated as \( E^{\circ} \) above. \( F \) and \( n \) are the Faraday’s constant and number of moles of electrons respectively. \( T \) is the temperature in kelvin, and \( R \) is 8.314 JK\(^{-1}\)mol\(^{-1}\). \( R \) is the concentration of the reduced species, while \( O \) is the concentration of the oxidized species at the interface of the electrode.

How does the scan rate affect the current curve? Figure 7 shows the variation of the current as the voltage is scanned for increasing scan rates. The size of the diffusion layer is affected by the scan rate. The flux, or change in concentration at the electrode surface, for an electrode surface is quite a bit smaller for a slow scan rate compared to a fast one.\(^{38}\) Because current is proportional to the flux, the current will be much greater at a faster scan rate than a lower one. The peak in a voltammogram can provide information about the electrochemical processes occurring at the electrode surface. As the scan rate
increases, the rate of change for the potential from $V_1$ to $V_2$ increases. The peak current designated $E_{\text{peak}}$ also increases.

Figure 7. Effect of increasing scan rate on linear sweep voltammetry. The rate of change for the voltage increases as a function of time with increasing scan rate (left). The peak current ($E_{\text{peak}}$) increases with increasing scan rate (right).

Linear sweep voltammetry was conducted in the cell that appears in Figure 8. In all cases, the cell was purged with the appropriate gas through a 22-gauge needle into the appropriate electrolyte for one hour before beginning the experiment to remove unwanted gases. An Ag/AgCl 3M NaCl reference electrode was used along with a Pt/Ti counter electrode previously used for the electrodeposition of catalysts. This technique can be utilized as a method of electrodeposition of catalysts, or used as a tool to investigate the effect of photocurrent as the potential is swept.
2.2.2 Cyclic Voltammetry

Cyclic voltammetry is a technique that can be used to unravel a plethora of information about the surface of a working electrode. This technique can be applied to deduce the effect of the chemical environment, electronic structure, and morphology on the oxidation/reduction peaks of a catalyst. It is like an extension of linear sweep voltammetry except the potential is cycled back to a starting point each time.
The potential of the system is cycled at a specified linear rate shown in part A) of Figure 9. In this technique, \( E_{\lambda 1} \) and \( E_{\lambda 2} \) are the switching potentials, and the potential of the working electrode vs. the reference will always be within this range.\(^{39}\) The system appearing in Figure 11 is a very typical 1mM Fe(CN)\(_6\)\(^{3-}\) (ferric cyanate) in 0.1 M KCl. This system is often used for calibration purposes of the potentiostat. Often there will not be a

Figure 9. Typical voltammogram during cyclic voltammetry experiments. A shows the potential as a function of time with \( E_i \) being the initial potential, and \( E_{\lambda 1} \) and \( E_{\lambda 2} \) being switching potentials. \( E_{pa} \) and \( E_{pc} \) designate the anodic and cathodic peaks respectively in B. Taken from reference 38. Reprinted with permission from (Mabbott, G. A. J. Chem. Educ. 1983, 60 (9), 697.). Copyright (1983) American Chemical Society.
change in subsequent cycles past the first scan, however, any differences can be used to
deduce important information about the surface reactivity of the electrode.

These experiments were conducted in the same cell as the linear sweep
voltammetry experiments. Cyclic voltammetry was used to investigate the trends in
overpotential for different metal oxide catalysts for the water oxidation reaction.

2.2.3 Electrolysis

Electrolysis involves holding the working electrode potential fixed and monitoring
the current as a function of time. The current yielded after a specific amount of time can
then be utilized to calculate a faradaic efficiency of the catalyst. All of the electrolysis
experiments were conducted in the photo reactor shown below in Figure 10. The
electrochemical cell has a volume of 5 mL and the reactor is made of Polyether ether ketone
(PEEK). The cell is filled with electrolyte via a peristaltic pump. A platinum mesh counter
electrode was used for these experiments to ensure enough surface area. The light source
was the same as for the linear sweep voltammetry experiments (a 100 mW/cm² white LED
from Thor Labs).
2.3 Other Characterization Techniques

2.3.1 Ultraviolet-visible Absorption Spectroscopy

Ultraviolet-visible absorption spectroscopy is a technique that is widely applicable to many different materials and refers to absorption spectroscopy in the ultra-violet visible region of the electromagnetic spectrum. Various types of material will absorb at different wavelengths depending on their composition and, as discussed previously, their band gap. This has been widely applied for quantitative analysis of specific thin films.  

The amount of an absorbing species can also be quantified using this method. It is described by the Beer-Lambert Law:

\[ A = \varepsilon bc \]  

(21)
Where $A$ is absorbance of the material, $\varepsilon$ is the extinction coefficient, $c$ is the concentration of the absorbing species, and $b$ is the path length. This technique was used to determine the band gaps of materials for the CO$_2$ reduction project. The band gap can be determined from the onset of absorption of the material.\textsuperscript{40}

\subsection*{2.3.2 X-ray Photoelectron Spectroscopy}

X-ray photoelectron spectroscopy (XPS) is a very widely used surface analysis technique.\textsuperscript{41} It is also known as Electron Spectroscopy for Chemical Analysis (ESCA). This technique is valuable because it can give element and oxidation state specific information for the surface composition of the sample. The typical depth of analysis for this process is 1-2 nm. Accordingly, XPS is a surface sensitive technique.

The photoelectric effect and its energy conservation is governed by equation 22:

$$E_{hv} = E_k + E_\phi + E_B(i)$$ \tag{22}

Where $E_{hv}$ is the X-ray energy, $E_\phi$ is a small correction for solid effects (also known as the work function), $E_k$ is the photoelectron kinetic energy, and $E_B(i)$ is the electron binding energy of the $ith$ level.\textsuperscript{42} The binding energy of the electrons are directly related to the environment around the atoms. The core binding energy of an electron is related to its oxidation state.
Figure 11 shows a schematic of the instrumentation. The incident X-ray radiation is from an X-ray tube, UV lamp, laser or a synchrotron source. In the case of this work, an X-ray tube was used as the photon source. The photoelectric interaction of the X-rays with a solid or gaseous sample causes electrons to be ejected from the material with specific kinetic energies. These kinetic energies are investigated by a hemispherical electron energy analyzer, which scans the kinetic energy spectrum to record $E_k$. For our experiments, a Kratos Axis Ultra system with Al Kα monochromatic radiation at an energy of 1486.2 eV used as the source was used for surface analysis of catalysts for CO$_2$ reduction.

![Diagram of X-ray photoelectron spectroscopy instrumentation](image)

Figure 11. A schematic of X-ray photoelectron spectroscopy instrumentation. An X-ray source is used to generate photons of energy $E_{hv}$. These photons interact with the sample and eject electrons. The electron kinetic energies are analyzed by a hemispherical electron analyzer.
2.3.3 Scanning Electron Microscopy

Classically, detailed information about the surface of samples was obtained using optical microscopy. Unfortunately, these techniques were often diffraction limited. Scanning electron microscopy (SEM) is a technique used to image and characterize sample surfaces on the micrometer (μm) to nanometer (nm) scale. This technique is used to image on a 10-10,000 X magnification of the surface usually. To obtain these magnified images of the surface, a beam of electrons is finely focused to irradiate the surface. Images can be obtained if the secondary electron emission is confined to a small volume near the beam impact area for specific choices of beam energy. These images have an approximate resolution to the size of the focused electron beam. Figure 12 shows an image of the setup for this instrumentation. In this technique, a well-focused electron gun is utilized to irradiate the sample area to be analyzed. The sample can either be rastered (moved as it is scanned to avoid damage to the sample) or it can be placed in one location for elemental analysis. Elemental analysis is often conducted by using the energy dispersive x-ray spectroscopy technique (EDX).
Figure 12. Setup of scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDX) detection capabilities. An electron gun generates a beam that is focused by lenses onto the sample. This occurs under vacuum. Backscattered and secondary electrons can be detected as well as X-rays.

