Photoelectrochemical Investigations on Novel Earth Abundant Solid State Catalysts for Solar Water Oxidation

Nathaniel Branimir Kurtz

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Photoelectrochemical Investigations on Novel Earth Abundant Solid State Catalysts for Solar Water Oxidation

Nathan Kurtz

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Submitted to the Honors College of
The University of Southern Mississippi
In Partial Fulfillment
of the Requirement for the Degree of
Bachelor of Science
in the Department of Chemistry and Biochemistry

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Abstract

In light of a looming fossil fuel scarcity, many forms of alternative, clean energy production are being researched in order to provide a more sustainable source of energy production for the future. One area of research is on using novel, abundant catalytic materials in conjunction with semiconducting materials to drive the splitting of water in order to produce hydrogen gas, an energy-rich fuel. Currently, efficiency is limited by the energy bottleneck posed by the oxygen evolution reaction (OER) half of water splitting. In this work, cobalt selenide (CoSe) catalyst paired with the semiconductor iron oxide (Fe$_2$O$_3$) has been identified as a particularly promising system. The results in this study show that CoSe is highly active for water oxidation and greatly increases the OER activity as compared to Fe$_2$O$_3$ alone. Studies have also been conducted to show the variation in maximum OER activity with changing electrodeposition time of CoSe, and an optimal deposition time has been identified. Using this deposition time, the water-splitting activity of CoSe/Fe$_2$O$_3$ was measured under both light and dark conditions. Scanning electron microscope (SEM) images of films have been taken to observe surface morphology and UV-Vis measurements have been taken to confirm the identity of the deposited films.

**Keywords:** Solar Energy, Solar Water Splitting, Photoelectrochemical, Semiconductor, Catalyst, Sustainability
Dedication

I dedicate this work to my brother, Ben, who has always supported me and celebrated my accomplishments. No one could ask for a better brother.
Acknowledgements

I would like to thank my advisor, Dr. Wujian Miao, for being a continual source of guidance and support. I would also like to thank Arun Siddarth Sridhar, for being a continual source of answers to my never-ending questions. Additionally, I would like to thank the Drapeau Center for Undergraduate Research for partially funding this project through the Eagle SPUR grant.
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>EDX</td>
<td>Energy-Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped Tin Oxide</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
</tr>
<tr>
<td>OCP</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen Evolution Reaction</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>TW</td>
<td>Terawatt</td>
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Chapter 1: Introduction

Photoelectrochemical (PEC) water splitting stores solar energy as chemical energy in the form of H₂ gas.¹ The basic components of a PEC cell consist of light, water, and a catalyst.¹ A catalyst is something that reduces the energy required to begin a reaction (activation energy). The energy from light by itself is not enough to drive the reaction, so a catalyst must be added to the system.²,³ In a PEC cell, there are two reactions occurring, the “oxidation” of water into O₂, and the “reduction” of water into H₂. Oxidation occurs at the photoanode, an electron-deficient material that takes electrons from water, causing O₂ to form. Reduction occurs at the photocathode, an electron-rich material that donates electrons to water, forming H₂. Of the two reactions, oxidation has the highest activation energy. The rate and efficiency of any reaction is limited by its most difficult (energy intensive) step. As such, efficiency can be most readily improved by designing a catalyst that lowers the activation energy of the oxidation half of the cell.⁴,⁵

To understand the goal of this project, the composition of the photoelectrodes (photoanode/cathode) must be further explained. Each electrode consists of a semiconductor material, usually a transition metal oxide such as titanium oxide or iron oxide, and a catalyst on its surface. Photons (light particles) are absorbed by the semiconductor and converted into electrons and electron-deficient “holes”. Electrons are moved to the surface of the photocathode, driving reduction, while the holes are moved to the photoanode, driving oxidation. At the surface of the electrodes, a catalyst reacts with the electrons and holes, respectively, and water to produce H₂ and O₂, respectively.⁶ Recent advances have seen promising improvements in oxygen evolution reaction (OER) activity by using catalysts that are based on earth-abundant transition metal chalcogenides and sulfides (M-S, M-Se), such as cobalt selenide, or nickel selenide. These
catalysts are attractive because they are stable, cost-effective, and can be easily deposited on the electrode surface at low temperatures.\textsuperscript{[7]}

