

## II.F.1 R&D Status for the Cu-Cl Thermochemical Cycle-2010

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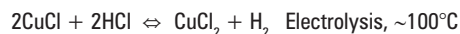
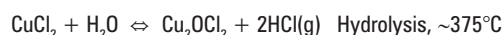
Start Date: June 2006  
Projected End Date: September 2015

- Demonstrated high yields from the hydrolysis reactor with lower steam usage. Lowering the steam requirement improves the process efficiency.
- Developed a method for quantifying the amount of  $\text{Cu}_2\text{OCl}_2$  produced from the hydrolysis reactor.



### Introduction

The U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE) is supporting the development of thermochemical cycles that use solar heat. Their focus is to identify thermochemical cycles that operate with solar heat and meet efficiency and cost targets. The lower temperature option for this cycle is attractive to DOE-EERE because the solar power tower provides heat near 550°C and is near commercialization. The three reactions in the Cu-Cl cycle are shown in the following. The experimentally verified temperatures for the two thermal reactions (hydrolysis and decomposition) are within the range of the solar power tower's process heat.



Based on preliminary experimental and modeling work, the Cu-Cl thermochemical cycle was chosen for further development for the following reasons:

- A maximum cycle temperature of  $\sim 550^\circ\text{C}$  has been verified.
- All reactions have been demonstrated at laboratory scale.
- No catalysts are needed for thermal reactions and no catalyst is needed for the anode in the electrolyzer.
- Conceptual process design is based on commercially practiced technologies.
- Preliminary mass and energy balanced flowsheet showed promising efficiency and the corresponding H2A showed estimated hydrogen production costs were within the proposed DOE target.

While the cycle has the attributes listed above, there are significant challenges in the electrolysis reaction and in the hydrolysis reaction. Copper crossover/cell degradation is observed in the former and a large excess of steam is required for complete conversion in the latter.

### Objectives

The strategic objective is to develop a robust process for producing hydrogen using the Cu-Cl thermochemical cycle. This year's objective is to facilitate the development of the electrolyzer capable of long-term operation. The long-term goal remains an integrated laboratory-scale demonstration for the Cu-Cl cycle.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (W) Concentrated Solar Energy Capital Cost

### Technical Targets

The proposed target for the cost of hydrogen production is \$6.00 per gasoline gallon equivalent (gge)  $\text{H}_2$ .

### Accomplishments

- Initiated a development and testing program for new membrane materials for the CuCl electrolyzer.
- Collaborated with the Atomic Energy of Canada Ltd. (AECL) and five Canadian universities funded by the Ontario Research Foundation.

## Approach

In the early electrolysis experiments, copper crossover was observed with both anion and cation exchange membranes. Copper crossover represents a potential showstopper as it degrades the electrolyzer's performance and prevents long-term operation of the electrolyzer at a stable cell voltage. A membrane development project has been initiated to identify and test promising membrane materials for the CuCl electrolyzer. Three types of cation exchange membranes are being tested in the first phase of this work: (1) commercial membranes such as Nafion<sup>®</sup> and CMX, (2) Nafion<sup>®</sup> coated with a low permeability layer for larger ions, and (3) new materials such as the polysulfone membranes, which can also be modified to obtain the desired cation selectivity and which were able to reduce sulfur crossover in the hybrid sulfur electrolyzer [1]. Screening tests include diffusivity, water uptake, conductivity, and ion exchange capacity measurements in high acid environments and water over a range of temperatures. The most promising samples will be tested for chemical stability and durability in electrolyzers at AECL and Pennsylvania State University (PSU). In the second phase of the work, tests will be conducted at elevated temperature and solutions with varying concentrations of CuCl, CuCl<sub>2</sub> and HCl. Since the electrolyzer tests are by definition long-term tests, the use of screening tests, which take a shorter time, should expedite the search for the 'best' membrane.