Several different types of signals can be utilized in this technique including backscattered electrons, characteristic x-rays, secondary electrons as well as other photons. The most important signals are usually the secondary and backscattered electrons because these are mainly due to differences in the surface topography. A schematic of this appears in Figure 13. 46 For our experiments, we were also interested in looking at the X-rays as this would give elemental composition of the surface.
2.3.4 Energy Dispersive X-ray Spectroscopy

In SEM, the characteristic X-rays can also be analyzed to get elemental information on the sample. Energy Dispersive X-ray Spectroscopy (EDX) is a technique often used alongside SEM.\textsuperscript{47} It is utilized in the same instrumentation as shown above in Figure 12.

Figure 13. The different types of signals from an SEM. An incident electron beam can produce Auger electrons, X-rays, backscattered electrons and secondary electrons. These different electrons can provide information about the sample analyzed through various detectors attached to the SEM.
This technique gives elemental analysis of a very small sample volume. It relies on the fact that characteristic X-rays are absorbed very differently for each element. The same high energy beam used in SEM can be used to excite electrons in the sample. In this technique, an inner shell electron is excited to an outer shell leaving a core hole. This is shown in Figure 14. After this, an outer shell electron of higher energy fills the hole; this releases X-rays with the amount of energy of the different between the electron that filled the hole and the hole. The number and energy of the X-rays are then measured to determine
the elemental composition. Different emission lines can be utilized for this (Kα, Kβ, Lα). These emission lines are named for the n levels of the electrons from which the electron fills the core-hole. Thus K corresponds to n=1, L corresponds to n=2, and M corresponds to n=3. The emission lines are named for the level the hole is located in that an electron fills as well as from what level that electron was originally in (α corresponds to a n=1 change in an electron, β corresponds to a n=2 change).

2.3 Product Detection

2.3.1 Ion Chromatography

Ion chromatography (IC) was used to quantify the products of catalysts for CO₂ reduction. Generally speaking, IC is a type of chromatography. The underlying basic principle of chromatography is the separation of analytes based on interactions of the analyte with a stationary phase. IC is a special type of liquid chromatography designed to separate various ions in solution. Anion or cation exchange columns are utilized to separate ions using typical high performance liquid chromatography instrumentation (HPLC).

The key principle used in these separations relies on ion-exchange processes between ions on the surface of a high molecular weight solid that is in essence insoluble and ions in solution of the same charge. This is also known as affinity to an ion-exchange column. Based on these interactions the ions will move through the column at different rates; the ions that bind very weakly to the stationary phase will elute first, while those more strongly attracted will elute last. In this way, ions in a mixture can be quantified.
This type of separation can be used on most charged molecules, including small organic molecules, ions, and proteins.

The stationary phase utilized for a cation or anion column are different.\textsuperscript{50} In our experiments, we were only interested in the products of CO\textsubscript{2} reduction (anions) so we only used the anion column. The anions are attracted to the column. These anions are then moved through the column using a carbonate/bicarbonate buffer. Detection in our case was done using a conductivity detector. The conductivity detector is non-selective, and a chromatogram is formed by plotting the conductivity as a function of time. The amount of time an analyte stays in the column is known as retention time, which is correlated to the ion time. The peak area and height is proportional to the amount of analyte present in the sample as long as it is within the linear range of the instrument. Due to matrix effects in the post-reaction solution, once acetate was identified as a product in our sample we used standard addition to quantify the concentration.

Figure 15 shows the instrumentation used for ion chromatography reproduced courtesy of Shimadzu Corporation.\textsuperscript{50} This instrumentation uses an anion exchange column and was ordered from Thermo-Fisher Scientific. It also uses a suppressor column from Dionex to remove background noise from the mobile phase and increase the peak response. This is accomplished by replacing potassium or sodium ions with hydronium ions from the electrolysis of water to control the ionic strength. This is especially useful with a conductivity detector, which is generally non-selective.
Nuclear magnetic Resonance spectroscopy (NMR) is a technique widely used to characterize organic compounds. This makes this technique a good choice to quantify products for CO$_2$ reduction. It is based on the principle that nuclei will absorb and re-emit electromagnetic radiation. The re-emitted energy is dependent on the magnetic properties of the isotope of the atoms and resonates at a specific frequency. These frequencies are often 60-1000 MHz, or similar frequencies to television broadcasts. The most common types of NMR are $^1$H and $^{13}$C.$^{40}$ This is because all isotopes that have an odd number of neutrons and/or protons have an intrinsic magnetic moment and angular momentum, which is also known as a non-zero spin.

NMR usually involves two general steps. The first step is the alignment of the magnetic nuclear spins within a constant magnetic field known as $B_0$. The final step is

Figure 15. A schematic of ion chromatography with anion detection. A suppressor column is used to increase sensitivity. Taken from reference 49 courtesy of Shimadzu Corporation.

2.3.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic Resonance spectrometry (NMR) is a technique widely used to characterize organic compounds. This makes this technique a good choice to quantify products for CO$_2$ reduction. It is based on the principle that nuclei will absorb and re-emit electromagnetic radiation. The re-emitted energy is dependent on the magnetic properties of the isotope of the atoms and resonates at a specific frequency. These frequencies are often 60-1000 MHz, or similar frequencies to television broadcasts. The most common types of NMR are $^1$H and $^{13}$C.$^{40}$ This is because all isotopes that have an odd number of neutrons and/or protons have an intrinsic magnetic moment and angular momentum, which is also known as a non-zero spin.

NMR usually involves two general steps. The first step is the alignment of the magnetic nuclear spins within a constant magnetic field known as $B_0$. The final step is
utilizing a radio frequency pulse to perturb the alignment of spins. The frequency required to perturb the field is dependent on the static magnetic field (H₀) and the sample of interest.⁴⁰
Chapter 3: CO₂ Reduction Photoelectrocatalysis

3.1 Introduction

CO₂ reduction is a very large and complex global problem affecting energy efficient technologies due to auto emissions. One of the main pathways to renewable energy involves reducing these emissions into a fuel we can use. So far, many advances have been made to reducing CO₂ to C1 products. However, reducing CO₂ to products that can be utilized as fuels is still an area of enormous growth in the scientific community. Reducing carbon dioxide to any useable product is an uphill battle thermodynamically. Therefore, efficient catalysts must be utilized in this process. The challenge then, is to design catalysts that are selective to CO₂ reduction, but do not participate in the hydrogen evolution reaction (HER).

Another possible complication is that while proton reduction actively competes with CO₂ reduction, protons must be used in the process to reduce CO₂. If the thermodynamics could be carefully tuned, product selectivity to high energy dense products could be realized. Because of the ability to tune the band gaps in metal oxides via doping or mixing metals, transition metal oxides make good model systems to study trends in electronic structure to lead to specific reaction pathways through photoelectrocatalysis.

Earth abundant metal oxides would be excellent catalysts for this reason if they were practical. Unfortunately, metal oxides are often not stable in the slightly acidic conditions during CO₂ reduction catalysis. Studying metal oxides, however, does provide
a way to investigate how electronic structure of catalysts influences selectivity to high energy dense products for CO₂ reduction.

The band gaps of specific metal oxides are optimal for this process.³⁰ The goal of this project was to determine how single and mixed transition metal oxides compositions lead to different CO₂ reduction products. As stated previously, we wanted to investigate metal oxides with band gaps greater than the thermodynamic requirement to reduce CO₂ to C1 products.

