PERFORMANCE OPTIMIZATION OF AN ELECTROLYZER FOR THE HYBRID COPPER-CHLORINE THERMOCHEMICAL CYCLE

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ABSTRACT

A background of electrolyzers and thermochemical cycles for hydrogen production is first given to introduce the Cu-Cl hybrid thermochemical cycle. The research performed on improving performance of the electrolysis step of the Cu-Cl cycle is then presented. This research involved studying the effect of catalyst loading technique, quantifying the effect of reducing catalyst loading from the cathode and anode, quantifying the temperature dependence of cell performance, and observing the effect of anolyte and catholyte flow rate on the overall cell performance. By improving the performance of the Cu-Cl electrolyzer, the proposed Cu-Cl hybrid thermochemical cycle under development is pushed closer to an economically viable technology for producing hydrogen gas efficiently from renewable heat and electricity sources. A 62 % increase in current density at an applied potential of 0.6 V was achieved by switching catalyst application technique from painting to spraying at a loading of 0.8 mg/cm² platinum. It was found that platinum catalyst was more effective at the cathode than the anode. When sprayed platinum loadings were reduced from 0.8 mg/cm² on both the cathode and anode, to 0.4 mg/cm² and 0.1 mg/cm², respectively, the required amount of platinum catalyst was reduced by 69 % while only decreasing current density by approximately 24 % at an applied potential of 0.6 V. The findings of this research improved Cu-Cl electrolyzer design in terms of catalyst application, therefore improving economics behind proposed projects based on the Cu-Cl hybrid thermochemical cycle. Studies presented in this paper were also included in a transaction paper for the Journal of the Electrochemical Society (Hall et al. 2013).
# TABLE OF CONTENTS

List of Figures ............................................................................................................................ iii

List of Tables ............................................................................................................................... v

Acknowledgements ..................................................................................................................... vi

Chapter 1 INTRODUCTION TO THE COPPER-CHLORINE HYBRID THERMOCHEMICAL CYCLE ........................................................................................................ 1

  1.1 Thermochemical Cycles and Hybrid Thermochemical Cycles ................................. 2
  1.2 Previous Work on the Cu-Cl Electrolyzer for the Hybrid Thermochemical Cycle ... 4

Chapter 2 RESEARCH MOTIVATION ......................................................................................... 6

Chapter 3 MATERIALS AND METHODS ................................................................................ 8

  3.1 Testing System: Lab Scale Electrolyzer ................................................................. 8
  3.2 Electrode Preparation: Airbrushing Platinum Catalyst onto Carbon Cloth ............ 12
  3.3 Solution Preparation ............................................................................................... 12
  3.4 Electrochemical Measurements ............................................................................... 13

Chapter 4 RESULTS AND DISCUSSION ............................................................................... 14

  4.1 Performance Dependence on Catalyst Application Technique: Painting vs. Spraying ............................................................................................................... 14
  4.2 Performance Dependence on Loading for Sprayed Electrodes ............................ 18
  4.3 Current Efficiency of the Electrolyzer .................................................................... 25
  4.4 Temperature dependence of the lab-scale electrolyzer performance .................... 26
  4.5 Flow Rate Dependence of the Electrolyzer ............................................................ 28

Chapter 5 SUMMARY AND CONCLUSION ......................................................................... 30

BIBLIOGRAPHY ......................................................................................................................... 32
LIST OF FIGURES

Figure 1: Lab scale electrolyzer used for catalyst loading, temperature, flow rate, and pressure dependence testing; 1 – catholyte tank containing 7 mol/L HCl(aq); 2 – anolyte tank containing 2 moles of CuCl(aq) per liter of 7 mol/L HCl(aq); 3, 4 – catholyte and anolyte pumps respectively; 5 – damping column; 6 – regeneration column containing layers of copper shot and glass beads; 7 – electrolyzer cell; 8, 9, 10, 11 – hydrogen measurement system including HCl removal, dessicator, flow meter, and hydrogen storage tank respectively.

Figure 2: Simplified diagram of the electrolyzer cell showing the solutions and reactions occurring at both the cathode and anode.

Figure 3: Comparison of brushed and sprayed carbon cloth electrodes on the lab scale electrolyzer performance; LSV scan rate 10 mV/s; temperature 80 °C; catalyst loading 0.8 mg Pt/cm²; 5 cm² geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.

Figure 4: SEM image of a carbon cloth painted with Vulcan XC-72R catalyst ink.

Figure 5: SEM image of a carbon cloth sprayed with Vulcan XC-72R catalyst ink.

Figure 6: SEM image of a carbon cloth sprayed with Vulcan XC-72R catalyst ink at 273x magnification.

Figure 7: Comparison of reduced catalyst loadings at the cathode and anode on the lab scale electrolyzer performance; LSV scan rate 10 mV/s; temperature 80 °C; 5 cm² geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.

Figure 8: EIS plot of the independently reduced loadings on the cathode and anode at an applied potential of 0.1 V. Frequency range: 0.005 to 100,000 Hz; temperature 80 °C; 5 cm² geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.

Figure 9: Zoomed in view of the high frequency area of Figure 8.