The challenge for the hydrolysis reaction was that the reactor used a large excess of steam to convert all of the CuCl<sub>2</sub> to Cu<sub>2</sub>OCl<sub>2</sub>. This high steam demand adversely impacts the efficiency of the cycle and the cost of hydrogen production. The goal of the current research was to verify the model's prediction that subatmospheric pressure operation would reduce steam demand. At one bar, a steam to CuCl<sub>2</sub> molar ratio of 20-23 was required for >97% conversion experimentally, somewhat higher than the model's value of 17. However, at 0.25 bar, the model predicts a steam to CuCl<sub>2</sub> molar ratio of only 7 is needed for complete conversion. A low-cost, commercially used method to obtain a partial vacuum, i.e., an aspirator or ejector, was tested. Since CuCl has been found in all of the hydrolysis products, experiments to determine the mechanism of CuCl formation were also planned. Possible mechanisms for the formation of CuCl are the decomposition of CuCl<sub>2</sub> or Cu<sub>2</sub>OCl<sub>2</sub> or a combination of both. CuCl<sub>2</sub> decomposition results in the formation of Cl<sub>2</sub> and CuCl, while the decomposition of Cu<sub>2</sub>OCl<sub>2</sub> results in CuCl and oxygen. The corrosive nature of the gaseous products prevents measurement of the mechanism and kinetics by standard techniques. However, experiments following changes in the environment around the Cu ion will provide this information. Synchrotron radiation allows this type of

measurement and is available at the Advanced Photon Source at Argonne National Laboratory. Extended X-ray absorption fine structure analysis has been a key technique for determining the substitution of O with Cl or vice versa in the first coordination sphere of the copper species [1]. X-ray absorption near-edge spectroscopy (XANES) at Cu K-edge would allow us to determine the coordination geometry of Cu in the samples. The XANES spectra of the Cu species of interest have been reported in literature to be very distinctive [2] and therefore a method to obtain quantitative information on the composition of the samples during reaction. A matrix of experiments has been designed to measure CuCl<sub>2</sub> and Cu<sub>2</sub>OCl<sub>2</sub> decomposition as a function of temperature and time and to measure the formation of Cu<sub>2</sub>OCl<sub>2</sub> as a function of time, temperature and steam to CuCl<sub>2</sub> molar ratio.

## Results

### Membrane Development

The membrane development project is new and is a collaborative effort involving several institutions. Argonne National Laboratory is preparing low permeability membranes for the anode by applying low-permeability coatings on commercial Nafion<sup>®</sup> 115 membrane. The coatings consist of either (a) substituted aromatic hydrocarbons or (b) a non-aromatic that forms a flexible network through the pores to inhibit the transport of copper ions without sacrificing the ion exchange capacity of the precursor Nafion<sup>®</sup> membrane. These membranes are then processed according to published literature. Polymer chemists at PSU and Sandia National Laboratories are developing polysulfone membranes, whose selectivity can be tuned by the choice and number of side groups [3,4]. Electrolysis experiments are conducted at PSU and AECL.

Membrane samples are now being examined. Diffusivity measurements of Cu species through the membranes are being used as the primary screening technique. The diffusion cell consists of two compartments separated by a membrane and is shown in Figure 1. The solute-rich side contains the solution of CuCl<sub>2</sub> dissolved in a hydrochloric acid solution and the solvent-rich side, either a solution of HCl or water. The diffusion of copper species into the solvent-rich side versus time is measured by following the change in concentration of the Cu species on the solvent-rich side.

The concentrations of Cu species are being determined by measuring the absorbance using ultraviolet-visual spectroscopy and correlating it with the absorbance of standards prepared by dissolving a known amount of CuCl<sub>2</sub> into the desired solution, in this case 10.2 M HCl. Standards spanned CuCl<sub>2</sub> concentrations from 25 to 1,000 ppm. The maximum absorbance was



**FIGURE 1.** Diffusion cell set up for testing membrane with a solution of  $\text{CuCl}_2$  in 10.2 M HCl solution on the solute-rich side and 10.2 M HCl solution on the solvent-rich side.

measured at 380 nm. The HCl concentration for both the solute-rich and solvent-rich sides is 10.2 M because these conditions were used by AECL in their longest duration test.