Previous studies of copper oxides, both I and II, have resulted in the reduction of CO₂ to products both through electrocatalysis as well as photoelectrocatalysis.⁵¹ However, this is typically reduced to carbon monoxide and hydrocarbons. These are not practical for fuel storage. Because the band gap of a material can be finely tuned by doping with another metal, we opted to investigate the electronic structure effects of CuO, CuFeO₂ of a mixed type, as well as α-Fe₂O₃ (hematite). CuO and CuFeO₂ have large enough band gaps that absorption of visible light has enough energy to produce CO₂ reduction products, however, Fe₂O₃, does not. Our catalyst is able to surprisingly reduce CO₂ to acetate, a C₂ product. This is a step in the right direction for controlling selectivity for CO₂ reduction.

The Choi group was the first group to produce a p-type delafossite structure of CuFeO₂ by thin-film electrodeposition.³⁰ This catalyst was electrodeposited in a DMSO solution on FTO and had an approximate band gap of 1.55 eV. They didn’t study this catalyst for carbon dioxide reduction, but instead were interested in the material’s application to the HER. It was observed that this catalyst was a poor choice for hydrogen evolution. However, they found that the delafossite CuFeO₂ catalyst absorbed across most
all of the visible spectrum, leading them to believe it had some applications in water or oxygen reduction.

Because the CuFeO$_2$ catalyst was found to be poor for the hydrogen evolution reaction, the Bocarsly group wanted to see if they could use this to promote CO$_2$ reduction over hydrogen evolution.$^{52}$ By doping the CuFeO$_2$ with even small amounts of Magnesium (0.05%), they were able to tune the band gap of the material. This led to a 14% increase in photon to energy conversion efficiency. This catalyst produced formate from the reduction of CO$_2$, but with a very poor faradaic efficiency. This is primarily possible because photon to energy conversion efficiency only takes into account the number and not the energy of photons. The Bocarsly group was able to experimentally determine the band gap of this material, and demonstrate that diverse products can be selected for by tuning the band gap of the material.

More recently, the Park group produced a mixed phase CuFeO$_2$/CuO p type catalyst that was able to reduce CO$_2$ to formate at a much higher efficiency.$^{31}$ This catalyst showed 90% selectivity to formate with a 1% overall energy efficiency. It was even able to operate as a photoanode without bias over the course of a week. Our studies were motivated by understanding charge transfer in this material, and how such high selectivity for formate formation could be achieved. We wanted to understand the high selectivity of this catalyst to formate. Herein, we compare the catalysis of CO$_2$ reduction using CuO and Fe$_2$O$_3$ to our mixed phase heterojunction CuFeO$_2$ catalyst. A surprising 70% faradaic efficiency to acetate from this catalyst produced in our group.

3.2 Catalyst Preparation and Characterization
All of these catalysts were prepared as previously described in chapter 2. In short, each catalyst was electrodeposited using our Biologic® SP-50 potentiostat onto clean FTO. The catalysts for these experiments appear below in Figure 16.

Figure 16. The as-deposited catalysts are shown. CuO appears on the left, Fe$_2$O$_3$ appears in the middle, and CuFeO$_2$ appears on the right.

The absorption spectra were taken with an Ocean Optics portable UV-vis spectrometer. Clean FTO was used as a blank for these spectra appearing in Figure 19. From this we can see the different materials have different band gaps useful for CO$_2$ reduction. Fe$_2$O$_3$ has a band gap of 2.0 eV, CuFeO$_2$ has a band gap of 1.7 eV, and CuO has a band gap of 1.3 eV. The band gap of the material affects what wavelengths of light
can be absorbed and used to reduce CO$_2$ to valuable products. This was demonstrated by our UV-vis spectra.

![Absorption spectra of catalysts in the UV-visible range. Clean FTO was used for a baseline subtraction.](image)

After characterizing the catalysts by UV-vis spectroscopy, we wanted to investigate how the electronic structure of these catalysts affect their ability to catalyze the reduction of CO$_2$. To do this we found the photocurrent via chopped light on/off linear sweep voltammetry with a sweep rate of 100 mV/s. This data appears in Figure 18.
Figure 18. Photocurrent in Argon and CO₂ saturated 0.1 M NaHCO₃ buffer with a scan rate of 50 mV/s and 1 Hz chopped on/off light.
As shown in the Figure 18, the Fe$_2$O$_3$ catalyst shows no photocurrent in the presence of CO$_2$ or its absence. CuO, on the other hand, shows a distinctive photocurrent in both Argon (Ar) and CO$_2$ saturated 0.1M NaHCO$_3$. Interestingly, our CuFeO$_2$ mixed phase catalyst shows selective photocurrent only in the presence of CO$_2$. This information suggests that Fe plays a key role in the active site of CO$_2$ reduction catalysis. The amount of photocurrent generated can be found from the difference of the light off curve from when the light is on. In the figure, more negative currents are generated when the electrode is illuminated with a white LED than without illumination. The current due to this illumination is known as the photocurrent. Once we determined that CuFeO$_2$ produced selective photocurrent for CO$_2$ reduction, the next step was to investigate the products formed when CO$_2$ was reduced.

Products were detected first using ion chromatography. In these studies, the catalyst was deposited on a square piece of FTO. Backside illumination was used during photo-electrolysis inside the PEEK reactor. The potential was held constant and the current was monitored as a function of time. Ion chromatography was the first technique used because Kang et al. previously found 90% selectivity to formate with a very similar catalyst.\textsuperscript{31} We were initially expecting to find formate as a product from our CO$_2$ reduction studies. However, to our surprise, the main product formed was acetate. Figure 19 shows the products eluted as a function of time. The analyte eluting between 4.0 and 4.25 minutes for retention time was determined to be acetate. This product could be quantified using the standard addition method with this technique. The largest photocurrent over the dark
current was found at -0.4 V vs. Ag/AgCl (3M NaCl). Because of this, the product was first quantified at this potential after electrolysis for two hours.

Figure 19. Elution of analytes using ion chromatography with a flow rate of 1 mL/min using a suppressor with a 4.5 mM Na$_2$CO$_3$ and 1.4 mM NaHCO$_3$ buffer as the mobile phase. Acetate elutes between 4.0 and 4.25 minutes. The large peak between 2.75 and 3.0 minutes is due to the buffer used in electrolysis.

A standard addition calibration curve was generated from the data collected in 0.1 M bicarbonate buffer solution as shown in Figure 20. In the standard addition process,
additions of a sodium acetate solution were added to the sample matrix. A linear best fit equation was used to determine the concentration of acetate in the sample matrix. This standard addition plot was taken after electrolysis occurred at -0.4 V vs. Ag/AgCl. This potential was chosen because there was the largest amount of photocurrent produced at this potential (as you can see in figure 24). This concentration can be linearly fit. Once the concentration of acetate formed is calculated, the faradaic efficiency can be calculated as discussed shortly.

![Graph](image)

**Figure 20.** Addition of various amounts of acetate to sample matrix at -0.4 V vs Ag/AgCl. This information was used to determine concentration of acetate in the reaction mixture a blank of 0.1 M bicarbonate buffer was baseline subtracted.

We wanted to also compare this to how acetate formation was affected at other potentials. To do this, electrolysis was performed at -0.2 V and -0.3 V vs Ag/AgCl. The standard addition chromatograms for these potentials appear in Figure 21 along with their calibration curves. Each of these were also baseline subtracted using 0.1 M bicarbonate buffer solution.
Figure 21. Standard Addition plots and calibration curves for -0.2 V vs. Ag/AgCl (bottom) and -0.3 V vs. Ag/AgCl (top).