Figure 10: Comparison of 0.4 mg/cm² platinum catalyst loading on both the anode and cathode to 0.0 mg/cm² at the anode and 0.4 mg/cm² at the cathode on the lab scale electrolyzer performance. LSV scan rate 10 mV/s; temperature 80 °C; 5 cm² geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.
Figure 11: Comparison of 0.4 mg/cm$^2$ on both the anode and cathode to 0.1 mg/cm$^2$ at the anode and 0.4 mg/cm$^2$ at the cathode on the lab scale electrolyzer performance; LSV scan rate 10 mV/s; temperature 80 ºC; 5 cm$^2$ geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte. ................................................................. 24

Figure 12. Temperature dependence of the current density of the lab-scale electrolyzer with a cathode loading of 0.4 mg/cm$^2$ platinum and an anode loading of 0.1 mg/cm$^2$; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rate 220 mL/min. ...................................................................................... 27

Figure 13. Current density dependence of the lab-scale electrolyzer on the flow rate of the anolyte and catholyte; Cathode loading of 0.1 mg Pt/cm$^2$ and an anode loading of 0.4 mg Pt/cm$^2$; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; applied potential 0.7 V; temperature 80 ºC. ................................................................. 28

Figure 14: LSV comparison of different flow rates on the performance of the lab scale electrolyzer. 0.4 mg/cm$^2$ platinum at the cathode, 0.1 mg/cm$^2$ at the anode; scan rate 10 mV/s; temperature 80 ºC; 5 cm$^2$ geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; anolyte: 2 mol/L CuCl(aq) in 7 mol/L HCl(aq); catholyte: 7 mol/L HCl(aq). ...................................................................................... 29
LIST OF TABLES

Table 1: Hydrogen production measurements compared to theoretically calculated hydrogen production to calculate the current efficiency over an 8 minute time interval at 80 °C.................................................................26
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Chapter 1

INTRODUCTION TO THE COPPER-CHLORINE HYBRID THERMOCHEMICAL CYCLE

Hydrogen gas is valuable for society, used as both an energy carrier and chemical feedstock.\(^1\) Approximately 55 million tons of hydrogen were produced annually as of 2013, and production has been increasing by roughly 6 \% annually.\(^2\) Currently around 96 \% of hydrogen gas is produced from hydrocarbons, with nearly 50 \% generated by steam reformation of natural gas. Oil and naphtha reforming account for about 30 \% of hydrogen production, followed by coal gasification and reformation of other hydrocarbons.\(^2\) Water electrolysis accounts for approximately 3.9 \% of today’s hydrogen production, with the remaining 0.1 \% representing all other sources.\(^2\)

Although hydrogen production by reformation of fossil fuels is relatively cheap, it results in the emission large quantities of CO\(_2\)(g).\(^2\) The push for sustainability and increased use of renewable sources of energy, along with fears about climate change, has created an incentive to cut back on emissions of greenhouse gasses such as CO\(_2\). Electrolysis of water is the process of directly splitting water into hydrogen and oxygen gas using electricity. Although many different types of electrolyzers are currently available, some of the most common types are alkaline electrolyzers, proton exchange membrane (PEM) electrolyzers, and solid oxide electrolysis cells (SOEC).\(^3\) The overall electrolysis of water reaction

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2
\]

does not directly result in the release of CO\(_2\). However, the electricity used to split the water will contribute to CO\(_2\) emissions unless it originated from a renewable source.
Depending on electrolyzer design, the efficiency of the electrolytic process taking place in water electrolyzers is typically in the range of 56 – 73 %. Overall efficiency, however, must take into account the thermal efficiency of converting heat into electricity that powers the electrolysis process. In the United States, the average thermal efficiency of electricity provided to the grid from generating sources is approximately 33 %. As a result, the overall efficiency of an electrolyzer powered from the grid, calculated as the product of the electrolysis and electricity generation efficiencies, is usually in the range of 18-24 %.

1.1 Thermochemical Cycles and Hybrid Thermochemical Cycles

A thermochemical cycle is a process for splitting water into hydrogen and oxygen gas through a series of chemical and sometimes electrochemical reactions at elevated temperatures. Heat and water are the only inputs in a thermochemical cycle; all other chemicals are recycled and reused throughout the process. A number of thermochemical cycles have been proposed since the 1970s as candidates for producing hydrogen gas more efficiently than direct electrolysis of water. Some examples of thermochemical cycles that have been considered as promising candidates are the cerium–chlorine (Ce–Cl), copper–chlorine (Cu–Cl), iron–chlorine (Fe–Cl), vanadium–chlorine (V–Cl), copper sulfate (Cu-SO4), and magnesium–iodine (Mg–I) cycles.

The Cu-Cl cycle can be transformed into a hybrid thermochemical cycle if it is developed so that one of the reaction steps is electrochemical, and therefore would require a small electrical input in addition to heat and water. The Cu-Cl hybrid thermochemical cycle can be represented by three main reactions, one of which is a relatively low temperature electrolysis reaction (Reaction 1), while the other two reactions are high temperature hydrolysis (Reaction 2) and decomposition (Reaction 3).
\begin{align*}
2 \text{CuCl} \cdot n\text{H}_2\text{O}(\text{aq}) + 2 \text{HCl} \cdot m\text{H}_2\text{O}(\text{aq}) &\rightarrow 2 \text{CuCl}_2 \cdot (n + m)\text{H}_2\text{O}(\text{aq}) + \text{H}_2(\text{g}) \quad [1] \\
\text{is an electrolysis reaction at 50–100}^\circ\text{C} \\
2 \text{CuCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) &\rightarrow \text{CuCl}_2 \cdot \text{CuO}(\text{s}) + 2 \text{HCl}(\text{g}) \quad [2] \\
\text{is a hydrolysis reaction at 310–375}^\circ\text{C} \\
\text{CuCl}_2 \cdot \text{CuO}(\text{s}) &\rightarrow 2 \text{CuCl}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \quad [3] \\
\text{is a decomposition reaction at 450–530}^\circ\text{C} \\
\end{align*}

