

## II.F.2 Membrane/Electrolyzer Development in the Cu-Cl Thermochemical Cycle

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### Fiscal Year (FY) 2011 Objectives

The strategic objective is to develop a robust process for producing hydrogen that meets DOE's targets for cost and energy usage; the tactical objectives are the following:

- Identify methods that prevent copper deposition at the cathode of the electrolyzer while meeting targets for cell potential (0.7 V) and current density (500 mA/cm<sup>2</sup> to be met in three years).
  - Identify membranes with low copper permeability and sufficient proton conductivity.
  - Optimize operating conditions and electrolyzer design to further minimize copper crossover.
- Continue collaborative work on the thermal reactions with Canada.

### 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 technical targets are the cost of hydrogen production and the process energy efficiency.

- For 2017, these are \$3.00 per gasoline gallon equivalent (gge) H<sub>2</sub> and >35% (lower heating value, LHV), respectively.

### FY 2011 Accomplishments

- Identified several membranes with low copper permeability at 80°C.
- Conducted electrolysis tests that showed no visible copper crossover with two membranes—double layer Nafion<sup>®</sup> and CG2, a porous separator. The hydrogen production efficiency exceeded >80-90% when the cell potential was 0.7 V and the current density was 100-150 mA/cm<sup>2</sup>.
- Scaled up the electrolyzer from 5 to 31 cm<sup>2</sup> and obtained a stable current for almost 800 hours with CG2 and a cell potential of 0.7 V and a current density exceeding 100 mA/cm<sup>2</sup>.
- Developed a speciation model of the electrolyzer's anolyte to calculate any thermodynamic property such as decomposition potential, solubility of CuCl(s) in HCl(aq) anolyte, concentration of HCl(aq) to dissolve Cu(s) in catholyte, etc. over a wide temperature range from 25 to 100°C.
- Continued collaborations with Atomic Energy of Canada Limited and a group of Canadian universities.



### Introduction

The U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE) is supporting the development of H<sub>2</sub> production technologies that use solar heat. One approach involves thermochemical cycles whose heat source is the solar power tower, which is near commercialization and provides heat near 550°C now and up to 650°C in the future. The CuCl cycle is unique because its maximum temperature is 550°C.

The three major reactions in the Cu-Cl cycle are shown in Table 1. All reactions have been verified at the temperatures shown. Note that the maximum temperature is less than 550°C.

**TABLE 1.** Three Major Reactions in the Cu-Cl Cycle

$\text{CuCl}_2 + \text{H}_2\text{O} \leftrightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl}(\text{g})$	Hydrolysis, ~375°C
$\text{Cu}_2\text{OCl}_2 \leftrightarrow 2\text{CuCl} + \frac{1}{2}\text{O}_2$	Decomposition, 450-525°C
$2\text{CuCl} + 2\text{HCl} \leftrightarrow \text{CuCl}_2 + \text{H}_2$	Electrolysis, ~80 -100°C

No separations or phase changes are specified in this high level representation. There is a significant challenge in the electrolysis reaction because of copper crossover, which has been observed at the Atomic Energy of Canada Limited and at laboratories in the U.S. Copper crossover can lead to catastrophic failure of the cell. Work in the past year has therefore been focused on reducing copper crossover.

## Approach

A collaboration involving several laboratories with expertise in different types of membranes was established. Pennsylvania State University investigated s-Radel (polysulfone-type) membranes, some of which were crosslinked, as well as double layered Nafion<sup>®</sup>. Argonne National Laboratory modified Nafion<sup>®</sup> by copolymerizing it with intertwining various aliphatic and aromatic polymers to reduce the pore size and also developed a cross-linked polybenzimidazole. Seven commercial separator-type membranes, which were available to Gas Technology Institute (GTI) for use in another study and were characterized by their manufacturers as having low metal ion transport and good chemical and thermal stability, were also examined. Screening evaluations were conducted with permeability and conductivity measurements. Electrolysis tests were conducted with the most promising membranes at 80°C.