To ensure that the product was a product of CO$_2$ reduction, calibration curves were produced under illumination in pH 7 phosphate 0.1 M buffer after electrolysis at -0.4 V vs. Ag/AgCl as well. This plot along with the calibration curve appears in Figure 22. Even in phosphate buffer it is clear that acetate is formed under bias and illumination.
In the standard addition plots, the concentration of the unknown can be found from finding the x-intercept. Tables 2, 3, 4, and 5 show the calculated faradaic efficiency at various potentials for acetate formation in both bicarbonate and phosphate buffers. This is calculated as previously described in chapter 2. Once the concentration of acetate in the solution is known, the current during the electrolysis experiment is used to calculate faradaic efficiency. The highest faradaic efficiency was achieved at -0.4 V vs. Ag/AgCl at over 55%. From the data in tables 2, 3, and 4 it can be seen that the amount of acetate formed is a function of the potential for electrolysis.

Interestingly, the faradaic efficiency was highest when using the pH 7 phosphate buffer. This is likely due to the formation of an intermediate or the change in pH from the bicarbonate to the phosphate buffer. A CO₂ saturated 0.1 M bicarbonate buffer has an

Figure 22. Standard Addition plot and calibration curve for -0.4 V vs. Ag/AgCl bias along with calibration curve in 0.1 M pH 7 phosphate buffer.
approximate pH of 6.8, whereas the pH of the phosphate buffer is likely still very close to pH 7 even when purged with CO₂. For reference, the pH of an Ar saturated phosphate buffer is 7.2.
Table 2. Calculation of faradaic efficiency for acetate formation for illumination with -0.4 V vs. Ag/AgCl bias in a 0.1 M bicarbonate buffer.

<table>
<thead>
<tr>
<th>Theoretical concentration (μM)</th>
<th>Theoretical yield (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>251</td>
<td>0.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Actual concentration (μM)</th>
<th>Actual yield (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>141.9</td>
<td>0.54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard error</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.2</td>
<td>0.07</td>
</tr>
</tbody>
</table>

**Faradaic Efficiency**

56.5%

**Standard error**

7.7%

Table 3. Calculation of faradaic efficiency for acetate formation with illumination along with a -0.2 V vs. Ag/AgCl bias in a 0.1 M bicarbonate buffer.

<table>
<thead>
<tr>
<th>Theoretical concentration (μM)</th>
<th>Theoretical yield (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>0.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Actual concentration (μM)</th>
<th>Actual yield (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.6</td>
<td>0.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard error</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Faradaic Efficiency**

29.8%

**Standard error**

2.9%
Table 4. Calculation of faradaic efficiency for acetate formation for illumination along with a -0.3 V vs. Ag/AgCl bias in a 0.1 M bicarbonate buffer.

<table>
<thead>
<tr>
<th>Theoretical concentration (µM)</th>
<th>Theoretical yield (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>258</td>
<td>0.93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Actual concentration (µM)</th>
<th>Actual yield (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>117.8</td>
<td>0.42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard error</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Faradaic Efficiency

<table>
<thead>
<tr>
<th>Faradaic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.7%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8%</td>
</tr>
</tbody>
</table>

Table 5. Calculation of faradaic efficiency for acetate formation for illumination along with a -0.3 V vs. Ag/AgCl bias in a 0.1 M pH 7 phosphate buffer.

<table>
<thead>
<tr>
<th>Theoretical concentration (µM)</th>
<th>Theoretical yield (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>339</td>
<td>1.36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Actual concentration (µM)</th>
<th>Actual yield (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230.4</td>
<td>0.92</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard error</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.7</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Faradaic Efficiency

<table>
<thead>
<tr>
<th>Faradaic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.0%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.7%</td>
</tr>
</tbody>
</table>

As a control the same experiment was performed with and without illumination, under Ar and CO₂ saturated conditions, as well as with all of the different catalysts and a
FTO blank to control for the effect of other variables. A summation of the results collected appears in Table 6. With or without illumination, there is acetate formation with the CuFeO<sub>2</sub> catalyst. However, illumination increases the amount of acetate formed over the course of 2 hours of electrolysis. To insure that the acetate formed is a product of CO<sub>2</sub> reduction and not an effect of the electrolyte, electrolysis with subsequent product detection by IC was performed in both Ar and CO<sub>2</sub> saturated electrolyte. Acetate formation only occurs in CO<sub>2</sub> saturated solution. Additionally, acetate is only formed with the CuFeO<sub>2</sub> catalyst in any sort of quantifiable amount.
Table 6. This table contains the amount of acetate formed from CO$_2$ reduction under various conditions. Acetate is only formed with the CuFeO$_2$ catalyst under CO$_2$ saturated conditions. 50% more acetate is formed when bias and illumination is used compared to illumination alone.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Catalyst</th>
<th>Illumination</th>
<th>Gas</th>
<th>Acetate Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light On and off</td>
<td>CuFeO$_2$</td>
<td>On</td>
<td>CO$_2$</td>
<td>226 uM</td>
</tr>
<tr>
<td>Carbon source</td>
<td>CuFeO$_2$</td>
<td>On</td>
<td>CO$_2$</td>
<td>231 uM</td>
</tr>
<tr>
<td></td>
<td>CuFeO$_2$</td>
<td>Off</td>
<td>CO$_2$</td>
<td>117 uM</td>
</tr>
<tr>
<td>Material</td>
<td>CuO</td>
<td>On</td>
<td>CO$_2$</td>
<td>&lt; 10 uM</td>
</tr>
<tr>
<td></td>
<td>Fe$_2$O$_3$</td>
<td>On</td>
<td>CO$_2$</td>
<td>&lt; 10 uM</td>
</tr>
<tr>
<td></td>
<td>FTO</td>
<td>On</td>
<td>CO$_2$</td>
<td>/</td>
</tr>
</tbody>
</table>
NMR studies were performed to confirm the presence of acetate in the reaction mixture. This is because the formation of acetate would be based on a complex mechanism, and in order to confirm the formation of such a product, more than one quantification method should be used. As you can see in Figure 23, the product is also confirmed by $^1$H NMR studies.

![Figure 23. Formation of products detected by $^1$H NMR. In the top of the figure is the post-electrolysis solution. The bottom shows the signal from standard solutions of acetate and formate. It is clear from these figures that acetate is formed by the catalyst CuFeO$_2$.](image-url)
After detecting the formation of acetate from CO\textsubscript{2} reduction with our catalyst, we wanted to understand how the electronic structure of our catalyst led to the formation of acetate. The formation of acetate from CO\textsubscript{2} is by an eight electron process, and the mechanism proposed for this process on a recent nanodiamond structure is as follows in equation 23\textsuperscript{54}.

\[
CO_2 \rightarrow CO_2^{\cdot \cdot} \rightarrow (COO)_2^{\cdot \cdot} \rightarrow CH_3COO^- \tag{23}
\]

In the reduction of CO\textsubscript{2} to acetate, we believe that oxalate is the critical intermediate. We are looking for the formation of oxalate via ion chromatography as a function of time. We intend on proving this in future experiments to study the formation of this intermediate in situ via vibrational spectroscopy.

As described in Chapter 2, XPS is a surface sensitive technique that is often used to probe the structure of catalysts within the top 1-2 nm. In order to elucidate the reason for our high selectivity to acetate formation, we used this technique to compare the catalysts before and after the annealing process. Figure 24 shows a comparison of before and after annealing at the Cu and Fe 2p peaks for the non-aqueous prepared CuFeO\textsubscript{2} using the XPS in CBC. As you can see in the figure, the Cu 2p\textsubscript{3/2} peak shifts to a higher binding energy after the annealing process. This is likely an indication of a shift from a Cu\textsuperscript{1+} to a Cu\textsuperscript{2+} surface state. The magnitude of the signal also decreases significantly after the annealing process. We believe this to be an indication of a segregation to the bulk by copper ions. Looking at the Fe 2p\textsubscript{3/2} peak, we see a peak splitting due to spin orbit coupling in both the pre-annealed and annealed samples. However, there is little change in the intensity before
and after the annealing process. The peak in the middle corresponds to tin from our FTO substrate, due to the presence of pinholes in the catalyst.