In addition to the three main reactions, four other processes are involved in the cycle.\textsuperscript{5}

\begin{align*}
\text{H}_2\text{O}(\text{l}) &\rightarrow \text{H}_2\text{O}(\text{g}), \text{evaporation} \\
2 \text{CuCl}(\text{s}) + n\text{H}_2\text{O}(\text{l}) &\rightarrow 2 \text{CuCl} \cdot n\text{H}_2\text{O}(\text{aq}), \text{dissolution} \\
2 \text{CuCl}_2 \cdot (n + m)\text{H}_2\text{O}(\text{aq}) &\rightarrow 2 \text{CuCl}_2(\text{s}) + (n + m)\text{H}_2\text{O}(\text{l}), \text{crystallization} \\
2 \text{HCl}(\text{g}) + m\text{H}_2\text{O}(\text{l}) &\rightarrow 2 \text{HCl} \cdot m\text{H}_2\text{O}(\text{aq}), \text{dissolution} \\
\end{align*}

The inputs of the Cu-Cl hybrid thermochemical cycle are liquid water, \text{H}_2\text{O}(\text{l}), heat (from sources around 550 °C), and electricity.\textsuperscript{5} The outputs of the hybrid thermochemical cycle are the same as a thermochemical cycle: hydrogen and oxygen gas. Note that the waste heat from the high temperature reactions can be used for the electrolysis reaction to increase efficiency. One of the main advantages of the Cu-Cl hybrid thermochemical cycle are the moderate temperature requirement, 550 °C as opposed to other cycles that can range up to 1000 °C.\textsuperscript{4} The moderate temperature requirement enhances materials stability in the system design, and potentially allows for the heat to be supplied from Gen IV nuclear power plant reactors or concentrating solar power
plants. Furthermore, overall energy efficiency of the Cu-Cl cycle is reported to be in the range of 42-44 % which represents a significant increase in efficiency over electrolysis of water.  

1.2 Previous Work on the Cu-Cl Electrolyzer for the Hybrid Thermochemical Cycle

Research on the Cu-Cl hybrid thermochemical cycle has been funded by the U.S. Department of Energy (DOE) in an effort to develop a more efficient method of producing hydrogen gas. Under a subcontract with Argonne National Laboratory, the Electrochemical Technologies Lab of the Penn State Energy Institute has been researching the electrolysis step of the cycle [oxidizing Cu⁺(aq) to Cu²⁺(aq) species at the anode and reducing H⁺(aq) to H₂(g) at the cathode] in an effort to improve the overall efficiency of the cycle and reduce its costs. Studies included the construction of a lab scale electrolyzer system capable of variable flow rates of the anolyte and catholyte, and temperature control.

Previous work has focused on optimizing anolyte and catholyte concentrations, thermodynamic modeling of the CuCl-CuCl₂-HCl aqueous system, and measuring and optimizing membrane durability. An initial proof of concept study included developing the lab scale electrolyzer, and comparing CuCl(aq)/HCl(aq) electrolysis to electrolysis of water. Early testing used a CuCl-HCl-CuCl₂ aqueous solution as the anolyte and pure water as the catholyte. Thermodynamic modeling of the system, verified with experimental testing, obtained a decomposition potential for CuCl hydrogen production around -0.45 V. The measured decomposition potential of CuCl(aq)/HCl(aq) electrolysis was over 3 times lower than that of water electrolysis, consistent with proposals that CuCl electrolysis in the thermochemical cycle could result in hydrogen production using much lower amounts of electrical energy.

Copper deposition at the cathode, as a result of permeation through the membrane, is an issue as a result of copper inhibiting catalyst sites, and the parasitic copper deposition reaction
reducing the hydrogen production efficiency. Research into decreasing membrane permeability to copper, through hot-pressing and optimizing solution concentration, was successful in allowing the electrolyzer to run continuously for 100 hours with no observed copper deposition and minimal reduction of performance. Further testing of increasing the concentrations of HCl(aq) and CuCl(aq) to 6 mol/L and 2 mol/L respectively, and using 6 mol/L HCl(aq) as the catholyte, was successful in exceeding the 2015 design point set forth by the DOE of 0.5 A/cm² at an applied potential of 0.7 V, with current efficiency over 95% for a 24 hour period.
Chapter 2
RESEARCH MOTIVATION

The majority of hydrogen gas is currently produced from fossil fuels, resulting in the release of large quantities of CO$_2$ into the atmosphere. Demand for hydrogen gas is expected to continue to rise, and fears of climate change have resulted in an incentive to reduce the emission of greenhouse gasses such as CO$_2$. As a result, there is a need for development of cheap and efficient methods for producing hydrogen gas to support the growing demand, while simultaneously lowering emissions of CO$_2$. The Cu-Cl hybrid thermochemical cycle is one potential candidate being investigated as a means for producing hydrogen gas from water, heat from Gen IV nuclear power plants or concentrating solar plants, and small amounts of electricity compared to water electrolysis.

Desire to improve performance of the electrolysis step of the Cu-Cl hybrid thermochemical cycle, defined in terms of quantity of hydrogen produced at a given electrical power input, with larger quantities of hydrogen equating to better performance, results from increased viability of projects based on the proposed cycle with each incremental performance improvement. Electricity is expensive, and contributes to CO$_2$ emissions if not supplied from a renewable source of energy. Increasing the amount of hydrogen produced at a given electrical potential (performance of the electrolyzer) therefore lowers both the cost and potentially CO$_2$ emissions associated with a given quantity of hydrogen produced by the Cu-Cl cycle. In addition, platinum catalyst used for electrodes in the Cu-Cl electrolysis step represents a significant cost for proposed cycle designs. As a result, reduction of catalyst loading while still maintaining a desired level of performance enhances the economic viability.
This research adapted and used a lab scale electrolyzer developed at the Electrochemical Technologies Lab of the Pennsylvania State University Energy Institute and described in previous studies.\textsuperscript{5,9,10} The goals of this research were to maximize the Cu-Cl electrolyzer cell performance, and minimize the amount of platinum catalyst required to be used for the electrodes. In addition, other aspects of the electrolyzer performance such as the effect of changing temperature, and the performance dependence on flow rate of the anolyte and catholyte solutions through the cell were explored.
3.1 Testing System: Lab Scale Electrolyzer