Given the promising scope of these materials, there are very limited studies on their application as co-catalysts for photoelectrochemical water splitting and effects of catalyst composition for electrocatalytic and photoelectrocatalytic activity. The main goal of this project is to focus on the photoelectrochemical solar water splitting applications of these co-catalysts tailored at different compositions and deposition conditions, which could lead to the optimization of efficient photoelectrodes for low applied bias water splitting and also possibly result in the fundamental understanding of the role of active catalyst components in the photoelectrode. These proposed studies would be helpful to provoke further investigations in this area and towards the development of tandem solar water splitting cells.
Chapter 2: Literature Review

2.1 Global Energy Crisis and the Need for Solar Energy Storage

One of the most pressing scientific challenges currently being faced is the issue of rising energy needs along with the rapid consumption of fossil fuels. Currently there are sufficient technology and coal reserves to provide enough energy to keep up with centuries’ worth of population growth and economic development, but not without environmental catastrophe.\(^8\) The power consumption for the global population of nearly 7 billion people in 2011 was 15 TW (terawatts, \(10^{12}\) W), and these numbers are expected to increase to 30 TW and 9 billion people by 2050.\(^9\) To combat this it is necessary to transition to clean, renewable forms of energy to provide for the increasing global energy needs. Of the sources of renewable energy, solar energy has the potential to deliver 20 TW of the world’s energy supply.\(^8,10\) In order for solar cells alone to provide this 20 TW of energy, a total surface area equivalent to France and Germany combined would need to be covered in solar cells, which would require producing 650 m\(^2\) of solar cell panels per second, 24/7 for 365 days per year, for the next 40 years.\(^9\) Besides the daunting logistics needed to accomplish this, as the contribution of solar energy to total energy supply increases, electricity network operators will have increasing difficulty dealing with the intermittent nature of solar energy (day/night cycle, clouds).\(^9\) Thus if the full potential of solar energy is to be exploited, a large-scale method of storing solar energy in the form of fuel will be needed.

2.2 PEC Water Splitting Background

Of the conventional fuels which can be used to store solar energy, hydrogen is the most attractive, having the highest volumetric energy density and being a non-carbon energy source.\(^11,12\) There are several methods\(^13,14\) for producing hydrogen gas from solar energy, such as photocatalytic water splitting, photovoltaic electrolysis, thermochemical conversion,
photobiological hydrogen production, and PEC water splitting. PEC has several major advantages in that hydrogen and oxygen are produced at separate electrodes, avoiding serious safety concerns,[11] and allowing the gasses to be easily separated. It can be carried out at room temperature, and a PEC cell can be constructed entirely out of inorganic materials, lending the system robustness which is difficult to achieve with organic systems.[9]

In a PEC water splitting cell, the energy from light is absorbed by a semiconducting electrode to produce electron hole pairs. The holes drive the oxidation of water to O2 gas at the anode (Eq. 2.1), and the electrons drive the reduction of water to H2 gas at the cathode (Eq. 2.2).

\[
2\text{H}_2\text{O} + 4h^+ \rightleftharpoons 4\text{H}^+ + \text{O}_2 \quad E^\circ = 1.23 \text{ V vs NHE} \quad (\text{Eq. 2.1})
\]

\[
4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2 \quad E^\circ = 0 \text{ V vs NHE} \quad (\text{Eq. 2.2})
\]