Figure 24. XPS of non-aqueous prepared CuFeO₂ at the Cu and Fe 2p binding energies. The black line is before annealing and the red line is after annealing.
Because the Fe concentration at the surface of the catalyst doesn’t change before or after annealing, we believe this has some influence on the active site for catalysis during CO$_2$ reduction. It was also important to ensure that the catalyst wasn’t losing copper in the annealing process. Even though this was unlikely, SEM with EDX analysis of the catalyst was performed. EDX is also a surface technique, however, its probe depth is much deeper compared to XPS as discussed in chapter 2. The probe depth for this technique can be up to 80 nm into the material. Figure 25 shows the imaging collected from the SEM and the elemental analysis from the EDX data. The color coated images show the location of individual Cu and Fe atoms. Table 7 shows the composition of different elements using EDX for the catalyst post-annealing.

Table 7. Elemental analysis of surface composition using EDX. From this data it can be concluded that Cu isn’t getting removed from the material, but is instead segregating to deeper in the bulk.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.23</td>
</tr>
<tr>
<td>O</td>
<td>69.99</td>
</tr>
<tr>
<td>Si</td>
<td>2.66</td>
</tr>
<tr>
<td>S</td>
<td>0.43</td>
</tr>
<tr>
<td>Fe</td>
<td>2.53</td>
</tr>
<tr>
<td>Cu</td>
<td>3.79</td>
</tr>
<tr>
<td>Sn</td>
<td>16.37</td>
</tr>
<tr>
<td>Total:</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Figure 25. SEM image and EDX elemental analysis of composition. SEM scaling is as marked. SEM imaging was also taken at the $k\alpha_1$ and $k\alpha_2$ emission lines to see the atomic distribution of Cu and Fe. The large amount of Sn in the EDX analysis is from the FTO substrate.
In order to better understand the reason behind the surprising selectivity of our catalyst to reduce CO$_2$ to acetate, we investigated how the preparation method affected the composition of the catalyst. Using the same salt concentrations, but in an aqueous electrolyte and applying the same potential bias, CuFeO$_2$ was produced on FTO substrates. However, this catalyst does not produce a selective photocurrent in the presence of CO$_2$. An XPS comparison of both preparation methods appears in Figure 26. From the XPS spectra, it is apparent that very little Fe is present on the surface of the aqueous prepared catalyst.
Figure 26. XPS spectra of CuFeO$_2$ prepared by electrodeposition in aqueous and non-aqueous electrolyte. Very little Fe is present on the surface of the catalyst.
3.5 CO₂ Reduction Conclusions

CuO, Fe₂O₃, and a mixed phase heterojunction of CuFeO₂ were produced by electrodeposition on FTO substrates. The activity of these catalysts were compared under illumination by a white LED along with various bias using linear sweep voltammetry. Only the CuFeO₂ catalyst showed selective photocurrent under CO₂ reduction conditions. The product of CO₂ reduction was monitored using NMR and IC. The primary product of CO₂ reduction with the CuFeO₂ catalyst was shown to be acetate. This product was quantified by IC and shown to be produced with a 70% faradaic efficiency. The catalysts were then characterized by XPS. It is believed that a long lived Fe²⁺ redox state is responsible for the selective catalysis. This is also suggested by the Fe rich surface of our CuFeO₂ catalyst. Probing the electronic structure of our catalyst by time-resolved soft x-ray spectroscopy will provide information on charge transfer in this material and lead to more informed design of metal oxide catalysts in the future. We plan to do this in future studies described further in chapter 4.
Chapter 4: Oxygen Evolution Reaction Electrocatalysis and Future Work

4.1 Introduction

Application of PEC to water splitting is a very complex, but potentially rewarding area of research. Metal oxides are earth abundant and inexpensive as well as quite stable in basic conditions. Metal oxides have been studied as electrocatalysts for the OER as well as to be used in conjunction with photoabsorbers for the photocatalytic oxygen evolution. If a metal oxide is to be used in conjunction with a photoabsorber, then at least a 10% efficiency of solar conversion much be upheld for practical application. From the literature it seems that overpotentials should be compared at values of 10 mA/cm$^2$.\textsuperscript{56,57} For this specific current density, materials with overpotentials between 0.33 and 0.5 V is considered promising for solar applications.\textsuperscript{58} It is best to calculate overpotentials vs. RHE because the OER will thermodynamically occur at 1.23V vs. RHE no matter what the pH.\textsuperscript{59} Because the OER follows a different kinetic pathway depending on the pH, it is important to understand how the overpotential of the OER changes as a function of pH dependence.

4.2 The Dependence of Overpotential on pH

From the equations appearing in chapter 1, it is clear that water splitting proceeds by a different mechanism depending on the pH of the solution. Unfortunately, the exact mechanism is difficult to study, although various groups have tried. This could be approximated as a series of one electron transfer steps. At neutral pH, it is likely that first water is oxidized to hydroxide and then a similar mechanism to basic conditions might
occur. It is also possible that a completely different mechanism occurs from neutral to basic pH.

As previously stated in chapter 2, the CV technique is able to provide a lot of information about what is occurring on a catalyst surface as a function of applied potential. The surface composition is likely to change after several cycles of potential change. It is crucial to see the change in the catalysts in subsequent cycles to look at stability. This number of cycles was chosen because the CV scans were relatively stable after this time frame. This purging was continued in the headspace of the cell over the setup during CV scans. As you can see in the figure, the cycling appeared to stabilize after 5 cycles. During the first cycle, the substrate (FTO) is often also oxidized, which can interfere with results.

Thus it is important to look at potential changes beyond the first cycle. Figure 27 shows a demonstration of this for nickel oxide in 0.1 M NaOH at the approximate pH of 13. The scan rate was 20 mV/s with a sweep in potential from 0 vs. Ag/AgCl to 1 V vs. Ag/AgCl and back again for each cycle. In the literature, it is often believed that the position of the Ni oxidation peak correlates with the overpotential of water oxidation at a specific current density. From the collected data for the various cycles, this also appears to be true of our collected data. If the overpotential is taken from the forward scan, the overpotential clearly decreases with the shift of the Ni oxidation peak as the cycle number increases in Figure 28.

Using this knowledge, various metal oxides were then tested at both pH 7 and pH 13 for their overpotentials, primarily using the forward scan of the fifth CV cycle as a
determinant for overpotential. The variation of metal oxide used as an electrocatalysts for water oxidation had a dramatic effect on the overpotential for water oxidation.
Figure 27. Effect of Water Oxidation Overpotential as a function of cycling at pH 13 with a scan rate of 20 mV/s. As the cycle number increases, the overpotential decreases at a specific current density. In addition, the nickel oxidation peak shifts to a lower potential with a higher intensity.
Figure 28. Correlation of Ni oxidation peak with the overpotential for water oxidation at pH 13 with a scan rate of 20 mV/s. This is a zoomed in version of figure 30. From cycle 1 to cycle 2 the Ni oxidation peak appears. As the cycle number further increases, the Ni redox peak increases in intensity and shifts to a lower potential vs. RHE. This is consistent with the idea that this oxidation peak is related to the overpotential for water oxidation.61

Figure 29 shows a fifth cycle comparison of all the prepared metal oxide catalysts at pH 7. For these experiments, a 0.1 M pH 7 phosphate buffer was prepared and 0.1 M sodium sulfate (Na₂SO₄) inert electrolyte was added to the solution to increase conductivity and decrease uncompensated resistance of the cell at neutral pH.4 This salt is typical of water oxidation experiments in the literature.62 As can be seen from the 5th cycle CV comparisons, cobalt and nickel oxides are the best catalysts at this pH with the lowest
overpotentials at most current densities. Manganese oxide (from this preparation method) clearly has the highest overpotential at every current density value. This could be because this form of manganese oxide was not “activated” by cycling as it was also tested in the original preparation method by Huynh et al. In this case, the original MnO$_x$ underwent a phase change. When the catalyst was subsequently conditioned anodically, the catalyst became a disordered birnessite-like phase that was highly active for the OER. In future experiments it will be interesting to compare this highly active MnO$_x$ to that of the “deactivated” one and other metal oxides.