The lab scale electrolyzer was an experimental testing system designed to continuously monitor and operate an electrolytic cell. The main components of the electrolyzer, shown in Figure 1, were an electrolytic cell that housed the membrane electrode assembly (MEA), the anolyte and catholyte tanks with their respective solution pumps, a regeneration column for the anolyte solution, a damping column for the catholyte solution, an oil bath used to maintain the anolyte and catholyte solutions at a desired temperature, and a hydrogen measurement system. The entire system was controlled by LabVIEW on a computer. Thermocouples were used to monitor the temperature at individual components of the system, and heating elements controlled by solid state relays maintained a desired temperature at the cell, regeneration column, and damping column.
Figure 1: Lab scale electrolyzer used for catalyst loading, temperature, flow rate, and pressure dependence testing; 1 – catholyte tank containing 7 mol/L HCl(aq); 2 – anolyte tank containing 2 moles of CuCl(aq) per liter of 7 mol/L HCl(aq); 3,4 – catholyte and anolyte pumps respectively; 5 – damping column; 6 – regeneration column containing layers of copper shot and glass beads; 7 – electrolyzer cell; 8,9,10,11 – hydrogen measurement system including HCl removal, dessicator, flow meter, and hydrogen storage tank respectively.

The catholyte and anolyte solution tanks were each filled with 1.5 liters of solution and submerged in an oil bath to control the solution temperature. The catholyte solution was 7 mol/L HCl(aq) purged with hydrogen gas. Catholyte solution was pumped from the solution tank to a damping column that acted to steady the flow rate of the solution from the pump. The solution then entered the cell passing through serpentine flow channels across the cathode before exiting the cell back into the solution tank. Hydrogen gas produced at the cathode was carried out of the cell by the catholyte solution and into the catholyte tank. Hydrogen gas exited the top of the catholyte tank into the hydrogen measurement system. The hydrogen gas was first bubbled through a column of water to remove any HCl vapor. Water vapor was removed by a column of
packed desiccant before the gas entered a flow meter to measure the rate of production. Hydrogen gas then exited the flow meter into a storage tank. A pressure transducer connected to the storage tank allowed for proper calculations of the molar flow rate.

The anolyte solution was 1 mol CuCl$_2$(aq) per liter of 7 mol/L HCl(aq) solution. The anolyte solution was pumped from the solution tank into the bottom of the regeneration column. The regeneration column consisted of layers of glass beads and copper shot. In the regeneration column, 1 mole of CuCl$_2$(aq) reacted with solid copper to form 2 moles of CuCl(aq). The solution then exited the top of the regeneration column and was fed into the cell where it followed serpentine flow channels across the anode. The solution then exited the cell back into the anolyte solution tank where it was recalculated. Before testing, anolyte solution was circulated through the regeneration column for several minutes converting the [1 mol/L CuCl$_2$(aq) + 7 mol/L HCl(aq)] solution to [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)].

The main components of the electrolyzer cell were the membrane electrode assembly (MEA), two graphite bipolar plates with flow channels for the anolyte and catholyte, a fluorosilicone gasket used to seal the MEA between the graphite plates, Hastelloy X plates used to protect the exterior of the bipolar plates, bolts used to secure the cell together, and heating tape applied to the Hastelloy X plates to control the cell temperature. The bolts holding the cell together were tightened to 15 in-lb of torque. Solutions, reactions, and the flows of electrons and
protons for the cell are shown in Figure 2.

![Figure 2: Simplified diagram of the electrolyzer cell showing the solutions and reactions occurring at both the cathode and anode.](image)

Membranes used in this research were Nafion 117 (Ion Power Inc.) hot pressed, chemically cleaned, and protonated before use as described in previous papers.\textsuperscript{9,10} Chemical treatment of the membrane consisted of soaking in 3 wt.% H\textsubscript{2}O\textsubscript{2}(aq) to remove any impurity or residue from the membrane surface, followed by rinsing in deionized water, soaking in 1 mol/L H\textsubscript{2}SO\textsubscript{4}(aq) to protonate the membrane, and lastly a final rinse in deionized water. The membrane was placed in each solution for 1 hour, and all solutions were held at 80 °C. Membranes were stored in a desiccator, and soaked in deionized water for 15 minutes before use.
3.2 Electrode Preparation: Airbrushing Platinum Catalyst onto Carbon Cloth

Electrodes used for testing in the lab scale electrolyzer were previously made by painting a platinum/carbon ink bound by Nafion 117 solution onto 5 cm$^2$ carbon cloth. For this research, however, a transition was made to spraying catalyst ink onto carbon cloth electrodes using argon as a carrier gas. Catalyst ink was prepared by mixing Vulcan XC-72R loaded with 20% platinum, Nafion 117 solution, deionized (DI) water, and isopropyl alcohol (IPA) in that order. 15% Nafion 117 solution was mixed with Vulcan XC-72R in a ratio of 2.86:1 Nafion 117 to Vulcan XC-72R by mass. DI water was added in a 4:1 DI water to Vulcan XC-72R by mass, and IPA was added in a 20:1 IPA to Vulcan XC-72R by mass. The ink was mixed thoroughly in a small test tube and sonicated to completely suspend catalyst particles in a homogeneous mixture. IPA was added as necessary to break up any catalyst chunks and completely suspend the catalyst particles. The ink was loaded into a gravity fed Aztek airbrush connected to an argon gas cylinder with pressure set to 1.38 bar. Flow was adjusted so that the ratio of argon to ink created a fine mist of catalyst and prevented wetting of the carbon cloth. Ink was sprayed across the two 5 cm$^2$ carbon cloth electrodes as they were periodically rotated to ensure an even coating. The electrodes were weighed before and after spraying to calculate catalyst loading. Before weighing, the electrodes were placed in a desiccator to completely dry. Additional spraying was done to reach the desired loading if necessary.