Equations 1 and 2 show that the PEC water splitting process has a standard potential of 1.23 V. In actuality, however, an additional “overpotential” is needed to activate the process. Under real conditions the required potential to split water is 1.9-2 V. An ideal PEC system would have the necessary potential provided by the generation and separation of electrons and holes at the interface between the semiconductor and the electrolyte. This has been the pursuit of much research for the past four decades.[15-19]

### 2.3 Improvements on PEC Performance

Among the advancements made toward improving the efficiency of the PEC cell, the dual-absorber system (Figure 2.1) is notable.[20] This strategy involves using two light absorbing semiconducting materials on each electrode, rather than one. These would then be referred to as the photoanode and photocathode,
respectively. Using multiple light absorbers allows for an increased range of wavelengths to be absorbed to produce greater numbers of electron hole pairs, producing a greater potential, and thus lowering the overpotential needed.

An essential part in increasing the efficiency of PEC water splitting is the incorporation of catalysts.\cite{21,22} Catalysts are chosen individually for the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Catalysts reduce the kinetic overpotential required to activate water oxidation and reduction, enhance charge separation, prevent electron-hole recombination, and improve the durability of the semiconductor photoelectrodes by protecting them against photocorrosion. The reduction of the required activation energy brings the bias required for water splitting closer to the theoretical value of 1.23 V.

### 2.4 Improving OER Performance

As the OER is the more energy-intensive half-reaction, much of the current research has been focused on improving the OER catalyst. $\text{IrO}_2$\cite{24,27,28} and $\text{RuO}_2$\cite{23-26} have been the highest performing OER catalysts, however, their cost makes them undesirable, spurring research into earth-abundant non-noble metal-based catalysts. Current research into such alternatives are focused on $\text{Ni}$-, $\text{Mn}$-, and $\text{Co}$-based metal oxides and hydroxides\cite{21} due to their redox properties and stability that is comparable to noble metals. Ni and Co selenides are also emerging as potential new catalysts with good stability and low overpotentials.\cite{29-32} To date, there have been no optimization studies on these new catalysts as to how thickness or composition ratio affects the efficiency of the OER half-reaction in conjunction with a photoanode.

This project will focus on studying $\text{CoSe}$ as a catalyst in conjunction with $\text{Fe}_2\text{O}_3$ as a photoanode. CoSe is being examined as the catalyst of choice over other cobalt catalysts such as $\text{CoP}$ or $\text{CoS}$ because of its reported superior performance for OER.\cite{33}
Chapter 3: Methodology

3.1 Electrode Preparation via Electrodeposition

Unless otherwise stated, fluorine-doped tin oxide (FTO) was used as the substrate, and was cleaned by sonication in 3:1 deionized water and ethanolamine solution, followed by deionized water prior to deposition. Electrodeposition is a method of growing thin films in which a conductive substrate is placed in an electrolyte solution containing the salt of the desired film. A potential is applied between the substrate and the counter electrode, causing redox chemistry to take place at the substrate surface, depositing the desired material on the substrate. For some films, a post-deposition thermal annealing was performed at 500 ºC, causing structural rearrangements.[34] The film growth can be optimized by controlling a variety of parameters such as electrolyte composition, pH, potential, and deposition time.[35]

3.2 Performance Measurements

Once the photoanodes were prepared, a variety of methods were employed to characterize the electrodes and measure their performance in terms of photocurrent production, capacitance, charge carrier density, and stability.

3.2.1 PEC Impedance Spectroscopy

Electrochemical impedance spectroscopy is a technique in which an electrochemical system is perturbed by an AC signal of variable frequencies in order to measure the impedance. This provides information on the charge transfer resistance, solution resistance, and double layer capacitance at the electrode-electrolyte interface. This information is usually obtained in the form of Nyquist plots.
3.2.2 Three Electrode $j$-$V$ and Photocurrent Onset Measurements

Three electrode $j$-$V$ and photocurrent onset measurements test a material’s ability to produce photocurrent ($j_{ph}$) at a given potential, and aid in the measurement of photocurrent onset potential ($E_{onset}$). Figure 3.1 shows a representative three electrode photocurrent measurement for a photoanode.