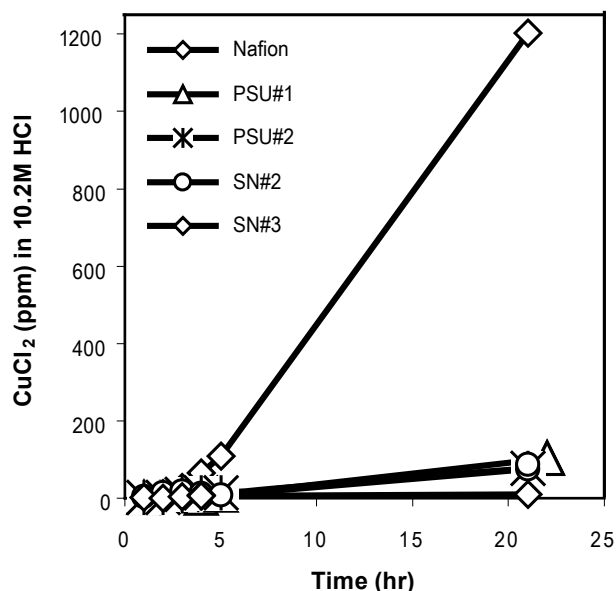
Figure 2 shows the results of the diffusivity measurements of Nafion<sup>®</sup>, Nafion<sup>®</sup> with three polymeric coatings, and two samples of s-Radel, a polysulfone-type membrane. As can be seen, the new membranes have lower diffusivity with respect to copper than does Nafion<sup>®</sup>. Based on these results, new membranes are being modified to further reduce transport of Cu species.

Conductivity measurements are in progress as are measurements of the ion exchange capacity and water uptake. Samples have been sent to PSU and AECL for testing copper crossover in their electrolyzers. Higher temperature tests are either in progress or will be started shortly.

### Hydrolysis Reaction

The model as well as Le Chatelier's Principle shows that reduced pressure operation should result in lower steam demand for complete conversion to the desired products in the hydrolysis reaction. An aspirator, a relatively low-cost method to obtain a partial vacuum, was added to the exit of the hydrolysis reactor. A schematic of the set-up and details of the experimental method are described elsewhere [5,6]. Experiments were conducted at 0.4, 0.7 and 1 bar. The amount of  $\text{Cu}_2\text{OCl}_2$  in the products was quantified using oxygen evolution from the decomposition of the solid products. The amount of  $\text{O}_2$  produced was calibrated using a known amount of Cu to form CuO in presence of 5%  $\text{O}_2/\text{He}$ . The yield of  $\text{Cu}_2\text{OCl}_2$  was calculated based on the ratio of the measured  $\text{O}_2$  to the theoretical value. The amount of CuCl was measured using a wet chemistry method.

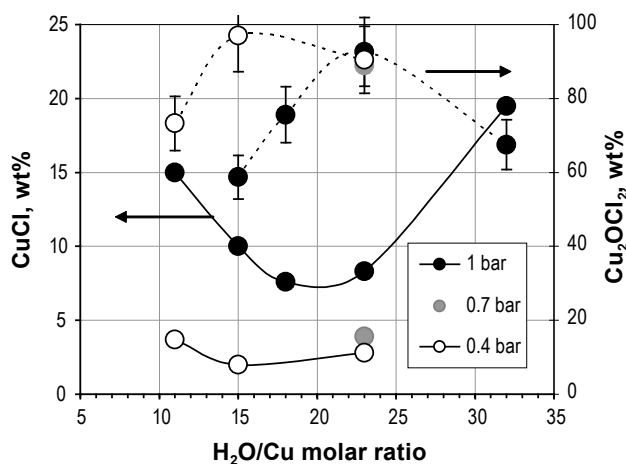
Figure 3 shows the amount of CuCl and  $\text{Cu}_2\text{OCl}_2$  formed at the three pressures. At 0.4 and 0.7 bar, the



**FIGURE 2.** Concentration of Cu(II) in the solvent-rich compartment (no  $\text{CuCl}_2$  at  $t=0$ ) as a function of time for various membranes.

amount of CuCl formed is significantly lower than that formed at 1 bar at all steam to  $\text{CuCl}_2$  molar ratios. The maximum amount of  $\text{Cu}_2\text{OCl}_2$ , about 98%, is formed at a steam to  $\text{CuCl}_2$  ratio of 15, a noteworthy reduction from the 20-23 used in the tests at 1 bar. From a practical standpoint, the observed increase in  $\text{Cu}_2\text{OCl}_2$  formation at reduced pressure is consistent with the modeling results, where a favorable effect of low pressure was predicted. However, the decrease in CuCl formation was not predicted. Assuming that CuCl forms due to thermal decomposition of  $\text{CuCl}_2$  or  $\text{Cu}_2\text{OCl}_2$  or both, it is unclear why decreasing the pressure inhibits this decomposition. This effect maybe associated with the relative rates of the hydrolysis and decomposition reactions and the hydrodynamics of the experimental reactor. If the decomposition reaction rates are much slower at 375°C than the hydrolysis rate, the formation of CuCl should critically depend on the residence time, which is determined by particle size and flow conditions in the reactor. Additional details of this analysis are published elsewhere [5]. This analysis demonstrates the critical need for the kinetic and mechanistic studies of these reactions.