3.3 Solution Preparation

Catholyte solution of 7 mol/L HCl(aq) was prepared by weighing out the desired mass of 37% mass basis hydrochloric acid from Sigma Aldrich. The hydrochloric acid was then poured into a volumetric flask. Deionized water from a Millipore water purification system was slowly
poured into the volumetric flask, and periodically shaken or inverted to thoroughly mix the solution. The flask was filled with deionized water up to the etched line, and inverted a few times to ensure complete mixing of the solution. Additional water was added if necessary to compensate for the volume change due to mixing.

Anolyte solution was made by first preparing a solution of 7 mol/L HCl(aq) solution as described for the catholyte. The desired amount of 97% pure copper (II) chloride powder from Sigma Aldrich was then weighed out and placed in a container for mixing. The 7 mol/L HCl(aq) solution was then poured into the mixing container and shaken vigorously until complete dissolution of the CuCl₂ powder.

### 3.4 Electrochemical Measurements

Electrochemical measurements were performed using a Gamry Reference 3000 potentiostat (Gamry Instruments). Linear sweep voltammetry (LSV) was performed at scan rates of 10 mV/s from an applied potential of 0 to 0.7 V to measure the current response of the cell. LSV scans were compared at an applied potential of 0.7 V when possible. Due to current limitations of the Gamry Reference 3000 some LSV scans on higher catalyst loading configurations did not make it completely to the 0.7 V applied potential, and therefore comparison was made at 0.6 V. Electrochemical impedance spectroscopy (EIS) was performed on the cell from 0.005 Hz to 100,000 Hz in order to obtain the ohmic, charge transfer, and mass transfer impedances of the cell.
Chapter 4
RESULTS AND DISCUSSION

4.1 Performance Dependence on Catalyst Application Technique: Painting vs. Spraying

Performance of the lab scale electrolyzer is defined by current density (ampere (A) per geometric cm$^2$ of carbon cloth) at a given applied potential (V), with higher current densities corresponding to better performance. Electrical power, measured in watt (W), is the product of V and A. Faraday’s law of electrolysis relates the charge passed through an electrochemical cell to the quantity of hydrogen produced. Increasing the current density (charge passed per area per unit time) of the Cu-Cl electrolyzer at a given applied potential therefore increases the amount of hydrogen gas produced at a given electrical power input.

Reactions at the cathode and anode of a Cu-Cl electrolyzer occur at the phase boundary between the catalyst particles and the aqueous solutions. Previous research on the Cu-Cl electrolyzer used carbon cloth painted with an ink of XC-72R catalyst/Nafion 117 for both the cathode and anode electrodes. Various studies on fuel cells and electrolyzers have demonstrated that spray-based methods of catalyst application have been effective in increasing cell performance. For this research, a transition to spraying the catalyst ink onto the carbon cloth electrodes was made in order to quantify the effect of spraying catalyst when adapted to the Cu-Cl electrolyzer.

Performance was measured using a Gamry Reference 3000 potentiostat to perform LSV sweeps at 10 mV/s between the cathode and anode of the electrolytic cell and are shown in Figure 3.
Figure 3: Comparison of brushed and sprayed carbon cloth electrodes on the lab scale electrolyzer performance; LSV scan rate 10 mV/s; temperature 80 °C; catalyst loading 0.8 mg Pt/cm²; 5 cm² geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.

The transition from painting to spraying catalyst ink on the carbon cloth electrodes resulted in a dramatic performance increase for the electrolyzer as seen in Figure 3. Although 0.7 V is the design point applied potential of the electrolyzer, and where normal comparison is made, the current density of the sprayed electrodes at 0.7 V could not be measured due to the current limitations of the Gamry Reference 3000 potentiostat at a little over 3 A. At an applied potential of 0.6 V the current density of the painted ink electrodes was 0.309 A/cm². At the same applied potential, the current density for the sprayed electrode was 0.500 A/cm² marking a 62 % increase in performance transitioning from paint to spray application of catalyst.
With all other testing parameters held constant, the 62% increase in current density at the same applied potential must be a result in changes of the electrode characteristics from catalyst application technique.

Figure 4: SEM image of a carbon cloth painted with Vulcan XC-72R catalyst ink.

Painting catalyst ink onto a carbon cloth electrode involves applying a coating of wet ink to the carbon cloth surface, and allowing that coating to dry. Figure 4 shows the surface of a carbon cloth electrode painted with catalyst ink. The cracked chunks are the catalyst ink, while the slightly curved lines seen between the chunks are weaves of carbon cloth. The painted catalyst does not appear to bond well to the individual strands of carbon, and instead forms chunks around the weaves. As a result, the individual strands of carbon are primarily left bare without catalyst.
Spraying catalyst ink onto carbon cloth involves using argon gas to carry ink to the carbon surface in a fine mist. As seen in Figure 5, the fine mist of catalyst ink bonds well to the individual weaves of carbon cloth. The strands of carbon are each coated with a layer of platinum/carbon catalyst, and therefore the surface area coated with catalyst appears to be much greater than for the painted electrode seen in Figure 4.
A close up view at 273x magnification of individual strands of carbon coated in catalyst can be seen in Figure 6. The sprayed catalyst ink completely surrounds individual strands of carbon, and bonds well without cracking off into chunks. The performance increase transitioning from painted to sprayed electrodes can be visually explained by SEM images of the electrode surfaces. Sprayed surfaces show a much more even and complete bonding of catalyst ink to individual carbon cloth strands, resulting in a much higher surface area of catalyst exposed to the solutions.