3.2.3 Stability Measurements

Measurements were made to study how stable the catalyst is after prolonged use by measuring the photocurrent produced at a constant potential and observing how much the photocurrent is reduced over time.

3.3 Characterization

3.3.1 Scanning Electron Microscope (SEM) Imaging

SEM imaging was used to obtain images of the films grown in order to determine their morphology as well as compare their degradation prior to and after stability studies were performed.

3.3.2 Energy-Dispersive X-Ray (EDX) Spectroscopy

EDX spectroscopy will be used to determine the weight percent composition of grown films in order to verify that the films which are grown are in fact of the composition that was intended.

3.3.3 UV-vis Spectroscopy

UV-vis spectroscopy will be used to help determine the band structure of certain materials and films by studying the light absorbed as a result of electron energy transitions.
3.4 Materials

Iron (III) chloride hexahydrate (97%), lithium chloride (99%), cobalt (II) acetate tetrahydrate (reagent grade), sodium tetraborate decahydrate (>99.5%), and ethanolamine (>98%) were obtained from Sigma-Aldrich. Sodium fluoride (>99.0%) was obtained from Fluka Chemika. Potassium chloride (A.C.S. reagent) was obtained from Fisher Chemicals. Sodium Selenite (99.75%) was obtained from Alfa Aesar. Deionized water produced using a Millipore Advantage 5 system was used as a solvent for preparing all aqueous solutions.

3.5 Experimental Procedure

3.5.1 Electrode Preparation

Fe₂O₃ photoanodes were prepared by potentiostatic electrodeposition.[34] The working electrode consisted of 1 cm² FTO, which was cleaned by sonication in a 3:1 deionized water and ethanolamine solution, followed by deionized water, for 30 minutes each. Ag/AgCl (3.0 M KCl) and Pt foil were used as the reference and counter electrodes, respectively. The deposition was carried out by cycling from -0.47 V to 0.43 V vs Ag/AgCl (3.0 M KCl) for 25 cycles in a bath consisting of 5 mM FeCl₃, 0.1 M KCl, 5 mM NaF, and 1 M H₂O₂. The resulting orange-colored films were then rinsed with deionized water, allowed to air dry, and annealed in air at 773 K for 1 h to produce the yellow-orange FTO/Fe₂O₃ electrode for study. The CoSe catalyst was deposited[35] on FTO/Fe₂O₃ by electrodeposition at -0.45 V vs Ag/AgCl (3.0 M KCl) in a bath consisting of 0.065 M Co(CH₃COO)₂, 0.2 M LiCl, and 0.035 M Na₂SeO₃ at pH 4.7 (adjusted with HCl) to produce the FTO/Fe₂O₃-CoSe photoanode.

Figure 3.2 is the UV-vis spectrum of FTO/Fe₂O₃, showing absorption in the visible region. The absorption edge at 590 nm corresponds to a band gap of 2.10 eV.
Figure 3.2 UV-vis spectrum of FTO-Fe$_2$O$_3$ (Blanked with FTO). The absorption edge at 590 nm corresponds to a 2.10 eV band gap.

3.5.2 Physico-chemical Characterization

Scanning electron microscope (SEM) images and energy-dispersive X-ray data (EDX) of FTO/Fe$_2$O$_3$-CoSe were obtained with a Zeiss Sigma VP FEG SEM. An Evolution 300 Thermo-Scientific spectrophotometer was used to obtain the UV-vis spectrum of photoelectrodes, with FTO substrate used as a blank.

