CO₂ Reduction on Cu Oxide Photoelectrodes

by

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Submitted in Partial Fulfillment of the Requirements
for the Degree of
Master of Science
in the
Chemistry
Program

YOUNGSTOWN STATE UNIVERSITY

May, 2012
CO₂ Reduction on Cu Oxide Photoelectrodes

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Abstract

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Copper electrodes were made with three different types of surfaces: copper metal, cuprous oxide, and cupric oxide. The metal electrode was made from a polished and chemically etched sheet, while the oxides were made by varying the thermal treatment of the copper metal in air. The electrodes were characterized by X-ray Photoelectron Spectroscopy and X-ray Diffraction. Background voltammetric behavior was consistent with theory as indicated by the Pourbaix diagram for Cu in aqueous media. The electrodes were then tested for activity toward catalytic electroreduction of carbon dioxide, CO₂. Cyclic voltammetry with and without CO₂ gave similar results, so that it was determined that any CO₂ reduction was occurring within the voltage range for H₂ evolution, which started at -0.7 V versus Ag/AgCl. Photoelectrochemical experiments were performed using a Xe arc light source. Cyclic voltammetry and chronoamperometric studies showed enhanced current behavior in the light. While chronoamperometry at -1.0 V generally showed current decay with time, the CuO electrode actually rose, supporting currents in excess of 100 mA after 10 min. Electrolyte samples taken after extended amperometry over an hour’s time and tested via Infrared Spectrometry showed a reduction product or products possessing O-H and C-H bonds.
Acknowledgements

My advisor
Dr. Clovis Linkous

My committee
Dr. Larry Curtin and Dr. Timothy Wagner

Others
Dr. Stephen Rhoden, Dr. Ruigang Wang, Dr. Linkous’s Research Group

NETL funding
DOE/NETL - URS Energy & Construction subcontract #RES1000286, "Co-catalyst Development for Photocatalytic Fixation of Carbon Dioxide at YSU"

DOE/NETL grant #DE-EE0004094, "Advance Automotive Fuels Research, Development, and Commercialization Cluster (OH)"

YSU Department of Chemistry and School of Graduate Studies for giving me this opportunity
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**Introduction:**

Carbon dioxide (CO₂) is one of the main greenhouse gases. It is emitted as a combustion product of fossil fuels from industrial processes and from automobiles. As the atmospheric concentration of CO₂ increases it is becoming more important to find a way to emit less CO₂. Much research interest is focused on ways to convert the CO₂ that is being formed every day through industrial processes into other more useful chemical compounds. These compounds include methanol, formaldehyde and formic acid, which are frequently the products of CO₂ reduction reactions. One way to reduce CO₂ levels in the atmosphere is through sequestration, of which there are many types. One of which is CO₂ fixation, which mimics natural photosynthesis that occurs in plants. This process, unfortunately, does not typically yield concentrations of organic compounds that are of great use industrially; therefore they would have to undergo further reactions, requiring the use of more resources to form compounds that the industries need. These compounds include; formic acid formaldehyde, and methanol. The introduction of a potential catalyst makes sense in this situation. A catalyst that could take CO₂ and water (H₂O) to form compounds such as methanol and formic acid in high yields would make the process better. This will be the focus of my research. Copper oxides have shown an ability to take the reaction products selectively to methanol, while producing negligible amounts of side products.
**Background:**

Fossil fuels are fuels formed from natural resources. These fuels include: coal, natural gas and petroleum. These fuels are thought to be formed from the fossilized remains of plants and animals, along with heat and pressure from the earth’s crust over millions of years. The amount of time required for these natural fuels to form lends to their name as non-renewable resources (01). A recent U.S. Department of Energy study states that an estimated 6.3 billion metric tons of CO₂ is added to the atmosphere annually (02).

**Figure 1:**

![Carbon Flux Diagram](image)

**Source:** Intergovernmental Panel on Climate Change, *Climate Change 2001: The Scientific Basis* (U.K., 2001)

*Shows naturally occurring CO₂ versus anthropogenic CO₂ (02)*
CO₂ sequestration is essentially a process which captures CO₂ from industrial processes, or flue gas, and stores it or converts it into other chemical compounds. Some of the more common sequestration techniques include underground storage in reservoirs, aging oil fields, carbon sinks and ocean water. Another technique is to take the flue gas and convert it into another chemical compound, such as methanol. This process is called carbon fixation (03).

**Solar Chemical/ Photochemical Energy:**

Solar chemical energy uses photons from the sun to drive a chemical reaction. In a photoelectrochemical cell, the photons that are absorbed generate electricity. When photons are absorbed by the semiconductor, electrons in the valence band of the semiconductor become free electrons in its conduction band. These free electrons create an electron deficient area otherwise known as an electron hole. When the free electrons move from the valence band to the conduction band, a voltage is created. When an external “load” is attached, electricity will flow out of the cell. This is demonstrated in Figure 2 (04).
Electronic Motion in a Photovoltaic Cell (04)

In photosynthesis, plants and algae use sunlight, CO₂ and H₂O to produce sugars and other organic compounds they can use as food, while simultaneously releasing oxygen (O₂) as a product (05). Carbon fixation also uses sunlight and a reaction of CO₂ and H₂O to form organic compounds such as methanol, formaldehyde and formic acid. CO₂ can also be reduced to carbon
monoxide (CO), which can then be reacted with other compounds to make more industrially useful compounds, such as methanol, formaldehyde and formic acid (06).