4.2 Performance Dependence on Loading for Sprayed Electrodes

The effect of reducing catalyst loading on both the anode and cathode was quantified using LSV with a 10 mV/s scan rate. Sprayed electrodes with catalyst loadings of 0.4 mg/cm² and 0.8 mg/cm² platinum were compared at an applied potential of 0.6 V averaged across multiple
LSV scans to account for random error. The average current density for the 0.8 mg/cm$^2$ platinum loading at a 0.6 V applied potential was 0.495 ± 0.007 A/cm$^2$, while the average current density for the 0.4 mg/cm$^2$ platinum loading was 0.359 ± 0.011 A/cm$^2$. Reducing catalyst loading by 50% therefore resulted in an approximately 28% reduction in current density at an applied potential of 0.6 V. At the design applied potential of 0.7 V, the average current density of the 0.4 mg/cm$^2$ platinum loading electrodes was 0.508 ± 0.016 A/cm$^2$, which was in range of the design target current density of 0.5 A/cm$^2$.

In order to further reduce catalyst loading without sacrificing performance to a level below the design target of 0.5 A/cm$^2$, reduction of catalyst at the anode and cathode independently was explored. The reaction occurring at the cathode is a hydrogen evolution reaction, for which it is well known that platinum is an effective catalyst. The rate determining step in the cell has yet to be established, however, and therefore the effect of reducing catalyst at each electrode on overall cell performance is unknown. In order to test the effect of reducing catalyst from the anode and cathode, LSV sweeps were run on sets of electrodes with loadings of 0.4 mg/cm$^2$ platinum at the cathode and 0.1 mg/cm$^2$ platinum at the anode, and a second set of electrodes with loadings of 0.1 mg/cm$^2$ at the cathode and 0.4 mg/cm$^2$ at the anode.
Figure 7: Comparison of reduced catalyst loadings at the cathode and anode on the lab scale electrolyzer performance; LSV scan rate 10 mV/s; temperature 80 ºC; 5 cm$^2$ geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.

Comparing the LSV sweeps in Figure 7, one can see that reducing catalyst loading at the anode resulted in much better performance compared to reducing catalyst loading at the cathode. Therefore, it is clear that platinum is more important as a catalyst for reactions at the cathode then it is for reactions occurring at the anode in terms of performance of the Cu-Cl electrolytic cell.

EIS measurements were taken to look for differences in impedances between the two sets of electrodes, and provide insight into why reduction of catalyst at the cathode resulted in much lower performance. Measurements, shown in Figure 8, were taken as cathode vs. anode, so the
measured impedances take into account contributions from reactions occurring at both electrodes. It therefore was not immediately possible in this study to separate the individual impedance contributions from the anode and cathode reactions. However, an attempt was made to incorporate a silver-chloride reference electrode into the cell design and take electrochemical measurements on reactions occurring at both electrodes separately, but in initial designs the reference electrode failed to maintain sufficient contact with solution for accurate measurement.

Figure 8: EIS plot of the independently reduced loadings on the cathode and anode at an applied potential of 0.1 V. Frequency range: 0.005 to 100,000 Hz; temperature 80 °C; 5 cm² geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.
EIS were obtained at an applied potential of 0.1 V, which is close to the experimental decomposition potential of the cell. The first small arc seen in Figure 9, the high frequency arc starting when the imaginary impedance crosses the x-axis, is commonly taken as the charge transfer resistance. The charge transfer arc is orders of magnitude smaller than the large arc seen in Figure 8, the lower frequency arc, which is commonly taken as the mass transfer resistance parameter. The relative sizes of the charge transfer and mass transfer resistances indicate that the Cu-Cl electrolyzer system is primarily limited by mass transfer under these conditions. In addition, as seen in Figure 9, the charge transfer arc is larger for the situation of reduced catalyst loading on the cathode then it is for the reduced catalyst loading on the anode, indicating that the charge transfer resistance is also larger. The finding of reduced catalyst loading on the cathode leading to larger charge transfer resistances suggests that the charge transfer reaction at the cathode is comparatively slower than at the anode, and is consistent with the results seen in
Figure 7, where the LSV for reduced catalyst on the cathode showed lower performance than reduced catalyst on the anode.

The degree to which catalyst is required on the anode was tested by exploring the extreme situation where platinum catalyst was completely removed from the anode (a blank carbon cloth was used), and 0.4 mg/cm$^2$ platinum catalyst remained at the cathode.

![Graph showing LSV for reduced catalyst on the cathode and anode](image)

Figure 10: Comparison of 0.4 mg/cm$^2$ platinum catalyst loading on both the anode and cathode to 0.0 mg/cm$^2$ at the anode and 0.4 mg/cm$^2$ at the cathode on the lab scale electrolyzer performance. LSV scan rate 10 mV/s; temperature 80 °C; 5 cm$^2$ geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.

A comparison of the control setup, where 0.4 mg/cm$^2$ platinum catalyst was used at both the anode and cathode, and the setup where catalyst was completely removed from the anode is
seen in Figure 10. There was a noticeable performance drop, from 0.535 A/cm$^2$ to 0.449 A/cm$^2$ at an applied potential of 0.7 V when catalyst was completely removed from the anode. Therefore, it can be seen that the Vulcan XC-72R catalyst helped with both the anode and cathode reactions, and from Figure 7 it can be seen that the catalyst was more important on the cathode than the anode.