3.5.3 Photoelectrochemical Studies

As shown in Figure 3.3, PEC measurements were carried out in a three-electrode setup using a 50-mL quartz beaker as the cell, an Ag/AgCl (3.0 M KCl) as the reference electrode, a Pt wire as the counter electrode, and 1 cm$^2$ FTO/M (where M = Fe$_2$O$_3$ or Fe$_2$O$_3$-CoSe) as the working electrode, respectively. A 0.050 M pH 9.0 borate buffer solution was used as the electrolyte for all
experiments with or without the presence of catalyst M of different thicknesses. Electrochemical impedance spectroscopic (EIS) measurements were carried out under open circuit potential (OCP) with a 5.0 mV AC signal superimposed. Mott Schottky plots were obtained at a frequency of 962 Hz. An electrochemical workstation (CH instruments, Model 660 A) was used to conduct electrochemical experiments. Simulated solar light for PEC studies was provided by a 150 W Xe lamp solar simulator (ABET technologies) with an AM 1.5 G filter providing a light intensity of 1000 W/m² (1 sun).

Figure 3.3 Representative cell scheme for photoelectrochemical water splitting using FTO/Fe₂O₃-CoSe. Incident light passes through the transparent conducting working electrode FTO, reaching light-sensitive Fe₂O₃ to generate electrons and holes. Holes move to the catalyst, CoSe, to be used in the OER while electrons move to the Pt counter electrode to be
used in the HER. Current is measured between the working and counter electrode, while potential is measured between the working and Ag/AgCl reference electrode.
Chapter 4: Results and Discussion

4.1 Optimization of FTO/Fe$_2$O$_3$-CoSe Films

Figure 4.1 CoSe catalyst deposition time vs current density for FTO/Fe$_2$O$_3$-CoSe photoanodes at 0.8 V vs Ag/AgCl. The optimal deposition time is shown to be 10 min, producing the most photocurrent.

Figure 4.1 shows the effect of different deposition times of CoSe on current density. Initially, increasing deposition time resulted in increased current density, up to 10 minutes, after which current density decreases with increasing deposition time. This can be attributed to the fact that, at first, as deposition time increases, there is more catalyst assisting in electron/hole separation, resulting in higher OER activity. After 10 minutes, however, the thickness of the film becomes inhibitory due to increased resistance. A thicker film also means that charge carriers are more likely to recombine before being able to participate in water splitting activity. The optimized
deposition time for CoSe on FTO/Fe₂O₃ has been identified as ten minutes, with a maximum photocurrent density of -3.98 mA/cm².

Figure 4.2 500 X magnification SEM images of FTO/Fe₂O₃-CoSe photoanodes at depositions times (a) 5 min, (b) 10 min, and (c) 15 min. This shows “islands” of Fe₂O₃ surrounded by a CoSe “sea,” with the amount of CoSe increasing with increasing deposition time.
Figures 4.2a-c and 4.3a-c show SEM images and their corresponding EDX spectra of FTO/Fe$_2$O$_3$-CoSe photoanodes at 5-, 10-, and 15-minute deposition times for CoSe, respectively. From the SEM images (Figure 4.2) it can be seen that the Fe$_2$O$_3$ is not a single, uniform layer. Rather, the Fe$_2$O$_3$ exists as “islands,” with CoSe filling the space between the islands. As deposition time is increases, there is a greater amount of CoSe between the islands of Fe$_2$O$_3$, similar to a rising sea level. From the EDX map images shown in Figure 4.4, which populate the SEM image with different colors corresponding to different elements, it can be seen that the darker, flat regions correspond to Fe$_2$O$_3$, while the lighter, spherical regions correspond to CoSe.

![EDX Spectra of FTO/Fe$_2$O$_3$-CoSe at deposition times of (a) 5 min, (b) 10 min, and (c) 15 min. The peaks relate the relative number of atoms of particular elements found in the films.](image-url)
Figure 4.4 EDX color map of 15 min deposition FTO/Fe$_2$O$_3$-CoSe. A color is assigned to each element, showing the composition of the films visually. This confirms that the “islands” correspond to Fe$_2$O$_3$, since that is where the images are populated by blue (iron) and red (oxygen). Less cyan (cobalt) and purple (selenium) in those regions shows that the CoSe is filling in between the “islands.”