**Photocatalytic/ Membrane Approach:**

For the long term goal of this research a proton exchange membrane (PEM) is needed for the inside of the photoelectrochemical cell. One of the most common classes of PEM’s are perfluorosulfonic polymers, which create Nafion. Nafion is a semi-permeable membrane of ionomers, which holds water. The hydrated membrane acts as a barrier for gas permeation or gas transport (07). How do PEM’s work? When sunlight shines on a PEM containing a semiconductor material, protons and electrons become readily available on their respective side of the membrane, the protons can move freely through the membrane causing reactions to take place. Figure 3 shows a Nafion membrane that is being irradiated with light. The light causes electrons to come free from their valence shells and react, in this case, splitting water and allowing the resulting protons to move freely through the membrane to react with H⁺ on the other side forming H₂, or hydrogen gas (07).
Figure 3: 

PEM Membrane Diagram
Objective:

The scope of this project will be to create a catalyst to drive a photocatalytic reaction to reduce CO₂ in the presence of water vapor producing methanol among a few other organic compounds which may be industrially useful. This will be accomplished by using a light source and a photoelectrochemical cell containing the catalyst. CO₂ will be pumped through the electrolyte in the presence of H₂O to drive the following reactions:

- Carbon monoxide formation: \( \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O} \)
- Formic acid formation: \( \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCO}_2\text{H} \)
- Formaldehyde formation: \( \text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \)
- Methanol formation: \( \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \)
- Methane formation: \( \text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \)

Figure 4:

A Representation Of The Above Reactions (8)
The main drawback is the use of H₂O in this reaction, as CO₂ is not very soluble in water and therefore photoreduction will have to compete with hydrogen (H₂) and hydrogen peroxide (H₂O₂) formation. As shown below it is easier to form H₂ and H₂O₂ than it is to reduce CO₂, so there may be tendency to form these compounds instead of reduce CO₂. This is represented in the following reactions:

\[
\text{Photocatalyst} + 4hν \leftrightarrow 4e^- + 4h^+
\]

Water decomposition \[ 2\text{H}_2\text{O} + 4h^+ \rightarrow \text{O}_2 + 4\text{H}^+ \]

Hydrogen formation \[ 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2 \]

Hydrogen peroxide formation \[ \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \]

To circumvent the formation of these byproducts, various transition metal catalysts have been used. Some of those include cupric oxide (CuO), cuprous oxide (Cu₂O), titania or titanium dioxide (TiO₂) and zirconium dioxide (ZrO₂) just to name a few (08). The catalysts that have been chosen show great potential to selectively form methanol, which is one of the most industrially useful compounds. CuO and Cu₂O will each be used individually as catalysts, and then be used in a mixture to determine which of the chosen catalysts showed the best efficiency and selectivity.
**CuO, Cu₂O, and TiO₂:**

According to Material Safety Data Sheets (MSDS) data CuO and Cu₂O are known to be both harmful and dangerous for the environment, though they are naturally occurring. CuO is a black solid with a monoclinic crystal structure (figure E) and a C2/c space group (09). Cu₂O on the other hand is a brownish red solid cubic crystal structure and a Pn3m space group (10). Both have semiconductor properties. TiO₂ is said to be the most common semiconductor material used for this type of application, as it is readily available, inexpensive, harmless, and photostable (11).

**Figure 5:**

![Diagram](image)

The ac-plane view of the crystal structure of CuO, where the red atoms represent Cu and the blue atoms represent O.

Photocatalysis uses semiconductors to promote reactions in the presence of light. Semiconductors have a region in which no energy states can exist, also known as a band gap, where no electron states exist. This region extends from
the top of the valence band which is the highest occupied molecular orbital, to
the bottom of the conduction band or lowest unoccupied molecular orbital.
Semiconductors work because of the generation of electron hole pairs, where
an electron from the valence band will gain energy from a photon of light and
jump to the conduction band, driving the reaction as seen in Figure 6 (06, 08).

\[
\text{Photocatalyst } \stackrel{\hbar \nu}{\longrightarrow} e^- + h^+
\]

\[e^- + h^+ \rightarrow \text{heat}\]

CuO has a narrow band gap energy at approximately 1.4 eV while the
band gap for Cu$_2$O is approximately 2.1 eV which corresponds to the required
energy to excite an electron from the valence shell to the conduction band
which is possible under photocatalytic conditions (10, 12). A comparison of
the band gap energies of copper oxides and a few other semiconductor
materials used for photocatalytic reactions are shown in Table 1 below. Also
seen below is Figure 6, which shows band gap formation (08).
### Table 1:

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>band-gap energy (eV)</th>
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<tbody>
<tr>
<td>Si</td>
<td>1.1</td>
</tr>
<tr>
<td>WSe₂</td>
<td>1.2</td>
</tr>
<tr>
<td>CuO</td>
<td>1.4</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>2.1</td>
</tr>
<tr>
<td>R-Fe₂O₃</td>
<td>2.2</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>2.7</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.8</td>
</tr>
<tr>
<td>SiC</td>
<td>3.0</td>
</tr>
<tr>
<td>TiO₂ rutile</td>
<td>3.02</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.1</td>
</tr>
<tr>
<td>TiO₂ anatase</td>
<td>3.23</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>3.4</td>
</tr>
<tr>
<td>SnO₂</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
</tr>
</tbody>
</table>

**Band Gap Energies of some Semiconductors (08)**

**Figure 6:**

[Diagram Showing Band-Gap Formation (08)]
CuO has been extensively researched because of its properties and potential applications. CuO has been studied for its possible use as an electrode in lithium ion batteries. It has also been studied for its photochemical and photoconductive properties and its ability to oxidize hydrocarbons to form CO₂ and H₂O (12). CuO and Cu₂O have also been studied as a catalyst for the reduction of CO₂ to hydrocarbons, which is the focus of this research.