![Graph showing current density vs. applied potential](image)

**Figure 11**: Comparison of 0.4 mg/cm$^2$ on both the anode and cathode to 0.1 mg/cm$^2$ at the anode and 0.4 mg/cm$^2$ at the cathode on the lab scale electrolyzer performance; LSV scan rate 10 mV/s; temperature 80 °C; 5 cm$^2$ geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; flow rates of 220 mL/min for both the anolyte and catholyte.

When the catalyst loading at the anode was reduced from 0.4 to 0.1 mg/cm$^2$ platinum, with the cathode loading held constant at 0.4 mg/cm$^2$, the current density of the LSV actually increased at the design applied potential of 0.7 V. The average current density for the 0.1 mg/cm$^2$
platinum anode loading at a 0.7 V applied potential was 0.555 ± 0.001 A/cm², while the average current density for the 0.4 mg/cm² platinum anode loading was 0.508 ± 0.016 A/cm². It is interesting to note that at lower potentials the current density for reduced catalyst loading at the anode is actually lower than the full catalyst loading, and there is a transition point around 0.55 V where the current density of the reduced anode loading surpasses that of the full loading. It is possible that at lower potentials, the charge transfer region, a lack of catalyst on the anode hinders performance because charge transfer impedances dominate. And at higher potentials, the mass transfer region, a lack of catalyst on the anode actually is beneficial for performance due to improved mass transfer and solution flow without having to permeate through the bulk catalyst layer.

In an overall comparison of the original sprayed platinum loadings of 0.8 mg/cm² on both the cathode and anode, to loadings of 0.4 mg/cm² and 0.1 mg/cm², respectively, the required amount of platinum catalyst was reduced by 69 % while only decreasing current density by approximately 24 % at an applied potential of 0.6 V.

4.3 Current Efficiency of the Electrolyzer

Faraday’s law relates the quantity of charge passed to the quantity of chemical produced assuming 100 % current efficiency. If undesirable side reactions take place such as the deposition of solid copper, however, the quantity of hydrogen produced will be lower than the theoretically calculated amount. In order to test for the presence of side reactions, hydrogen production was measured and compared to the theoretical volume produced through Faraday’s law and the ideal gas law.
Table 1: Hydrogen production measurements compared to theoretically calculated hydrogen production to calculate the current efficiency over an 8 minute time interval at 80 ºC.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Measured H₂ Production (mL/min)</th>
<th>Theoretical H₂ production (mL/min)</th>
<th>Current Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.57</td>
<td>11.97</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>11.64</td>
<td>11.97</td>
<td>0.97</td>
</tr>
<tr>
<td>3</td>
<td>11.80</td>
<td>11.96</td>
<td>0.99</td>
</tr>
<tr>
<td>4</td>
<td>11.56</td>
<td>11.96</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>11.71</td>
<td>11.96</td>
<td>0.98</td>
</tr>
<tr>
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<td>11.79</td>
<td>11.96</td>
<td>0.99</td>
</tr>
<tr>
<td>7</td>
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<td>11.95</td>
<td>0.98</td>
</tr>
<tr>
<td>8</td>
<td>11.37</td>
<td>11.95</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The average current efficiency over the time interval measured was 97 %, indicating that very little to no undesirable side reactions were taking place. Possible error results from small leaks in the hydrogen measurement system. The current efficiency results matched closely with previous studies.\textsuperscript{5,9,10}

4.4 Temperature dependence of the lab-scale electrolyzer performance

Temperature dependence of the lab scale electrolyzer was tested by taking LSV measurements with a scan rate of 10 mV/s at various temperatures as the temperature increased from 36 to 80 ºC. Current densities were then compared at an applied potential of 0.7 V. Flow rate of the electrolyzer was held constant at 220 mL/min for both the catholyte and anolyte throughout testing. Gauge pressure of the catholyte was 0.04 bar, with an atmospheric pressure of 1.002 bars.
Temperature has an effect on multiple aspects of the electrolyzer system, such as membrane resistance, reaction kinetics, and thermodynamics such as the activities of reacting species. The current density of the electrolyzer at an applied potential of 0.7 V appeared to increase linearly by 0.0042 A cm\(^{-2}\) °C\(^{-1}\) from 36 °C to 80 °C, with an \(R^2\) value of 0.9967. Increasing temperature from 36 to 80 °C therefore resulted in a 50 % increase in current density at the same applied potential. Given that temperature affects multiple aspects of the system, and yet a linear dependence on temperature is observed, it is likely that factors with linear temperature dependence were rate limiting, and had the greatest impact on performance over the temperature range tested.
4.5 Flow Rate Dependence of the Electrolyzer

The lab scale electrolyzer was equipped with pumps capable of variable flow rates for the anolyte and catholyte solutions. Increasing flow rates of the solutions results in enhanced transport of reactants to the electrode surfaces and removal of reaction products.\(^5\)

![Current density dependence of the lab-scale electrolyzer](image)

Figure 13. Current density dependence of the lab-scale electrolyzer on the flow rate of the anolyte and catholyte; Cathode loading of 0.1 mg Pt/cm\(^2\) and an anode loading of 0.4 mg Pt/cm\(^2\); [2 mol/L CuCl(aq) + 7 mol/L HCl(aq)] anolyte; 7 mol/L HCl(aq) catholyte; applied potential 0.7 V; temperature 80 °C.