Figure 3 also shows the results of reduced pressure operation for other steam to  $\text{CuCl}_2$  molar ratios. The amount of  $\text{Cu}_2\text{OCl}_2$  formed with a steam-to-Cu ratio of 11 is relatively low at <80% while the amount of CuCl was 4%. Thus a significant amount of  $\text{CuCl}_2$  remained, indicating insufficient mixing and/or residence time. Further optimization of the operating parameters is required.



**FIGURE 3.** Concentration of CuCl (solid lines) and Cu<sub>2</sub>OCl<sub>2</sub> (dashed lines) in the solid products as a function of H<sub>2</sub>O/CuCl<sub>2</sub> molar ratio at pressures 1 bar (closed symbols), 0.7 bar (grey symbols), and 0.4 bar (open symbols).

### Electrolysis Reaction

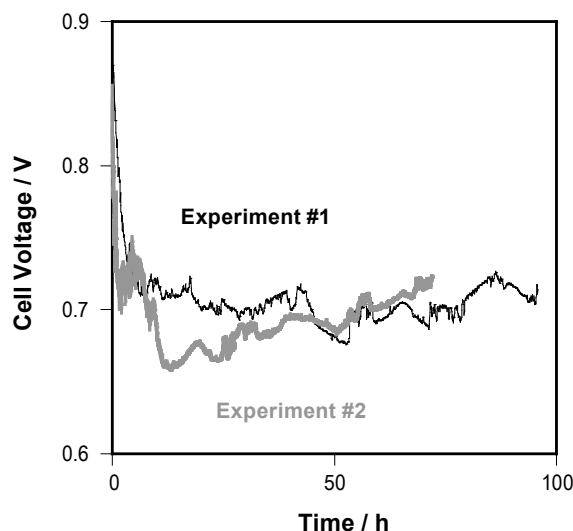
The ultimate test of the membrane development work is a demonstration of its performance in the electrolyzer. Early tests showed large increases in cell voltage within one hour of operation. Scanning electron microscopy showed copper deposits in the membrane or on the cathode. A recently completed electrolyzer test at AECL is shown in Figure 4. The two tests were run under identical conditions, 10.2 M HCl, 0.5 M CuCl and a Nafion<sup>®</sup> membrane. The reason for the differences in the results is under study. Nevertheless, these results are a significant improvement over the earlier tests as the cell voltage was stable for 72-96 hours and was near our target voltage of 0.7 V. The new membranes should provide longer duration cell performance since they have lower copper diffusivity.

### Large-Laboratory Demonstration of Cycle

Collaborators at the University of Ontario Institute of Technology are planning an integrated demonstration of the Cu-Cl cycle. Large laboratory-scale reactors and ancillary equipment have been purchased and set up in a newly refurbished building. Cold testing is ongoing. As part of the collaboration, Argonne National Laboratory will study the decomposition of CuCl<sub>2</sub> and Cu<sub>2</sub>OCl<sub>2</sub> and the hydrolysis of CuCl<sub>2</sub> as a function of time and temperature using synchrotron radiation. Kinetic data are needed to set operating conditions in these larger scale reactors and for further scale-up.

### Conclusions

Several types of membranes have been prepared. These include Nafion<sup>®</sup> with low selectivity coatings,



**FIGURE 4.** Cell voltage versus time in the AECL electrolyzer using a Nafion<sup>®</sup> membrane, 0.5 M CuCl and 10.2 M HCl. Note that the cell voltage is near the target of 0.7 V.

modified polysulfones, known as s-Radel, and a higher temperature version, known as EXSDAPP. Thus far, the diffusivities of the first two types have been measured. The results show that the new membranes are less permeable to Cu species than Nafion<sup>®</sup> and that the modifications have been successful. Based on these results further modifications are being made to further decrease the diffusivity of Cu species and to improve stability at elevated temperatures. Other characterization tests are ongoing. Electrolyzer tests will start as soon as the larger membranes required for the electrolyzers are prepared.

Operation of the hydrolysis reactor at reduced pressure provides an engineering method for reducing the steam demand. Further work is required to optimize conditions. The results of the present experiments indicated the need for measurement of the kinetics and mechanisms of the hydrolysis and the decomposition reactions of CuCl<sub>2</sub> and Cu<sub>2</sub>OCl<sub>2</sub>. Experiments to obtain these data are planned.