**What is in the literature?**

There are numerous articles in the literature which discuss the use of many different compounds and transition metal complexes as photocatalysts in the reduction of CO₂ to hydrocarbons. These compounds include TiO₂, CdS, ZrO₂, ZnO, MgO, Al(NO₃)₃, CuO and CuO₂ (08,13). These catalysts have been used individually, and also in mixtures. They have also used Cu metal as an electrode for the reduction of CO₂ (14). How were the catalysts made? There were many methods used to make these catalysts from synthesis to deposition. The methods which are the most relevant to this research are the ones which yielded the most methanol as a product. Kobayashi et al (15) used a method which mixed solutions to form a slurry from which they made their catalyst; other methods that formed methanol included a method for the sol-gel synthesis of Cu/TiO₂ by Yang et al (16) and TiO₂ powder impregnation with Cu, CuO and Cu₂O by Slamet et al (17). The common factor in all of these methods
is that they selectively produced methanol, utilizing an electrochemical or photochemical reaction (15-17).

**Photoelectrochemical Reaction:**

The reaction method which is intended for this research is photochemical, though the current research will be completed as photoelectrochemical. Slamet et al (17) described the use of a photochemical reactor which was a “horizontal stainless steel vessel with an inner diameter and height of the vessel 140 mm and 50 mm, respectively. A top plate cover of the vessel was made of Pyrex and equipped with a gas bubbler and sampling port.” The cell can be irradiated by a light source through the glass top plate (17). Researchers have used many different lamps as light sources including medium pressure mercury (Hg), high pressure xenon (Xe), medium pressure halide, and black light UV as the energy source to drive these reactions (16-20). Once a reaction was initiated, analysis of the products from the photochemical reaction is necessary. This can be done using Gas Chromatography GC or GC-FID (Gas Chromatography with a Flame Ionization Detector) (15, 17, 20).
**Figure 7:**

(Figure showing a schematic diagram of a photochemical cell with labeled parts: 1. Gas inlet, 2. Quartz Window, 3. Catalyst, 4. Gas outlet.)

**Future Research Directions/ What I will Try!**

There has been much research done on CO\textsubscript{2} fixation as it is becoming ever important to reduce CO\textsubscript{2} emissions and the amount of CO\textsubscript{2} in the atmosphere. The scope of this research is to catalyze the photoreduction of CO\textsubscript{2} in an effort to increase the efficiency of the reaction, and to produce the energy required to fuel the reaction from a natural source, the sun. One problem described in the literature was that unlike the photoreduction of water, the photoreduction of CO\textsubscript{2} is unable to be enhanced by introducing strong electron donors into the solution. One way researchers found around this problem was to find a “semiconductor catalyst that will undergo self-sacrifice with a rapid consumption of photogenerated holes.” (19).
CuO, Cu₂O and TiO₂ are all viable options to catalyze this reaction as seen in the literature. CuO and Cu₂O will be used as the catalysts for the reaction as they have been stated to work well. Using them together in a mixture as a catalyst will also be studied. This will be done to see if the mixture will yield any different results than each catalyst separately. These catalysts were shown to work well in organic media; however this work will be performed in an aqueous environment, as this more closely mimics the exhaust of a smokestack. The end product for this research is to use a catalyst on a semiconductor membrane to reduce CO₂ emissions by carbon fixation, which means that we take atmospheric CO₂ which would have been released by chemical processes and convert it into another chemical substance that is more industrially useful, or a chemical that is less toxic to the atmosphere.

To do this we will start with Cu foil, which will be the foundation of the electrode. On the surface of the electrode, place cupric (CuO) or cuprous (Cu₂O) oxide catalysts by electrochemically polishing Cu plate in 85% phosphoric acid or through electrodeposition (22). One other method that can be tried is to take Cu₂O and CuO powders, and make a pressed powder electrode (21). Once the electrode and catalyst are formed, simple electrochemical experiments will be used to determine if the catalyst does indeed form methanol, and if the reaction can be driven photoelectrochemically. If it does, the next step is to put these catalysts on a Nafion membrane. Once on the Nafion membrane it will be placed in a
photoelectrochemical cell through which CO₂ will be pumped, and methanol possibly formed.

**Why CuO and Cu₂O?**

Cuprous and cupric oxides have been shown through much research to work well for CO₂ reduction. They have also shown selectivity for methanol formation from the CO₂ reduction, and are also easily formed and inexpensive. These compounds also exhibit semiconductor properties which may aid in the movement of electrons in the system.

**Crystal structure/ how structure can affect activity.**

CuO and Cu₂O can both form many different crystal structure orientations, depending on their growing conditions as seen in the research done by Li et.al. (23) Luo et.al. (24) and Bijani et.al. (25). Li et.al. (23) added a room temperature hydrophilic ionic liquid in differing concentrations to his solution, and found that by differing the concentration of the ionic liquid they were able to electrodeposit different orientations of Cu₂O. They showed these results using SEM images. Luo (24) had a similar study where they varied the temperature and the concentration of NaOH. This resulted in their ability to synthesize different orientations. They also showed their results with SEM images. Bijani (25) was able to show changes in morphology by varying applied potential and the electrolytic bath pH.
Why is this research important? The variations in the morphology have been suggested to change the outcome of the experiment. This is something that will not be taken into account in the beginning of this research, though if there is time or the thought that one specific morphology, may work better for CO₂ fixation than what is already being studied during this research, looking further into the difference in morphology may be reconsidered.

**Experimental/ Results:**

Marcel Pourbaix published a book of diagrams known as the “Atlas of Electrochemical Equilibria in Aqueous Solutions.” These diagrams, named after him called the Pourbaix diagram, give information on the state of a substance in solution during electrolysis (26). These diagrams are based on the type or composition of the electrode, the amount of energy or voltage applied, and the pH of the electrolyte solution. The Pourbaix diagram for copper shows us that cuprous and cupric oxide both will exist on the surface of the copper electrode in aqueous solution, and at what conditions each will occur.