Over the range of flow rates tested 80 ± 5, 150 ± 5, and 300 ± 5 mL/min, the current density was observed to follow an increasing trend. The increasing trend indicates that reactions occurring in the cell are primarily limited by transport of the reacting species and removal of products under these conditions as opposed to chemical kinetic limitations.
Figure 14: LSV comparison of different flow rates on the performance of the lab scale electrolyzer. 0.4 mg/cm² platinum at the cathode, 0.1 mg/cm² at the anode; scan rate 10 mV/s; temperature 80 ºC; 5 cm² geometric area for the cathode and anode electrodes; hot-pressed Nafion 117 membrane; anolyte: 2 mol/L CuCl(aq) in 7 mol/L HCl(aq); catholyte: 7 mol/L HCl(aq).

When flow rates were adjusted at the cathode and anode independently, slightly higher current densities were achieved with flow rates of 220 mL/min at the anode and 80 mL/min at the cathode than 80 mL/min at the anode and 220 mL/min at the cathode. Overall, however, the performance difference between the reduced flow rates at the anode and cathode independently was small compared to conditions when both flow rates were increased or decreased at both electrodes. The small performance difference between independently reduced flow rates indicates that transport processes have significant impacts at both the cathode and anode in terms of overall cell performance.
Chapter 5

SUMMARY AND CONCLUSION

The Cu-Cl hybrid thermochemical cycle is a promising technology for efficient production of hydrogen gas due to the relatively low temperature requirement of the cycle. In this research, a lab scale electrolyzer was used to study the electrolysis step of the cycle. A 62 % increase in current density at an applied potential of 0.6 V was achieved for electrodes of 0.8 mg/cm² platinum catalyst loading by transitioning from painting to spraying as a technique for catalyst application. Comparing electrolyzer performance when the catalyst loading was reduced independently at the cathode and anode indicated that the catalyst was comparatively more effective at the cathode for overall cell performance. When sprayed platinum loadings were reduced from 0.8 mg/cm² on both the cathode and anode, to 0.4 mg/cm² and 0.1 mg/cm², respectively, the required amount of platinum catalyst was reduced by 69 % while only decreasing current density by approximately 24 % at an applied potential of 0.6 V. The larger charge transfer resistance observed with low platinum loading at the cathode suggested that the cathode reaction was slower relative to the anode. Over the temperature range and conditions tested, the current density of the electrolyzer at an applied potential of 0.7 V followed a linearly increasing trend with temperature, indicating that phenomena with linear temperature dependence such as membrane resistance improved the cell performance within this range. Furthermore, increasing the flow rates of the anolyte and catholyte over a range from 80 to 300 mL/min resulted in increases in current density, indicating that under these conditions transport processes that supply reacting species and removing products are rate limiting. Results of this study suggest that further improvements to the cell should focus on maximizing transport occurring at the
cathode and anode, working at increased temperature, and favoring catalyst loading on the cathode over the anode.


ACADEMIC VITA

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EDUCATION
The Pennsylvania State University, Schreyer Honors College, University Park, PA
Candidate for Bachelor of Science Degree, May 2014
Major: Energy Engineering
Minor: Electrochemical Engineering

PROFESSIONAL EXPERIENCE

Energy Institute  
Researcher, University Park, PA  
Spring 2013 – Present  
- Developed and tested Cu-Cl electrolyzer configurations to improve the efficiency of a hybrid thermochemical cycle  
- Used a potentiostat for EIS, LSV, and cyclic voltammetry analysis testing electrolyzers

Sithe Global  
Intern, New York, NY  
Summer 2012  
- Assisted with due diligence, energy models, budgets, and pro formas for energy projects in various countries  
- Prepared a feasibility study and project implementation guide for a micro-hydro project in Guyana  
- Created an energy calculation model for hydroelectric projects  
- Spent two weeks in the Philippines assisting with the commissioning of a 600 MW coal-fired power plant

Sigma Consultants, Inc.  
Intern, Acton, MA  
Summer 2010 and 2011  
- Reviewed and consolidated information from multiple Environmental and Social Management Plans to create an overall environmental budget for the proposed 165 MW Amaila Hydro Project in Guyana  
- Created a tracking register of environmental issues from construction inspection reports of a 170-km road under construction in the rainforest of Guyana  
- Prepared a zoning application for a 340 MW parabolic trough concentrating solar project in Arizona

LEADERSHIP EXPERIENCE

Department of Energy Engineering Accreditation Review  
Penn State University, University Park, PA  
Fall 2011  
- Selected by the Dean’s office and recommended by faculty of the Department of Earth and Mineral Sciences to consult with the independent Accreditation Board for Engineering and Technology (ABET) prior to the Department’s successful accreditation

Eagle Scout Project  
Handicapped Accessible Picnic Tables for Town Park, Sudbury, MA  
Spring 2009 – Winter 2010
• Designed handicapped accessible tables, obtained town approvals, recruited volunteers to assist in the construction, and organized the transport and installation of the tables

Lincoln Sudbury Regional HS Volleyball Team  
Fall 2006 – Spring 2010
Captain, Spring 2010

• Led team in practice and games, organized team fundraisers, and planned social events for parents and players

ADDITIONAL SKILLS
• Proficient in: Mathematica, Arduino programming, MS Office

PUBLICATIONS

SCHOLARSHIPS AND HONORS
• Phi Eta Sigma National Honor Society
• Energy and Mineral Engineering General Scholarship
• Virginia S. and Philip L. Walker Jr. Enrichment Scholarship

CAMPUS ACTIVITIES
• Phi Eta Sigma National Honor Society Thon Committee (fundraiser for cancer research)
• Energy Engineering Club
• Society of Energy Engineers
• Mixed Martial Arts Club