### Future Directions

- Continue membrane development and testing that includes diffusivity measurements and characterization tests, i.e., ion exchange capacity, conductivity and water uptake.
- Change composition on the solute-rich side by adding CuCl to the CuCl<sub>2</sub> and HCl solutions.
- Modify the equipment for elevated temperature use and test the most promising membranes at 60-80°C.
- Investigate the use of other types of proton exchange membranes as needed.

- Continue testing of the most promising membranes in the electrolyzers at AECL and PSU and assess long-term chemical stability and durability.
- Continue the investigation of engineering methods to reduce copper crossover, including flow rates, anolyte and catholyte concentrations, temperature, etc.
- Continue synchrotron radiation experiments that monitor the nearest neighbors of Cu(II) species as a function of temperature and time to obtain mechanistic and kinetic information for  $\text{CuCl}_2$  and  $\text{Cu}_2\text{OCl}_2$  decomposition and  $\text{CuCl}_2$  hydrolysis.
- Identify and test potential materials of construction.

## FY 2010 Publications/Presentations

### Publications

1. M.S. Ferrandon, M.A. Lewis, F. Alvarez, E. Shafirovich, Hydrolysis of  $\text{CuCl}_2$  in the Cu-Cl Thermochemical Cycle for Hydrogen Production: Experimental Studies Using a Spray Reactor with an Ultrasonic Atomizer, *Int. J. Hydrogen Energy* 35(2010) 1895-1904.
2. M.S. Ferrandon, M.A. Lewis, and D.F. Tatterson, A. Gross, D. Doizi, L. Croizé, V. Dauvois, J.L. Roujou, Y. Zanella, P. Carles, Production of  $\text{Cu}_2\text{OCl}_2$  using a spray reactor and formation of HCl and  $\text{Cl}_2$  during the hydrolysis of  $\text{CuCl}_2$  in the Cu-Cl thermochemical cycle, *Int. J. Hydrogen Energy* 35(2010) 992-1000.

### Presentations

1. M.A. Lewis, *An overview of R&D activities for the Cu-Cl cycle-2010*, Ontario Research Foundation Workshop, Oshawa, Canada, February 16, 2010.
2. M.A. Lewis, *An overview of R&D activities for the Cu-Cl cycle- March 2010*, STCH Technical Review, Florida Solar Energy Center, Cocoa, FL, March 23, 2010.

## References

1. G. Leofanti, A. Marsella, B. Cremaschi, M. Garilli, a. Zecchina, G. Spoto, S. Bordiga, P. Riscicaro, C. Prestipino, F. Villain, and C. Lamberti, *Alumina-Supported Copper Chloride-4. Effect of Exposure to  $\text{O}_2$  and HCl*, *Journal of Catalysis* 205, 375-381 (2002).
2. D.N. Briggs, K.H. Lawrence and A.T. Bell, *An investigation of carbon-supported  $\text{CuCl}_2/\text{PdCl}_2$  catalysts for diethyl carbonate synthesis*, *Applied Catalysis A366*, 71-83 (2009).
3. M. Hibbs K. Norman, C. Fujimoto and M. Hickner, *Membrane Development for Hybrid Sulfur Electrolysis at High Temperatures*, presented at the Hybrid Sulfur Electrolyzer Workshop and Information Exchange, Aiken, SC, April 21-21, 2009.
4. M. Hickner, personal communication, Argonne National Laboratory, April, 2010.
5. M.S. Ferrandon, M.A. Lewis, F. Alvarez, and E. Shafirovich, *Hydrolysis of  $\text{CuCl}_2$  in the Cu-Cl Thermochemical Cycle for Hydrogen Production: Experimental Studies Using a Spray Reactor with an Ultrasonic Atomizer*, *Int. J. Hydrogen Energy* 35(2010) 1895-1904.
6. M.S. Ferrandon, M.A. Lewis and D.F. Tatterson, A. Gross, D. Doizi, L. Croizé, V. Dauvois, J.L. Roujou, Y. Zanella, P. Carles, *Production of  $\text{Cu}_2\text{OCl}_2$  using a spray reactor and formation of HCl and  $\text{Cl}_2$  during the hydrolysis of  $\text{CuCl}_2$  in the Cu-Cl thermochemical cycle*, *Int. J. Hydrogen Energy* 35(2010) 992-1000.