One reason these experiments were run in pH 10 electrolyte solutions was that CuO and Cu₂O should both be easily seen according to the Pourbaix diagram Figure H below. The second reason that these experiments were run at pH 10 is that photoelectrochemical systems seem to work better in basic or acidic solutions rather than neutral pH; due to the splitting of water. This information will be important for the eventual goal of the research project, which is to design a photochemical cell with a membrane lined with a catalyst,
possibly copper, which will facilitate water splitting on one side, and CO$_2$ reduction on the other. A pH of 10 should allow for better equilibrium between the protons coming from the reduction of water through the membrane to react with CO$_2$ on the other side. Shifts in the balance toward neutral could cause the reaction not to work at optimal conditions, causing less CO$_2$ reduction.

*Figure 8:*
Pourbaix Diagram for Copper

For this research, CuO and Cu$_2$O were tested in two different electrolyte solutions of pH 10. The two different solutions that were examined including potassium nitrate KNO$_3$ and potassium carbonate K$_2$CO$_3$, the pH was changed using potassium hydroxide KOH to make the KNO$_3$ solution more basic until the pH of 10 was obtained. pH 10 K$_2$CO$_3$ was obtained by using HNO$_3$, or nitric acid to make the solution more acidic until it reached the optimal pH 10. Three different working electrodes were used in each solution: a copper metal electrode, a cupric oxide electrode, and a cuprous oxide electrode.

Working Electrode Preparation:

Working electrodes were made three different ways, but the initial set up and cleaning was the same for all electrodes. This was done with a one inch square of Puratronic copper from Alfa Aesar, which was 99.9999% pure copper foil 0.5 mm thick. The copper foil was cleaned with alumina powder to remove any surface oxide layer and dirt that may have been on the copper, it was then etched in concentrated hydrochloric acid (HCl) for approximately 2 minutes. The cleaned copper metal was then rinsed in deionized water (DI- water) and dried with a Kim-Wipe. For the copper electrode this was the final preparation step. For the other two electrodes, once dried they were placed on a ceramic boat in the oven at room temperature and one of the following procedures followed depending on the type of electrode desired.
The cuprous oxide electrode was made by placing a 1 inch square of copper in the oven at room temperature, and the oven temperature set to rise to 80 °C where it was held for 24 hours. The oxide electrode was then removed from the oven, allowed to cool and placed in a labeled container then stored for later use. This electrode was easily made on the first attempt, along with the plain copper metal electrodes, which required only cleaning to remove any surface oxide layers that were present at ambient room conditions.

The first couple of attempts at making a CuO electrode failed as the black oxide layer that formed in the oven quickly cracked and peeled off the surface of the electrode leaving a reddish colored metal underneath. The initial procedure followed to make this electrode was to place a freshly cleaned, etched and dried 1 inch square of copper in the oven at room temperature, and ramp the temperature to 500 °C and left for 1 hour after which time it was allowed to cool. It was during the cooling that problems started to occur, with the black layer flaking off the surface, examples of this can be seen in Figures 9 and 10.
1st Attempt At Making CuO

2nd Attempt At Making CuO

Thinking that maybe the surface layer was to thin, the second attempt was done by again placing a freshly cleaned 1 inch square of copper in the oven at room temperature. The oven temperature was then set to rise to 500 °C
where it remained for 24 hours before the oven was turned off, and the
electrode allowed to slowly cool in the oven until it reached room temperature.
One again this was a failed attempt. When the copper metal was removed from
the oven, the surface layer this time was thicker than that of the previous
attempt, but crumbled right off. This time the remaining copper metal was
pinkish in color, not the grayish black that was hoped for. This is seen in
Figure 10.

The third attempt was the most successful to this point at making a CuO
electrode, for this attempt the 1 inch square of copper metal was cleaned,
placed in the oven at room temperature, the oven was then set to heat to 400
°C and allowed to reach temperature. Once the oven reached 400 °C, the
surface of the electrodes was monitored closely as the temperature was set to
rise to 500 °C where it was held for 5 minutes, at this point the electrode
looked much better, there was not a thick layer on the surface, instead a
thinner grayish color layer, but unfortunately upon cooling the layer had still
cracked. The only explanation that one could use to explain this is thermal
expansion. A metal expands as it gets hot, and shrinks back to size when
cooled, causing a thick layer to crack off. This would lead me to believe that the
layer being formed maybe too thick, or the heating temperature too high.
Thinking a shorter heating time may lead to a thinner layer, A fourth attempt
was made with some small changes to determine if it was possible to make this
electrode. The fourth attempt was much like the third attempt, though this
time the cleaned 1 inch copper square was placed in the oven at room
temperature, the temperature was allowed to rise to 400 °C. Once the oven reached 400 °C, the oven temperature was raised once again and set to 500 °C, but was monitored closely by opening the oven door every couple of minutes and checking the progress of the surface layer to ensure that only a thin surface layer formed. The color of the electrode turned from a reddish brown color to a grayish black, sometimes silver looking color when the final desired surface coating had been reached. This typically took less than 10 minutes to complete, and the temperature never made it to 500 °C, usually never rising above 430 °C. If left unattended for too long, or if the temperature was set to 500 °C as the literature suggested, the surface layer would be thick, black in color layer, and would quickly peel or flake off upon cooling. Once the desired layer was formed the electrodes was removed from the oven and allowed to cool to room temperature. It was then placed in a labeled container and placed in the desiccator to be used later.
**Photo of metal electrodes left being cuprous oxide Cu$_2$O, middle cupric oxide CuO, and right plain copper metal**