## Results

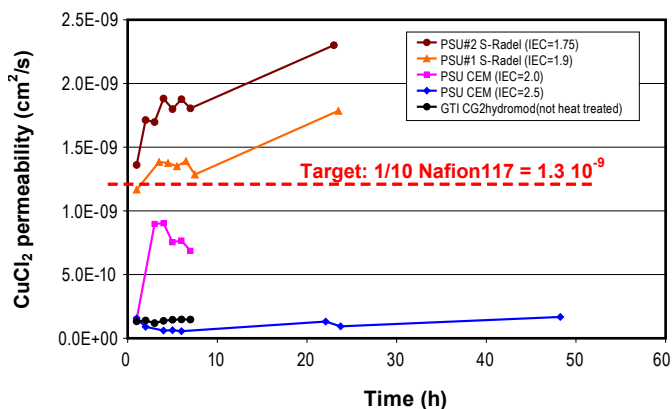
**Permeability Measurements:** The various membranes were screened by measuring copper permeability at 80°C and through-plane conductivity at room temperature. An initial target permeability of 10% of Nafion<sup>®</sup>'s was used. The permeability was measured in a diffusion cell, which consisted of two compartments, clamped together but separated by a membrane. The solute side contained a solution of CuCl<sub>2</sub> in 10.2 M HCl. The solvent side contained 10.2 M HCl. The permeability was calculated from the equation,

$$k = \left( \frac{IV_{\text{sample}}}{At_{\text{exp}}} \right) \ln \left( \frac{C_1}{C_1 - C_2} \right)$$

where  $l$  is the thickness of the wet membrane (cm),  $V_{\text{sample}}$  is the volume of the sample solution in our cell (cm<sup>3</sup>),  $A$  is the surface area of membrane (cm<sup>2</sup>),  $t_{\text{exp}}$  is the time of the exposure (sec),  $C_1$  is initial concentration of Cu<sup>2+</sup> in the first compartment (1 M), and  $C_2$  is concentration of Cu<sup>2+</sup> measured in the sample in the second compartment

at  $t = t_{\text{exp}}$ . Ideally  $k$  values should not be dependent on time as long as the properties of the membrane are stable and osmotic pressure does not result in significant solvent diffusion. The test period was 24 hours in most cases. However, large volume changes in the solute side due to osmotic pressure caused some permeability tests to be terminated after only several hours.

The membranes with the lowest copper(II) permeabilities are shown in Figure 1. Only one of the seven separator-type membranes examined, CG2, had very low copper permeability and further work, e.g., supports and pretreatments, was justified on this basis. The CG2 membrane is significantly thinner than Nafion<sup>®</sup> as shown in Table 2. Mechanical supports are therefore being developed to facilitate fabrication of membrane electrode assemblies (MEAs). CG2's proton conductivity is also relatively small (see Table 2) and various pretreatments are being investigated to increase this property. In addition, this membrane has the highest osmotic pressure and the diffusion tests can be run for very limited time periods. The membrane consisting of a double layer of Nafion<sup>®</sup> exceeded the permeability target by almost a factor of 6



**FIGURE 1.** Permeability measurements at 80°C vs. time. HCl concentrations are 10.2 M in both compartments of the diffusion cell.

**TABLE 2.** Properties of Membranes for Possible Use in the Cu-Cl Electrolyzer

Membrane	Pretreatment	Thickness, / (mm)	Conductivity, $\sigma$ (S/cm)	Permeability $k * 10^{-9}$ (cm <sup>2</sup> /s)	Selectivity $\sigma / k * 10^5$
Nafion <sup>®</sup> 117	20 h in 2 M HCl, 25°C	0.180	0.086	0.18	48
Double-layer Nafion	20 h in 2 M HCl, 25°C	0.350	0.083	5.80	143
Mit-1 (from GTI)	None	0.003	Inconclusive		
CG2 (from GTI)	None	0.030	0.0054	94	57
s-Radel, IEC 2.0	None	0.054	0.038	3.68	102
s-Radel, IEC 2.0, crosslinked	None	0.107	0.053	4.77	111
s-Radel, IEC 2.5, crosslinked	None	0.100	0.045	83.5	535
s-Radel, IEC 2.5, crosslinked	66 h in 3.3 M HCl + 1 M CuCl <sub>2</sub> , 25°C	0.109	0.045	1.48	300
s-Radel, IEC 2.5, crosslinked	2 h in 10 M HCl, 80°C	0.107	0.072	0.112	64

but this membrane had the highest proton conductivity and therefore the highest selectivity see Table 2. Two of the s-Radel membranes were very close to the target. After cross-linking, their permeabilities were below the target. Co-polymerized Nafion®-type membranes had low permeability at room temperature but exceeded the target at 80°C and further effort on this type of membrane was terminated. Studies are still ongoing with the crosslinked polybenzimidazole.