Figure 29. 5th cycle cyclic voltammograms of various metal oxide catalysts at pH 7 in 0.1 M phosphate buffer with 0.1 M Na$_2$SO$_4$. A scan rate of 20 mV/s was taken from 0V to 1.5 V vs. Ag/AgCl and these values were then converted to the RHE scale.
In between the CoO\textsubscript{x} and NiO\textsubscript{x} catalysts which had the lowest overpotentials and the MnO\textsubscript{x} that clearly performed the worst, copper, iron, and copper iron mixed metal oxides appear in Figure 29. From previous results with CO\textsubscript{2} reduction experiments, we were expecting the non-aqueous prepared CuFeO\textsubscript{2} to perform similar to Fe\textsubscript{2}O\textsubscript{3} because of the Fe-rich surface from the XPS data. As shown in the figure, the non-aqueous CuFeO\textsubscript{2} performed slightly better than Fe\textsubscript{2}O\textsubscript{3}. Aqueous prepared CuFeO\textsubscript{2} performed very similar to the CuO catalyst. This is also expected based on the XPS results from the CO\textsubscript{2} reduction project because this catalyst is very Cu-rich on the surface. At some current densities, the aqueous prepared CuFeO\textsubscript{2} might have lower overpotentials, and this might be due to the nature of the catalyst. The CuO catalyst was prepared in DMSO solvent\textsuperscript{27}, while the aqueous prepared CuFeO\textsubscript{2} was prepared in water\textsuperscript{31}, which often results in more porous films where ions are more permeable. For example, this has been noted for other metal oxide catalyst in the literature.\textsuperscript{32} Ion permeability into an electrocatalysts has been shown to impact the activity of the OER at the photoanode\textsuperscript{26}, so it is also possible that this could affect the electrocatalysts as well.

Most electrolyzers operate under alkaline conditions because hydrogen evolution is easiest under these conditions\textsuperscript{63}, so it is more essential to study the impact of the choice of electrocatalysts in the alkaline region. Because the mechanism is likely different under various pH conditions, it is also useful to investigate pH dependence. Also, the metal oxide electrocatalysts are much more stable under alkaline conditions than at neutral pH.

These interests led us to investigate the effect of overpotential on the composition of the metal oxide at pH 13 in 0.1 M NaOH. We were expecting that the overpotential at
every current density would be lower at pH 13 than at pH 7. Our results indicate this is true.

The same experiments above were then conducted in Ar saturated 0.1 M NaOH at a pH of approximately 13 (neglecting activity). Figure 30 shows the results of the 5th cycle CV scans at a scan rate of 20 mV/s. As with the pH 7 electrolyte, as expected cobalt and nickel oxides had the lowest overpotentials compared to the other catalysts. The overpotentials of the other catalysts were more differentiated in this solution compared to the pH 7 one. In any case, we see that MnOₓ performed poorly again, only slightly better than clean FTO that was used as a substrate for the other catalysts deposition.

In this electrolyte, it is also easier to differentiate the aqueous from the non-aqueous prepared CuFeO₂. Both the aqueous and non-aqueous CuFeO₂ had lower overpotentials at most any current density than CuO. Interestingly, the aqueous CuFeO₂ performed almost equivalent to the thin Fe₂O₃. However, even the non-aqueous CuFeO₂ had lower overpotentials than pure Fe₂O₃. This is likely due to the amount of Fe present on the surface of the working electrode. The aqueous CuFeO₂ likely has only minimum Fe incorporated into its porous structure, whereas the non-aqueous CuFeO₂ likely has a much thicker layer of Fe on the surface. Due to the difference between the thin (approx. 20 nm) and thick (approx. 100 nm) sample this seems likely. Interestingly, previous reports of Ni-Fe hybrid catalysts have reported that Fe isn’t very conductive.⁶⁰,⁶¹ This is likely why thicker Fe₂O₃ tend to have higher overpotentials than thinner catalysts.
Also appearing in Figure 30, is a nickel-doped \( \text{Fe}_2\text{O}_3 \) catalyst. The results of experiments with nickel doping will be discussed mostly in the next section of this chapter, however, the 10% Ni-doped \( \text{Fe}_2\text{O}_3 \) appears in Figure 34 for comparison. This catalyst appears to have intermediate overpotentials between that of nickel and iron oxides. This is somewhat expected, however, it is likely a greater shift than expected from the doping level. The doping of nickel in the \( \text{Fe}_2\text{O}_3 \) is probably much less than 10%.\(^{36}\) The doping level would need to be verified by elemental analysis before conclusions could be made regarding this.

![pH 13 Comparison of Overpotentials](image)

Figure 30. pH 13 5\textsuperscript{th} cycle cyclic voltammogram from 0 V vs. Ag/AgCl to 1 V vs. Ag/AgCl at a scan rate of 20mV/s. These potentials were then converted to respective potentials vs. RHE. Under these conditions, \( \text{CoO}_x \) and \( \text{NiO}_x \). The nickel oxidation peak is readily apparent at approximately 1.5 V vs. RHE.
In order to properly compare catalysts, proper conditions for comparing them must be chosen. For this, one of the most important points is a current density of 10 mA/cm$^2$.$^{57}$ This value as previously described, implies a 10% photon to energy conversion efficiency when the electrocatalysts is deposited on a photoanode for the OER reaction. The former CV scans appearing in Figures 29 and 30 were used to compare the current densities of the best catalysts at pH 13 and pH 7. However, current densities are normally taken using a rotating disk electrode with a high rpm to neglect mass transfer and diffusion terms.$^{56}$ This is because CV scans are complicated in terms of analyzing both the kinetics and thermodynamic properties of a system.$^4$ Because we are primarily interested in separating the kinetics at the electrode surface from the thermodynamics, this must be taken into account.

Tables 9 and 10 summarize the overpotentials calculated at current densities 1 mA/cm$^2$, 5 mA/cm$^2$, and 10 mA/cm$^2$ (if applicable) at pH 7 and pH 13 respectively. To determine the overpotential 1.23 V ($E_{\text{reversible}}$ for the OER) was subtracted from each potential reading vs. the RHE. This is neglecting an uncompensated resistance of the cell term, but this is likely only 4 mV or so. The reason the overpotential can be determined vs. the RHE in this manner is because the RHE’s potential dependence compared to the standard hydrogen electrode (SHE) for pH is the same.$^{64}$
Table 8. pH 7 overpotentials at various current densities. These were calculated by linear extrapolation of the two nearest points in current density values of the forward scan of the 5th cycle Cyclic voltammograms.