The one inch pieces of copper with oxide coatings, but they needed lead wires to them to be able to suspend them in the electrolyte solution while being connected to a potentiostat to regulate the current during experiments. There were two problems! What kind of wire should be used, and how should it be attached to the electrode. One solution, a solid 18 gauge wire, but, another problem, if the wire was to be left bare in solution it could potentially react with the electrolyte solution during electrolysis, giving skewed results. So the wire was covered with 1/16 inch heat shrink leaving a section bare at each end, one to attach to the surface of the electrode, the other to lead to the instrumentation to be used during electrolysis.
Prepared Wire

Our task was to attach a solid wire to a solid surface while maintaining enough surface contact to conduct electricity, and at the same time not damage the oxide surface layer on the electrode. The wire was attached to the back of the electrode, which was intentionally left unprepared, using conductive silver epoxy. The silver epoxy came in a two part mixture, and needed to be prepared at the time of use, so each time an electrode was made a small amount of each part was placed on a clean piece of weighing paper, and it was mixed using a clean spatula, then placed on one end of the copper wire which was then placed on the back of the electrode surface, and allowed to dry. Once again though, the potential arose for surfaces other than the prepared electrode surface to contact the electrolyte solution, potentially causing problems with the analysis. These problems were avoided by allowing the silver epoxy to completely dry, then covering the entire backside and uncovered part of the wire with 5 minute epoxy. This was done to keep all metal surfaces covered, and therefore for them not to interact with the electrolyte solution.
Figure 13-1:

**Completed Electrode Front View**

Figure 13-2:

**Completed Electrode Back View**
Reference Electrode preparation: Making of a Silver/Silver chloride (Ag/AgCl) Electrode:

The making of a Ag/AgCl reference electrode was fairly easy requiring silver wire, and a glass electrode tube with a vycor tip. The first step in making the reference electrode was to clean the silver wire this was done with ethanol to remove any organics which may have gotten on the surface of the wire during handling, then rinsed with deionized water. The next step was to make a 0.3 M nitric acid solution in which the silver wire was etched for 20 seconds before chloride deposition. The silver wire with a positive lead wire was placed in a 1 M HCl solution along with platinum mesh with an attached negative lead wire. A current of 50 mA was run through the wires, and the positively charged silver wire attracted the negatively charged chloride ions forming a AgCl layer on the surface of the wire. Next a 3 M KCl solution was made as an electrode storage solution, and a 4 M saturated AgCl solution was made as the electrode filling solution. To finish the electrode, the wire was placed in a special glass tube with a vycor tip. The electrode was then filled with the premade 4 M KCl filling solution, and capped with a septum cap through which the wire was fed to give an air, and watertight seal. The final electrode can be seen in Figure 14. The electrode was then placed in a Erlenmeyer flask filled with saturated KCl solution, and
fitted with a rubber stopper with a hole in it large enough to stick the electrode through allowing the tip of the electrode to be submerged in solution.

*Figure 14:*

![Image of Ag/AgCl Electrode]

**Ag/AgCl Electrode**

**Counter Electrode Preparation:**

The counter electrode is made from a piece of pure platinum (Pt) wire. The wire was wound into a tight spiral and the end fed through a piece of nylon round stock that acted as holder to keep the electrode in place in the electrochemical cell.
Figure 15:

Pt Counter Electrode

Experiments:

The first experiment run was using a plain copper electrode in 0.1 M potassium nitrate (KNO₃) solution at pH 10. This solution was prepared by using 2.53 g of KNO₃ in 250 mL of H₂O. The solution was mixed until all solids had dissolved, and then the pH was adjusted using powder from ground KOH pellets, stirring until the powder dissolved and reached the desired pH 10. The electrode was then placed in the electrochemical cell along with the electrolyte solution, and the reference and counter electrodes as seen below in Figures 16-1, and 16-2. The solution was then purged with nitrogen gas (N₂) and the cell connected to the potentiostat, where the electrode was swept negative from zero
to -0.8 V, then positive to +0.5 V, and back to zero. This procedure was repeated for the CuO, and Cu₂O electrodes.

*Figures 16-1:*

*Electrochemical Cell Diagram and photo of actual cell*
The second set of experiments used 0.1 M $\text{K}_2\text{CO}_3$ solution at pH 10. This solution was made by dissolving 3.46 g of $\text{K}_2\text{CO}_3$ in 250 mL of DI H$_2$O. The solution was stirred for a couple of minutes to allow all solids to dissolve, then a pH measurement was taken. The pH of this solution was higher than pH 10; therefore the pH needed to be lowered. This was done by slowly adding drops of concentrated nitric acid to the solution from a pipette until pH 10 was observed. This was done very slowly and stirred between drops and measurements to allow time for the acid to react forming bicarbonate in solution, and reducing the pH. Once the desired pH 10 was achieved, the solution was placed in the electrochemical cell, along with the counter,
reference and working electrode. The solution was then purged with N₂ gas to remove any possible contaminants from the atmosphere, and then attached to the potentiostat. Once again the voltage was swept negative first to -0.8 V then positive to +0.5 V and back to zero. This experiment was repeated for each of the Cu, CuO and Cu₂O electrodes.

The third set of experiments was performed much as the previous sets except for a couple small changes. This time using a 1 M K₂CO₃ solution pH adjusted to 10 with HNO₃, the electrochemical experiments were carried out. Gas sampling was done during the experiment to determine: 1.) if CO₂ was being reduced, and 2.) to see what was formed. To complete this experiment the electrochemical cell needed to be adjusted to allow for gases to flow in and a port was needed for the gas detector as a gas out of the system. This was accomplished by drilling an extra hole in the nylon round stock used as an electrode holder for the working electrode. The gas detector input fit snugly, but easily fit though the hole in the nylon round stock along with the lead wire for the working electrode to allow the use of the gas detector along with the current electrochemical cell.