**Conductivity Measurements:** Conductivity was measured using the two-electrode through-plane method in 2 mol/L HCl(aq) solution at ambient temperature and pressure. Conductivity values were calculated using measured membrane resistance ( $R$ ), thickness of wet membrane ( $\delta$ ), and exposed membrane surface area ( $A=0.74 \text{ cm}^2$ ), as follows:  $k = \delta / (R \times A)$ . The equipment and method are described in detail elsewhere [1]. No target was set for proton conductivity except that it had to be measurable. Those membranes which met the targets were tested in electrolyzers at GTI and Pennsylvania State University for a more realistic evaluation.

The results of the through-plane conductivity measurements are given in Table 2. Nafion® 117 membrane was used as a bench mark. Table 2 also summarizes permeability and selectivity data. The latter are calculated by dividing the conductivity by the permeability. Some of the samples were pretreated. The data in Table 2 for the cross-linked s-Radel membranes show that pretreatment affects selectivity. Pretreatment processes are still under development for CG2.

**Electrolyzer Results:** Electrolyzers were built at both Pennsylvania State University and GTI. Details of the electrolyzer at Pennsylvania State University are published elsewhere [1]. The performance of the electrolysis process was monitored by taking polarization data and comparing experimental and theoretical hydrogen production. Targets for the cell potential and the current density in the model are 0.7 V and 500 mA/cm<sup>2</sup>, respectively. However, short term targets specify lower current densities for cell potentials of 0.7 V.

Several MEAs were tested in the electrolyzers. The MEA fabricated from the double-layer Nafion® gave promising results in a 24-hour test at 80°C with 10.2 M HCl as the catholyte and 1 M CuCl in 10.2 M HCl as the anolyte. Hydrogen production followed Faraday's Law, as shown in Figure 2. There was, however, some degradation with time as shown by the polarization curve in Figure 3, which may be due to the consumption of CuCl. At the conclusion of the test, no copper deposition was observed on the cathode, membrane or gas diffusion layers. Photographs of the latter are shown in Figure 4. Similar results were obtained with CG2 using the same conditions but with deionized water as the catholyte. Lifetime tests at GTI were run intermittently for almost 800 hours with the intermittent addition of CuCl. The cell voltage was 0.7 V and the current density was stable near 150 mA/cm<sup>2</sup>. Hydrogen production followed Faraday's

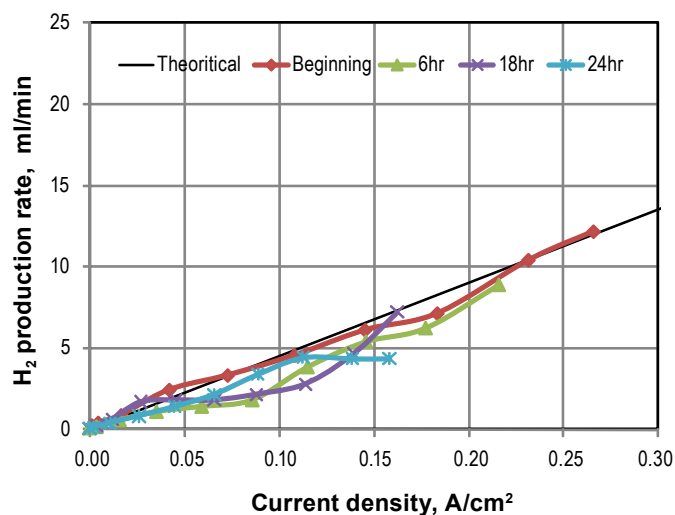


FIGURE 2. Hydrogen production as a function of cell voltage over 24 hours with the double layer Nafion® membrane.

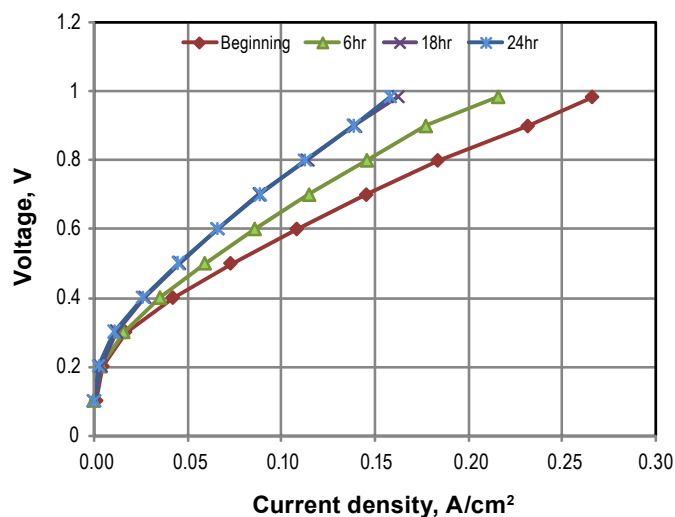


FIGURE 3. Current vs. voltage as a function of time with the double layer Nafion® membrane.