<table>
<thead>
<tr>
<th>Material</th>
<th>1 mA/cm²</th>
<th>5 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>0.740</td>
<td>--</td>
</tr>
<tr>
<td>Thick α- Fe₂O₃</td>
<td>0.636</td>
<td>0.897</td>
</tr>
<tr>
<td>CuFeO₂ non-aqueous</td>
<td>0.672</td>
<td>0.891</td>
</tr>
<tr>
<td>CuFeO₂ aqueous</td>
<td>0.677</td>
<td>0.900</td>
</tr>
<tr>
<td>NiOₓ</td>
<td>0.455</td>
<td>0.792</td>
</tr>
<tr>
<td>CoOₓ</td>
<td>0.244</td>
<td>0.683</td>
</tr>
</tbody>
</table>

Table 9. pH 13 Overpotentials at various current densities. These were calculated by linear extrapolation of the two nearest points in current density values in the forward scan of the 5th cycle cyclic voltammograms.

<table>
<thead>
<tr>
<th>Material</th>
<th>1 mA/cm²</th>
<th>5 mA/cm²</th>
<th>10 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>0.415</td>
<td>0.591</td>
<td>0.742</td>
</tr>
<tr>
<td>α- Fe₂O₃</td>
<td>0.511</td>
<td>0.602</td>
<td>0.695</td>
</tr>
<tr>
<td>CuFeO₂ non-aqueous</td>
<td>0.455</td>
<td>0.553</td>
<td>0.657</td>
</tr>
<tr>
<td>CuFeO₂ aqueous</td>
<td>0.457</td>
<td>0.542</td>
<td>0.630</td>
</tr>
<tr>
<td>NiOₓ</td>
<td>0.198</td>
<td>0.441</td>
<td>0.540</td>
</tr>
<tr>
<td>CoOₓ</td>
<td>0.229</td>
<td>0.417</td>
<td>0.486</td>
</tr>
<tr>
<td>MnOₓ</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>FTO</td>
<td>0.718</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Thin α-Fe₂O₃</td>
<td>0.447</td>
<td>0.544</td>
<td>0.634</td>
</tr>
<tr>
<td>0% Ni doped α-Fe₂O₃</td>
<td>0.558</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2% Ni doped α-Fe₂O₃</td>
<td>0.467</td>
<td>0.540</td>
<td>0.603</td>
</tr>
<tr>
<td>5% Ni doped α-Fe₂O₃</td>
<td>0.441</td>
<td>0.526</td>
<td>0.604</td>
</tr>
<tr>
<td>10% Ni doped α-Fe₂O₃</td>
<td>0.422</td>
<td>0.504</td>
<td>0.581</td>
</tr>
<tr>
<td>15% Ni doped α-Fe₂O₃</td>
<td>0.495</td>
<td>0.580</td>
<td>0.658</td>
</tr>
</tbody>
</table>
Figure 36 shows a summary of the calculated overpotentials for the particular catalysts at specific current densities in pH 13 solution (0.1 M NaOH) so that they can be readily compared. As a general trend, the current density increases as a function of overpotential (defined as the potential beyond 1.23 V vs. RHE) as also shown in figure 34. From this we see that at 1mA/cm$^2$ NiO$_x$ has the lowest overpotential followed by cobalt oxide. However, cobalt oxide has a slightly lower overpotential at 5 mA/cm$^2$ and a much lower overpotential at the 10 mA/cm$^2$ threshold. At all current densities (as seen in the previous CV scans) the 10% Ni-doped Fe$_2$O$_3$ has a lower overpotential. As also seen in the cyclic voltammogram, thin Fe$_2$O$_3$ has a significantly lower overpotential as thick Fe$_2$O$_3$.

Analogous to Figure 31 for pH 13, Figure 32 plots the overpotentials at specific current densities for the pH 7 electrolyte. However, no catalyst tested reached a current density of 10 mA/cm$^2$ in the selected region, so only the catalysts that achieve a 5 mA/cm$^2$ are compared in the figure. As previously stated, this is likely due to a different mechanism occurring for water oxidation at neutral pH than under alkaline conditions. At 1 mA/cm$^2$, cobalt oxide had the lowest overpotential, followed by nickel oxide. Thick Fe$_2$O$_3$ and non-aqueous CuFeO$_2$ had very similar overpotentials at this current density as well as at 5 mA/cm$^2$. There was a much larger increase in overpotential for cobalt oxide going from 1 mA/cm$^2$ to 5 mA/cm$^2$ than for nickel oxide over the same range of current densities.

Finally, it is important to compare catalysts tested at both pH 7 and pH 13. Figure 33 compares the overpotentials at both 1 mA/cm$^2$ and 5 mA/cm$^2$ for pH 7 and pH 13. These plots follow the same color coding as used in Figures 31 and 32 for ease of identifying
trends between materials. One interesting thing to note is that for CoOₓ the overpotential at 1 mA/cm² changes very little from pH 7 to pH 13. However, the overpotential is quite different for cobalt oxide between these two pH values. For both pH values Fe₂O₃ and the non-aqueous CuFeO₂ the overpotentials follow similar trends. However, at pH 7 the overpotentials at both current densities is lower for Fe₂O₃ than for non-aqueous CuFeO₂. At pH 13, the trend is reversed and CuFeO₂ has lower overpotentials at both current densities than Fe₂O₃. In future experiments it will be interested to investigate how the overpotential for water oxidation relates to the excited state soft X-ray spectroscopy spectrum.
Figure 31. Comparison of select catalyst overpotentials at 1mA/cm$^2$, 5 mA/cm$^2$, and 10 mA/cm$^2$ at pH 13.
Figure 32. Comparison of Overpotentials at 1 mA/cm² and 5 mA/cm² for select catalysts at pH 7.
Figure 33. Comparison of overpotentials for select catalysts at different current densities at pH 7 and pH 13.
4.3 Effect of Nickel doping on Overpotential of Fe$_2$O$_3$

As shown in the above section, the development of nickel iron oxides are one strategy of lowering the overpotential for water oxidation.$^{36}$ Liu et al. even found that nickel doped Fe$_2$O$_3$ can be photoactive for the evolution of oxygen. So far we have not been able to reliably reproduce photoactivity with this catalyst, however, it is possible we could make photocatalytic materials for water oxidation in the near future. The overpotential for the OER was compared to the doping content in 0.1 M NaOH at pH 13. These experiments were conducted under the same conditions as the above experiments at pH 13.

Figure 34 shows the effect of nickel doping on the overpotential at pH 13. It is interesting to note that pure NiO$_x$ has the lowest overpotential for water oxidation until a current density of about 17 mA/cm$^2$ is reached. This is different from some findings in the literature that show Ni-Fe oxides tend to show lower overpotentials than that of nickel or iron oxides alone.$^{65}$ Preparation method is well known to affect electrocatalysts.$^3$ Because the NiO$_x$ is prepared through a pulsed potential step method and the nickel doped Fe$_2$O$_3$ samples were prepared through a potential cycling method, this could affect surface morphology of the samples. SEM imaging with EDX analysis alongside XPS analysis of these electrocatalysts could help understand the effect of this on activity of these catalysts in the future. It is also interesting to note that the thicker 0% doped Fe$_2$O$_3$ catalyst has much higher overpotentials at all current densities.
The thick 2% and 5% nickel doped iron oxide catalysts have significantly lower overpotentials with 5% being better at lower current densities and 2% better at current densities above 9 mA/cm². The thicker 5% nickel doped Fe₂O₃ catalyst has nearly the same overpotential at all current densities as the thin Fe₂O₃ sample. Of the doped samples, 10% doping clearly has the lowest overpotential except at current densities higher than 20 mA/cm². Interestingly, 15% doping has higher overpotentials than any of the other doping percentages. The overpotential for the OER decreases up to 10% nickel doping and then the overpotential increases again by the time 15% doping is achieved. To verify these doping levels, either atomic absorption spectroscopy (AA) or inductively-coupled plasma mass spectrometry (ICP-MS) should be used to quantify metal content in the catalysts. Additionally, these catalysts were compared much like the other catalysts prepared at pH 7 and pH 13 before. Figure 35 compares these catalysts at 1 mA/cm², 5 mA/cm², and 10 mA/cm² (if applicable). This figure helps demonstrate what was just described in figure 34.
Figure 34. Effect of nickel doping of Fe$_2$O$_3$ on the overpotential for water oxidation. A scan rate of 20 mV/s was used sweeping in the positive direction from 0 V to 1 V vs. Ag/AgCl. These potentials were then converted to RHE values.
Figure 35. Comparison of nickel doped catalysts at pH 13 at various current densities. The overpotential at each current density was found by subtracting the OER equilibrium potential from the potential vs. RHE at various current densities.
4.4 Water Oxidation Conclusions