The fourth set of experiments was photoelectrochemical experiments. These experiments were initially set up using the same round bottom electrochemical cell as before, and were conducted using 1 M K₂CO₃ in pH 10 solution. The working electrode was once again copper metal, cuprous, or cupric oxide. The other counter and reference electrodes did not change from earlier experiments. When working with the electrochemical cell, the same
system connections were used as before, leading to the potentiostat, and the electrode was swept from -1 V to +1 V. The system was continuously purged with argon during the sweep. The only change was that the electrode was set in the pathway of a solar simulating light source, in this case a xenon arc lamp. The light source was illuminated, and the experiment was run to determine if in fact the electrode was photoactive, and if the photoactivity changed the results of the experiment when compared to earlier dark data.

Experiment set 5 was done using a photoelectrochemical cell made from aluminum metal, glass, and rubber sheet for gaskets. There were some changes in configuration between the electrochemical cell and the photoelectrochemical cell. For instance, there was no need for the nylon electrode holders; instead, the working electrode and the counter electrode were allowed to dangle through holes in the photochemical cell. The completed cell configuration can be seen in Figures 17-1, and 17-2 below.
Figure 17-1:

Photoelectrochemical Cell Diagram
Photo of Photoelectrochemical Setup for Experimentation

There were only two differences in experimental conditions from experiment 4, and they were the difference in cell type and the amount of liquid in the cell. The photocell could only accommodate 80 mL of 1 M $\text{K}_2\text{CO}_3$ solution. Another parameter that was changed for the photoelectrochemical
experiments was that after the initial sweep, the potentiostat control was set to hold the system at -1 V for 10 minutes to determine if anything different happened after a length of time in this area of the voltammogram, and to see if any other gas was evolved other than hydrogen. All of the peaks on the voltammogram can be explained using a Pourbaix diagram for copper metal. The H₂ evolution region is the only area in which we could suggest that these electrodes are photoactive for CO₂ reduction. The photovoltage was also determined using a voltmeter between the reference electrode and the working electrode, and then applying light from the solar simulator, looking for an increase in voltage across the electrode. This experiment was repeated for the Cu metal electrode, the cuprous oxide, and the cupric oxide electrodes, and was also repeated for all electrodes in the dark. This experiment was also repeated at pH 3 in the light and dark while bubbling in CO₂ to determine if the pH made a difference in the outcome of the experiment.

The photovoltage of each electrode type was checked to make sure that a photovoltage was in fact being seen. The Cu₂O electrode showed a small photovoltage, increasing by 1.2 mV, and the CuO electrode gave a change in photopotential of 20 mV as measured as the initial jump in current after being illuminated.

Another test that was completed was for the Hall Effect, using an Ecopia Hall Effect Measurement System with a 0.58 T magnet to determine if the copper oxides are truly p- type semiconductors. The instrument used to conduct this experiment worked by producing a voltage difference across an
electrical conductor, transverse to the electric current, and perpendicular to the magnetic field. This test was done to determine how the charge moved through the electrode, whether the flow is by electrons, or if holes are the charge carriers. In an n-type semiconductor charge is carried by the electrons, and in p-type, the charge is carried by the holes.

**Results/Discussion:**

**Electrodes:**

After successfully making all three electrode types, samples were sent to the NETL (National Energy Technology Laboratory) laboratory for XPS (X-Ray Photoelectron Spectroscopy) analysis (also known as ESCA Electron Spectroscopy for Chemical Analysis) to determine if the surface layers on the electrodes were indeed what was expected. The first sample analyzed was cleaned copper metal. According to the data, there was a chloride (Cl⁻) contaminant, as well as the presence of Cu^{1+} and Cu^{2+}, suggesting that the cleaned copper sample had oxidized slightly in the atmosphere before it was analyzed. The XPS spectrum can be seen in Figure 18.
**Figure 18:**

![XPS Spectrum of Cleaned Cu Metal](image)

**XPS Spectrum of Cleaned Cu Metal**

The second sample that was analyzed was a reddish colored slightly oxidized copper metal, thought to be purely Cu$_2$O; this was not the case. Instead of being pure Cu$_2$O, this sample was a slight mixture of oxidation states, making it a mixture of cuprous and cupric oxides. Though not what was expected, the result makes sense, as Cu$_2$O will slowly turn into CuO in moist atmospheric conditions. As these samples had to be sent out for analysis, complete control of their atmospheric surroundings was not possible. In the laboratory, all samples were stored in a desiccator to limit further oxidation from occurring once the
electrode was prepared. The XPS results for the Cu$_2$O sample can be seen in Figure 19.

*Figure 19:*

![XPS Spectrum Cu$_2$O](image)

**XPS Spectrum Cu$_2$O**

The third sample that was analyzed was expected to be exclusively CuO. According to the results of the analysis, it was determined that all of the Cu was in the 2$^+$/state, meaning that the entire surface of the sample is composed of CuO. This spectrum can be seen in Figure 20.
Figure 20:

XPS Spectrum CuO Electrode

What was seen was that both the Cu metal electrode and the Cu$_2$O electrode were in impure states, the natural tendency is for copper to oxidize the entirely to CuO. Cu$_2$O can be seen as an intermediate state, as the transition from Cu$_2$O to CuO takes time. The only way to have a pure Cu sample was to clean it and keep it in a dry atmosphere to limit exposure to moisture, which will in turn limit oxide formation, and can probably only be accomplished in a glove box. CuO is the only oxide that can easily be made as a pure surface layer using this method.
Data from XRD (X-Ray Diffraction) experiments confirmed the results of the XPS, showing that Cu electrode was plain copper metal. Also it showed that the Cu$_2$O appeared to be largely copper metal, and the CuO was mostly copper metal and CuO. The results suggest that the Cu$_2$O surface layer was very thin, approaching the limits of the instrument to measure.