Table 4.1 Effects of Deposition Time on CoSe Composition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5 min</th>
<th>10 min</th>
<th>15 min</th>
</tr>
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<tbody>
<tr>
<td>Element</td>
<td>Co</td>
<td>Se</td>
<td>Co</td>
</tr>
<tr>
<td>Mass ratio</td>
<td>0.8</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>Molar ratio</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Molar ratios of cobalt to selenium were calculated using EDX data, reported in Table 4.1. The EDX data shows that with increasing deposition time, the amount of CoSe by weight percent is increasing. Unlike the 1:1 molar ratio of Co:Se for the 5- and 10-min deposition times, the 15-
minute deposition time shows a molar ratio of 1:1.4, indicating a compositional change at longer deposition times.

4.2 Photocurrent Measurements

![Figure 4.5](image)

Figure 4.5 (A) Linear sweep voltammograms of FTO/Fe$_2$O$_3$ in the absence of catalyst under (a) dark and (b) simulated solar radiation conditions. (B) Linear sweep voltammograms of FTO/Fe$_2$O$_3$-CoSe photoanode under (a) dark and (b) simulated solar radiation conditions. Both FTO/Fe$_2$O$_3$ and FTO/Fe$_2$O$_3$-CoSe show increased photocurrent under light, with FTO/Fe$_2$O$_3$-CoSe showing several orders of magnitude higher current density.
Figure 4.6 Linear sweep voltammograms of FTO/Fe$_2$O$_3$ in the (a) absence and (b) presence of catalyst, shuttering light approximately every 3 sec. The large spikes in current for FTO/Fe$_2$O$_3$-CoSe show that the addition of CoSe increases charge separation for electrons and holes generated by Fe$_2$O$_3$.

The linear sweep voltammograms for FTO/Fe$_2$O$_3$ and FTO/Fe$_2$O$_3$-CoSe (10 min deposition) photoanodes under dark and irradiated conditions are shown in Figure 4.5. It can be clearly seen that in the presence of CoSe, the OER activity is greatly enhanced. Fe$_2$O$_3$ by itself shows a maximum current density of $-4.01 \times 10^{-3}$ mA/cm$^2$ at 0.8 V vs Ag/AgCl. In the presence of CoSe, the maximum current density achieved was $-4.56$ mA/cm$^2$ at 0.8 V. Comparison of the onset potential shows that in the presence of CoSe, a ~0.5 V negative shift in onset potential is observed. Figure 4.6 shows that upon illumination, FTO/Fe$_2$O$_3$-CoSe has a much larger photocurrent
response than FTO/Fe₂O₃. This shows that the addition of the CoSe catalyst greatly increases OER activity.

4.3 Electrochemical Impedance Spectroscopy and Mott Schottky Plots

Figure 4.7 Electrochemical impedance spectra of FTO/Fe₂O₃ photoanodes in the (a) absence and (b) presence of CoSe catalyst under simulated solar radiation. The decreased impedance in the presence of catalyst indicates that CoSe improves charge separation.
Figure 4.8 Mott Schottky Plots of FTO/Fe$_2$O$_3$ photoanodes in the (a) absence and (b) presence of CoSe catalyst under simulated solar radiation. The decreased slope in the presence of catalyst indicates increased capacitance and a greater charge carrier density.

Figure 4.7 shows the EIS measurements comparing FTO/Fe$_2$O$_3$ and FTO/Fe$_2$O$_3$-CoSe in the form of Bode plots. This can be used to compare the capacitance of the two photoanodes. FTO/Fe$_2$O$_3$-CoSe shows a lower maximum impedance, indicating higher capacitance, supporting evidence that CoSe improves charge separation for water splitting.