Nickel oxide is a great catalyst for water oxidation along with cobalt oxide. Cobalt or nickel oxide produces a lower overpotential over the other based on the current density investigated. The overpotentials of various catalysts were compared at current densities of 10 mA/cm², 5 mA/cm², and 1 mA/cm² for pH 13. The best catalysts from pH 7 were also compared at current densities of 1mA/cm² and 5 mA/cm². Doping hematite with even just a few percent nickel had a dramatic effect on the overpotential for the water oxidation reaction at pH 13. By varying the amount of nickel present in Ni-doped Fe₂O₃, you can change the overpotential for water oxidation. The overpotential decreases as more nickel is doped in the Fe₂O₃ up to a 10% doping. Beyond this, the overpotential increases again by 15% doping. 10% nickel doped Fe₂O₃ had an intermediate overpotential between that of NiOₓ and thick Fe₂O₃. Even though the nickel-doped iron oxide catalysts were nearly 4 times as thick as the thin iron oxide catalyst, there was still a lower overpotential for the 10% doped than the thin Fe₂O₃ sample.

4.5 X-ray Absorption Spectroscopy Future Studies

X-ray absorption spectroscopy (XAS) is an element, oxidation state, and spin specific technique. However, most XAS experiments are performed at synchrotron facilities such as Stanford or Argonne National labs. Unfortunately, synchrotron radiation makes it difficult to do time dependent studies, of which there is great importance in energy research to study charge transfer and electron-hole pair recombination. Synchrotron
facilities can be used to investigate time-dependent processes on a picosecond time scale. Charge transfer kinetics frequently happen in hundreds of femtoseconds.

Through the use of a pump and probe beam creating high-harmonic generation, it is possible to probe materials in the soft X-ray region (20-120 eV) on a femtosecond time scale. This is possible with a table-top soft X-ray system. Our future studies will focus on utilizing this system in our lab to investigate our hypothesis for both the CuFeO₂ heterojunction material for CO₂ reduction as well as Ni-doped Fe₂O₃ for the water oxidation reaction. Because there is a large overlap of 3 p and 3 d wave functions leads to 10-1000 times higher absorption cross section. This means that using the tabletop system to look at the M₂,₃ edge of metal oxides will be much more sensitive than other types of XAS spectroscopy. We will use this technique to study the different metal oxides prepared for CO₂ reduction and water oxidation experiments, and then study the ground and excited states of each.

Figure 36 shows a schematic of the instrumentation for soft X-ray transient absorption spectroscopy used in our group. In this instrumentation, an 800 nm laser beam from a Ti: Sapphire laser is focused inside a semi-infinite gas cell where X-rays are generated. These X-rays are then focused onto a toroidal mirror and then focused onto the sample. Once the radiation passes through the sample, it is spectrally dispersed by a holographic grating. The resulting spectrum is measured on a charge-coupled device (CCD). The entire beam line is contained in a series of vacuum chambers because air will absorb the radiation. Part of the 800 nm radiation is split and frequency doubled using a BBO crystal to produce a 400 nm pump beam. The 400 nm pump beam photoexcites the
sample from outside the vacuum chambers, while the X-rays are used to probe perturbations in absorption within the sample. A delay stage is used to overlap the pump and the probe beams in space and time. This delay can be controlled to probe charge transfer in a material.
Figure 36. Instrumentation for tabletop soft X-ray Transient Absorption Spectroscopy.
This technique has been used recently to investigate charge transfer in single hematite samples by Vura-Weis et al.\textsuperscript{67} In this study, a transient absorption soft X-ray spectroscopy system was used to investigate the M\textsubscript{2,3} edge of Fe. This edge corresponds to exciting an electron from a 3p state to a valence state (3d orbital). Pertinent figures from this work appear in Figures 37 and 38 for the purposes of explaining how this technique can be applied to transition metal oxides. In Figure 37 on the left is shown a general concept for the experiments ran by Vura-Weiss et al.\textsuperscript{67} The main objective of this work was to determine the excited state of hematite. The spectrum on the right shows the oxidation state specificity of this technique at the Fe M\textsubscript{2,3} edge. In this experiment, a 400 nm pump pulse was used to excite the sample and it was monitored in time by overlapping with an XUV pulse generated from a semi-infinite gas cell in a very similar setup to the one in our lab. In the figure, the black curve shows the Fe\textsuperscript{3+} ground state, the blue curve corresponds to the Fe\textsuperscript{2+} ligand-to-metal charge transfer (LMCT) excited state, and the red curve corresponds to a d-d excitation, where an electron doesn’t leave an Fe\textsuperscript{2+} atom, but instead excites an electron from a t\textsubscript{2g} to an e\textsubscript{g} orbital.

Figure 38 shows the experimental results of the studies with hematite. The fast decay (240 fs) of the Fe\textsuperscript{2+} excited state corresponds to hole thermalization from the O 2p orbitals to the Fe 3d orbitals. There is a strong bleaching at 57.4 eV on the graph on the left. In B we see traces at specific energies as a function of delay time between the pump and probe pulse.
Figure 37. Summary of work by Vura-Weis et al on hematite with tabletop XAS experiments. On the left appears the potential process that occurs during excitations, while A) shows the XAS calculated spectra for different excited states. Adapted with permission from (Vura-Weis, J.; Jiang, C.-M.; Liu, C.; Gao, H.; Lucas, J. M.; de Groot, F. M. F.; Yang, P.; Alivisatos, A. P.; Leone, S. R. J. Phys. Chem. Lett. 2013, 4 (21), 3667–3671.). Copyright (2013) American Chemical Society.  

So why would the copper iron oxide be different? Most literature agrees that the valence band maximum in CuFeO$_2$ is composed of Cu 3d orbitals, so hole thermalization in this material will leave the iron in the redox active 2+ excited state. Consequently, if we repeat the Vura-Weiss experiment for our active copper iron oxide catalyst, we would expect to observe a long-lived Fe$^{2+}$ excited state, contrary to the case for pure Fe$_2$O$_3$. Studies in the very near future for CO$_2$ reduction will focus on proving this hypothesis. By investigating excited and ground state spectra of our material we can determine where the hole is thermalizing to and the exact active site for CO$_2$ reduction to acetate.

For our future water oxidation studies, the intent is to use our XAS system to determine which active site or sites produce lower overpotentials for water oxidation. This would first involve the study of NiO$_x$ and Fe$_2$O$_3$ in their ground and excited states. We can then compare this to the excited state of different doping levels of nickel in the iron oxide. Additionally, it will be interesting to study the effect of the buried interface of the electrocatalysts with the semiconductor anode in more detail than has been done.$^{25}$

The work presented in this thesis represents a start in my studies of photoelectrocatalysis and electrocatalysis for important energy applications. By producing and studying single and mixed metal oxides, I hope to contribute to this exciting field in the realms of water oxidation and CO$_2$ reduction to high energy dense products.
References:

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