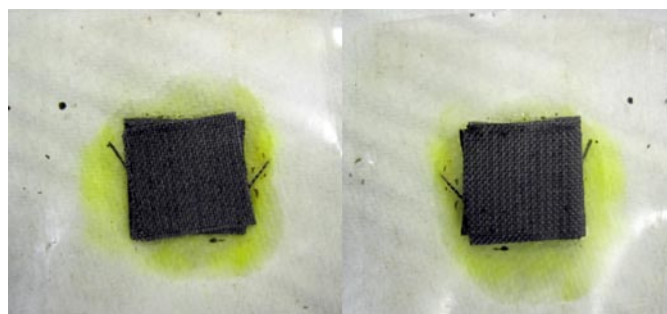


FIGURE 4. Photographs of the MEA diffusion layers facing the cathode (left) and anode (right) of the electrolysis cell used in the 24-hour electrolysis test with double layer Nafion® that show no visible copper deposits.

Law. No copper deposition was visible on the components of the cell after the test was terminated. Comparison of peak hydrogen production in the two electrolyzers showed essentially identical results. Electrolyzer tests with the cross-linked s-Radel membranes are planned.

Collaborations: Collaborations between the U.S. team members and their Canadian colleagues are focused on the study of the hydrolysis and oxychloride decomposition reactions using X-ray absorption near edge structure at the Advanced Photon Source. It is hoped that these measurements will result in kinetic measurements and mechanistic understanding of these two thermal reactions. Information is exchanged periodically, e.g., Ontario Workshop Foundation workshops (see presentation #2) and in discussions between the researchers, especially in modeling activities.

## Conclusions

- Identified two membranes that had low copper diffusion in permeability tests and had sufficient proton conductivity.
- Conducted electrolyzer tests that showed no visible copper deposition in/on the cell components.

## Future Directions

- Develop methods to improve the mechanical stability of CG2.
- Optimize the electrolyzer's performance by investigating other compositions for the anolyte and catholyte, flow rates, flow field design, electrode surface, mass transport media, etc. to obtain higher current densities at 0.7 V.
- Investigate the degradation mechanisms in the electrolyzer and develop methods to mitigate these.
- Continue collaboration with staff at Atomic Energy of Canada Limited and six Canadian universities.

## FY 2011 Publications/Presentations

### Presentations

1. CuCl Electrolyzer for Hydrogen Production via Cu-Cl Thermochemical Cycle, Oral presentations (R. Sharna, M. Fedkin, and S. Lvov, Penn State University) 219<sup>th</sup> ECS Meeting, Montreal, Canada May 1–6, 2011.
2. Current R&D Status for the Cu-Cl Thermochemical Cycle (2-2011), M. Lewis, C. Fan, R. Sharna, M. Fedkin, S. Lvov, M. Ferrandon, S. Ahmed and S. Niyogi, Ontario Research Foundation Workshop, Oshawa, Ontario, Canada, February 23, 2011.

### Publications

1. Balashov, V.N., Schatz, R.S., Chalkova, E., Akinfiyev, N.N., Fedkin, M.V., and Lvov, S.N., CuCl Electrolysis for Hydrogen Production in the Cu-Cl Thermochemical Cycle, *J. Electrochemical Soc.*, 2011, **158**, B266-B275.
2. Naterer, G.F. et al., Canada's Nuclear Hydrogen Program on the Thermochemical Copper-Chlorine Cycle, submitted to International Journal of Hydrogen Energy.

### References

1. Balashov, V.N., Schatz, R.S., Chalkova, E., Akinfiyev, N.N., Fedkin, M.V., and Lvov, S.N., CuCl Electrolysis for Hydrogen Production in the Cu-Cl Thermochemical Cycle, *J. Electrochemical Soc.*, 2011, **158**, B266-B275.