The Mott Schottky plots (Figure 4.8a-b) provide further supporting evidence for CoSe as a facilitator of charge separation. The higher slope of (Figure 4.8a) FTO/Fe$_2$O$_3$ ($5.27 \times 10^{10}$) compared to (Figure 4.8b) FTO/Fe$_2$O$_3$-CoSe ($7.32 \times 10^{9}$) indicates a lower capacitance in the absence of CoSe catalyst. In addition to this, the Mott Schottky plots can be used to determine the charge carrier density $N_D$ for each material (with an area $A$ and relative permittivity $\varepsilon_r$) using the following formula:$$1/C^2 = \frac{2}{q^2} \frac{1}{N_D} - \frac{2}{q^2} \frac{1}{A \varepsilon_r} \times \ln \left( \frac{2eE}{kT} \right)$$
\[ N_D = \frac{1.41 \times 10^{32} \text{cm} \times \text{F}^{-2} \times \text{V}^{-1}}{\xi \times A^2 \text{cm}^4 \times |\text{slope}| \text{F}^{-2} \times \text{V}^{-1}} \] (5.1)

Using the Mott Schottky slopes, a 1 cm² electrode area, and \( \xi_r = 10 \text{,} \) the \( N_D \) values were calculated to be 2.67\times 10^{20} in the absence of catalyst, and 1.93\times 10^{21} in the presence of catalyst. The increased charge carrier density in the presence of catalyst complements the previous observations that CoSe improves OER activity. The positive slope indicates n-type semi-conductivity, which is appropriate for OER.
4.4 Stability Study

Figure 4.9 Stability study of FTO/Fe$_2$O$_3$ photoanodes under simulated solar radiation for the time region of (A) 0-500 s, and (B) 3200-3500 s. Potentials applied at (a) 0 V vs Ag/AgCl and (b) 1.10 V vs Ag/AgCl. The lack of significant change in current density indicates that the Fe$_2$O$_3$ film is very stable over time and does not decompose during OER.
Figure 4.10 Stability study of FTO/Fe$_2$O$_3$-CoSe photoanodes under simulated solar radiation for the time region of (A) 0-500 s, and (B) 3200-3500 s. Potentials applied at (a) 0 V vs Ag/AgCl and (b) 1.10 V vs Ag/AgCl. An initial decrease in current density indicates some portion of the CoSe is not strongly bound to the electrode surface. For the remainder of time, little change is seen in current density, indicating the film remains stable after the initial loss of material.
The stabilities of FTO/Fe$_2$O$_3$ and FTO/Fe$_2$O$_3$-CoSe over time are shown in Figures 4.8 and 4.9, respectively. For FTO/Fe$_2$O$_3$, there is no significant decrease in current over time. The faradaic current remains stable near -0.97 mA/cm$^2$. For FTO/Fe$_2$O$_3$-CoSe, there is an initial significant decrease in current density from -6.98 mA/cm$^2$ to -3.80 mA/cm$^2$ within the first 50 seconds. After this period, it slowly decreases over time to 2.50 mA/cm$^2$. This suggests that the topmost layer of the CoSe is not strongly bound to the electrode, causing some of it to be removed during OER.
Chapter 5: Conclusion

FTO/Fe$_2$O$_3$-CoSe was studied as an earth-abundant photoanode for OER and compared to FTO/Fe$_2$O$_3$. The films were characterized using UV-vis spectroscopy, SEM, and EDX. The LSV measurements showed a significant increase in photocurrent in the presence of CoSe, indicating that CoSe acts as a catalyst for OER and increases electron/hole separation. This was confirmed by EIS and Mott Schottky plots, which showed increased capacitance and charge carrier density in the presence of CoSe. Future studies will focus on improving the stability of the CoSe catalyst to improve its current production over time by changing variables such as deposition bath composition, and pH. Different catalyst materials such as Mn$_2$O$_3$, NiSe, and WO$_3$ may be used with Fe$_2$O$_3$ and other photoanode materials such as BiVO$_4$ to probe other promising material combinations for photoelectrochemical water splitting.
Literature Cited