**Hall Effect:**

The electrode pieces were tested for the Hall Effect, as both of the oxides were expected to be p-type semiconductors. The instrument used to conduct this experiment works by producing a voltage difference across an electrical conductor, transverse to the electric current, and perpendicular to the magnetic field. This test was done to determine how the charge moves through the electrode, whether the flow is by electrons, or if holes are the charge carriers. In an n-type semiconductor charge is carried by the electrons, and in p-type, the charge is carried by the holes.
Table 2: The Hall Effect

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Bulk</th>
<th>Mobility (μ)</th>
<th>Resistivity ρ (Ω cm)</th>
<th>Avg Hall Coefficient A-C</th>
<th>Hall Coefficient B-D</th>
<th>Sheet Concentration</th>
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</thead>
<tbody>
<tr>
<td>Cu-1</td>
<td>4.73E+21</td>
<td>9.83E+02</td>
<td>1.34E-06</td>
<td>1.32E-03</td>
<td>3.24E-04</td>
<td>2.32E-03</td>
</tr>
<tr>
<td>Cu-2</td>
<td>3.29E+22</td>
<td>1.67E+02</td>
<td>1.14E-06</td>
<td>1.90E-04</td>
<td>-2.58E-03</td>
<td>2.96E-03</td>
</tr>
<tr>
<td>Cu-3</td>
<td>-3.11E+21</td>
<td>1.01E+03</td>
<td>2.00E-06</td>
<td>-2.01E-03</td>
<td>-4.94E-03</td>
<td>9.20E-04</td>
</tr>
<tr>
<td>CuO-1</td>
<td>2.42E+21</td>
<td>2.06E+03</td>
<td>1.25E-06</td>
<td>2.58E-03</td>
<td>-9.24E-04</td>
<td>6.09E-03</td>
</tr>
<tr>
<td>CuO-2</td>
<td>4.29E+21</td>
<td>5.31E+02</td>
<td>2.74E-06</td>
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<td>3.06E-03</td>
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<td>CuO-3</td>
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<td>9.24E+02</td>
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<td>-8.40E-04</td>
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<td>3.83E-04</td>
</tr>
<tr>
<td>CuO-4</td>
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<td>9.99E-07</td>
<td>2.90E-04</td>
<td>7.66E-04</td>
<td>-1.87E-04</td>
</tr>
</tbody>
</table>

Voltammograms: In the dark

These experiments were completed to determine how the electrodes worked without the presence of sunlight, and to establish any differences between electrolytes. For these experiments most of the peaks in the voltammograms can be identified by the location of the peaks in reference to the Pourbaix diagrams. The only peak that is unexplainable from the Pourbaix diagram is a peak that appears in all diagrams at approximately -0.7 V. This peak may be the reduction peak of something in the sample, or may be the beginning of hydrogen evolution from the surface of the electrode. The other reduction peaks, at approximately +0.1 V, and -0.3 V can be explained as transitions between CuO and Cu₂O states and Cu₂O to Cu metal respectively. The reduction peaks do
not seem to be dependent on the electrolyte, as they remain in approximately the same location in both potassium nitrate and potassium carbonate solutions. They do tend to change in magnitude as the number of sweeps on one electrode increases, causing the surface to change. After a few sweeps all of the electrode samples appear to turn blackish gray in color, and on occasion, in the carbonate samples, blue crystals formed on the surface of the electrode.

*Figure 21:*

![Graph showing voltammetry data.](ECUKNO33.BIN)

**Voltammogram of cleaned Cu metal electrode in 0.1M KNO₃ solution**
Figure 22:

Voltammogram of Cu$_2$O electrode in 0.1M KNO$_3$ solution
Figure 23:

Voltammogram of CuO electrode in 0.1M KNO₃ solution

Voltammograms: in the light:

The electrodes were examined in the light (solar simulated) to see if a photopotential develops and how the photopotential affects the voltammogram. For the light experiments, the voltammograms showed little variation for the location of the reduction peaks or number of peaks; however the magnitude of the peaks did differ from the light to the dark experiments. The magnitude of the peaks was larger in the
voltammograms in which the electrode was exposed to the Xe light source. An example of this can be seen in Figure 25.
**Chronoamperometry:**

The potentiostat experiments were completed for each electrode to see any variations that happened over time at -1 V, and variations between the electrode behavior in the light and the dark. If there was any reduction of CO$_2$, this is the region where it is expected to be, as all other peaks in the voltammograms were explainable using the Pourbaix diagrams. Though hydrogen evolution occurs at this potential, it is expected that CO$_2$ reduction does as well.

The copper metal electrode and cuprous oxide electrodes did not show much variation, an example of the chronoamperometric experiment can be seen in Figure 26 below. These samples were also tested for gas evolution using an Infotec gas detector. The detector was set to continuously monitor levels for, CO$_2$, H$_2$, and O$_2$. The copper metal and cuprous oxide showed little gas evolution beyond CO$_2$ gas, and a small amount of H$_2$. These results were as expected; these electrodes were not expected to be very active for CO$_2$ reduction.
Figure 25:

Potentiostat Data Cu$_2$O Electrode in the Light
**Figure 26:**

\[ \text{K2CO3 Cu2O electrode 5-3-12 dark Potentiostatic.cor} \]

**Potentiostat Data Cu2O Electrode in the Dark**

The cupric oxide on the other hand did show signs of being photoactive as there were drastic differences between the light and dark chronoamperometric data, and also with the gas evolution. The cupric oxide data for the light run appeared different from all the other potentiostatic data; the current rose quickly at the beginning instead of falling though it flattened out after the quick rise. This can be seen below in Figures 28 and 29. For this I cannot offer any logical explanation to say why this happened especially seeing the light data for this same electrode. It also seemed out of the ordinary. It did however start the
same way as all of the other data collected for the other electrodes. Subsequently, however, instead of the current quickly falling then flattening out, the current kept rising the entire length of the run. The same behavior was seen from this electrode in pH 3 solution as well. This may be explained by the gas data. The evolved gas showed that there was some H₂ in both samples, at pH 10 and pH 3. At pH 10, however, there was significant O₂ gas evolution recorded; this was not the case at pH 3, where there was some O₂ evolution, but not as much as there was at pH 10. Though we saw O₂ evolution this result did not seem to make sense. Why was there O₂ evolution in the negative regime? There may be an explanation. The gas detector works by using a mass spectrometer as a detector, and is set to determine a gas by its molecular mass. What happens when you have two possible gases that have the same molecular mass? The O₂ result was confusing until we determined that both O₂ gas and methanol, CH₃OH, vapor share a molecular mass at 32 g/mole. Now all of a sudden the results seemed to make sense. O₂ was not evolved, methanol was made in the reaction, and as a result, the gas detector was picking up its signal, and reporting it as O₂, as they shared a molecular weight. To confirm this finding, a new solution was prepared at pH 10, purged with argon gas, and spiked with methanol knowing that if the gas detector detected O₂, it was truly detecting methanol, as there would be
no $O_2$ in the system. The potentiostat data from the CuO electrode at pH 10 and pH 3 can be seen below in Figures 27 thru 30.

**Figure 27:**

![Potentiostat Data CuO in the Light At pH 10](image-url)
Figure 28:

Potentiostat Data CuO in the Light at pH 3

Figure 29:

Potentiostat Data CuO in the Dark at pH 10
**Figure 30:**

**Potentiostat Data at pH 3 in the Dark**

The last experiment run was a one-hour potentiostatically controlled reduction of CO₂ on a CuO electrode in pH 10 K₂CO₃ solution in the light. At the end of the hour, a sample was taken, and analyzed using Infrared Spectroscopy (IR) to determine reduction peaks by looking at the location of the IR stretching peaks. As shown in Figure 31, there are 5 peaks, which may suggest what type of compound was formed from the reduction. The first peak is approximately 3100-3300 wave numbers (cm⁻¹) and is a broad peak; the other peaks are at 2916.47, 2848.72, 1576.8, and 1543.5 cm⁻¹. The peak at
approximately 3200 cm\(^{-1}\) suggests a bonded \(-\text{OH}\) group. The peaks at 2916 and 2848 cm\(^{-1}\), suggest many different things including \(-\text{CH}, -\text{CH}_3\), and a bonded OH in a carboxylic acid. The peaks at 1543.5 and 1576.8 suggest a \(-\text{COO}\) group. What can be gathered from this information is that we reduced CO\(_2\) to make another carbon-containing product, according to the data shown, most likely, formic acid.

*Figure 31:*

**K\(_2\)CO\(_3\) sample IR analysis**
**Figure 32:**

**IR water background Sample**

Though the IR data is conclusive in showing that something other than CO₂ was seen in the solution, it is not confirmation that formic acid was actually made. For this, other experiments should be done, which could include possibly GC analysis, although to perform GC analysis, head space was the only method which could have been tried, as putting a pH 10 solution in the GC with a high concentration of potassium salts would do one of two things: plug the injection port or ruin the column. Therefore this experiment was not tried.
Conclusions and Future Work:

In conclusion, copper oxide electrodes were successfully made by heating 1 inch pieces of elemental copper metal in the oven under certain conditions to achieve the desired oxide surface layer. I am confident that CuO was made and was pure, but am not confident in the ability to make Cu$_2$O, as I think that this will always be a mixture of the two oxidation states, and never truly get a pure oxide layer with this method. Something that could be studied in the future with these electrodes is surface morphology to see differences in the surface structure, and how the structure may change after electrolysis.

I also believe that the CuO electrode was more active than the Cu$_2$O and plain copper metal in reducing CO$_2$. There was always more activity in the cell during electrolysis; I saw a lot more gas evolution with this electrode. Though I do not have a lot of proof, after an analysis method for the solutions is determined, all of the solutions can be checked for the expected reduction products. I believe that the CuO would show the greatest amounts of reduction products.
References:


02.) http://www.eia.doe.gov/oiaf/1605/ggccebro/chapter1.html


04.) http://www.eia.gov/energyexplained/index.cfm?page=solar_photovoltaics


09.) Wang, Xiaoqing; Xi, Guangcheng; Xiong, Shenglin; Liu, Yankuan; Xi, Baojuan; Yu, Weichao; Qian, Yitai. Solution-Phase Synthesis of Single-Crystal CuO Nanoribbons and Nanorings. Crystal Growth., 2007, 7 (5), 930-934.

10.) Zhao, He Ying; Wang, Ye Feng; and Zeng, Jing Hui., Hydrothermal Synthesis of Uniform Cuprous Oxide Microcrystals with Controlled Morphology. Crystal Growth. 2008, 8, (10), 3731–3734.


24.) Luo, Y; Li, S; Ren, Q; Liu, J; Xing, L; Wang, Y; Yu, Y; Jia, Z; Li, J. Facile Synthesis of Flowerlike Cu2O Nanoarchitectures by a Solution Phase Route. *Crystal Growth.* **2007**, *7* (1), 87-92.
