

II.B.1 Electrolyzer Development in the Cu-Cl Thermochemical Cycle

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Start Date: October 2010

Projected End Date: September 2013

Overall Objectives

- PSU: Determine effect of increased temperature on cell operation
- PSU: Reduce Pt loading
- GTI: Identify scale up issues
- ALL: Identify methods to reduce costs of H₂ production

Fiscal Year (FY) 2013 Objectives

- PSU: Complete 168-hour test in 5-cm² electrolyzer
- PSU: Design, build and test a 5-cm² electrolyzer operating at 100°C
- PSU: Reduce Pt loading by 50% in 5-cm² electrolyzer
- GTI: Scale up electrolyzer to 300 cm²
- GTI: Increase number of 300-cm² cells from 1 to 5 and operate stack for 100 hours

Technical Barriers

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

- (S) High-Temperature Robust Materials
- (T) Coupling Concentrated Solar Energy and Thermochemical Cycles

(W) Materials and Catalyst Development

(X) Chemical Reactor Development and Capital Costs

FY 2013 Accomplishments

- PSU: Completed a 168-hour test in a 5-cm² electrolyzer at the milestone value
- PSU: Reduced Pt loading by at least 50% in the 5-cm² electrolyzer
- GTI: Ran a 2-cell full-size stack with 65% conversion from Cu(I) to Cu(II)
- GTI: Ran a 5-cell, full-size stack at the milestone value of 0.2 A/cm² at 0.7 V and 60°C; a 100-hour test is ongoing

Technical Targets

The DOE cost target for H₂ production is \$2.00/gallon gasoline equivalent (gge) dispensed. However, it is recognized that solar thermochemical cycles are in their early stages of development and the 2015 target is \$14.80 and \$3.70 for 2020 [1]. Costs for H₂ production using the CuCl cycle were calculated in 2011 using H2A v.2 with estimates of capital and operating costs based on an Aspen process design as \$6.0/gge for 2015 and as \$4.0-4.4/gge for 2025, depending on the number of solar fields [2].



INTRODUCTION

The goal of this project is to couple the relatively low-temperature CuCl thermochemical cycle for hydrogen production with a solar power tower as a possible heat source. The power tower is near commercialization and could provide heat near the maximum process temperature of the CuCl cycle. The cycle consists of three major reactions, shown in Table 1. All have been proven in the laboratory.

TABLE 1. Major Reactions and Operating Temperatures in the CuCl Cycle

Reaction	Chemistry	Operating Temperature, °C
Hydrolysis	$\text{CuCl}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl}$	375
Decomposition	$\text{Cu}_2\text{OCl}_2 \rightarrow 0.5\text{O}_2$	450-525
Electrolysis	$\text{CuCl} + 2\text{HCl} \rightarrow \text{CuCl}_2 + \text{H}_2$	80-100(verified)-120

We have recently focused on the development of the electrolyzer. One reason was that catastrophic failure of the cell could result from copper deposition on an electrode or

membrane. It was subsequently shown that any electrolytic copper metal that may be formed dissolves immediately in the high concentrations of HCl. Another reason for emphasizing the electrolyzer was that our cost estimates for H₂ production showed that the major cost and energy usage drivers are the electrolyzer and its components. To meet the projected cost of hydrogen at \$6.0/gge, both the design and operation of the electrolyzer have to meet certain specifications. The current density, which controls the number of electrolyzer units, should be 0.5 A/cm² or higher and the applied cell potential should be 0.7 V (in 2015) and 0.5 V (in 2025). The cost of the noble metal catalysts is high and our plan is to reduce Pt loading (by 2015) and/or substitute other lower cost catalysts (by 2025). Longer term tests are also being conducted to determine the durability of the membrane and other components. Another avenue to reduce costs is possible if Cu(I) conversion to Cu(II) in the full-scale electrolyzer is about 90%, which would allow elimination of a separation step.

APPROACH

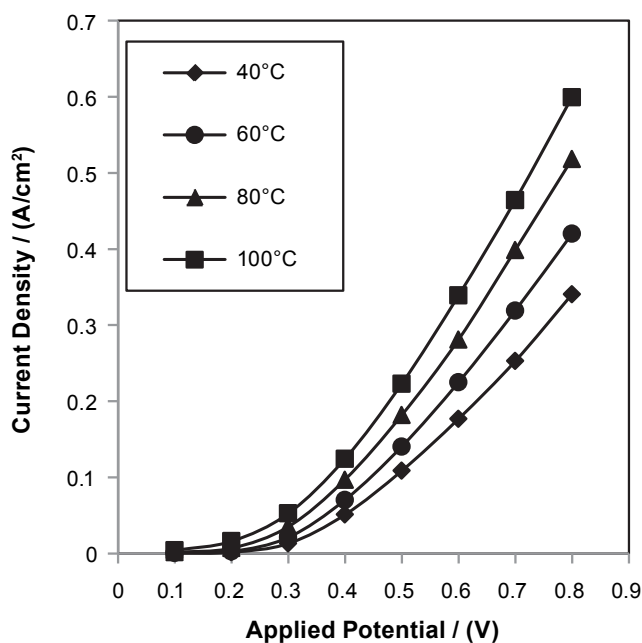
Our approach is twofold. One path is to conduct fundamental studies with a 5-cm² electrolyzer that include the effects of increased temperature, lower Pt loadings, and longer duration tests. Running the electrolyzer above 80°C is demanding because of the increase in vapor pressure of HCl (above 1 bar) and the higher pressure operation needed to contain the vapors. These experiments should provide an estimate of the magnitude of the expected increase in current density with increasing temperature. Various Pt loadings and application methods are being investigated to reduce catalyst costs. Longer duration tests are being conducted to determine if degradation occurs with time. In all of the tests, the current density was measured as a function of cell potential and the H₂ production efficiency was determined. Scanning electron microscopy (SEM) was used to study the catalytic surfaces. Electrochemical impedance spectroscopy (EIS) was used to identify important cell resistances as a function of time on stream and temperature. A second path is to identify and meet challenges associated with scale up to a full-size or 300-cm² electrolyzer. The issues related to scale up are expected to be quite different from those used for water electrolyzers. For example, the solubility of CuCl used in the electrolyzer is very dependent on the HCl concentration and both HCl and CuCl₂ are very corrosive materials. Scale up involves fabricating and testing the 300-cm² full-size cells and then combining them to form a stack, using sufficient holding force and appropriate seals and contacts so that the mass flow distribution is even and the electrical contact is the same for all of the cells. A 100-hour test is being conducted with a 5-cell stack.

RESULTS AND DISCUSSION

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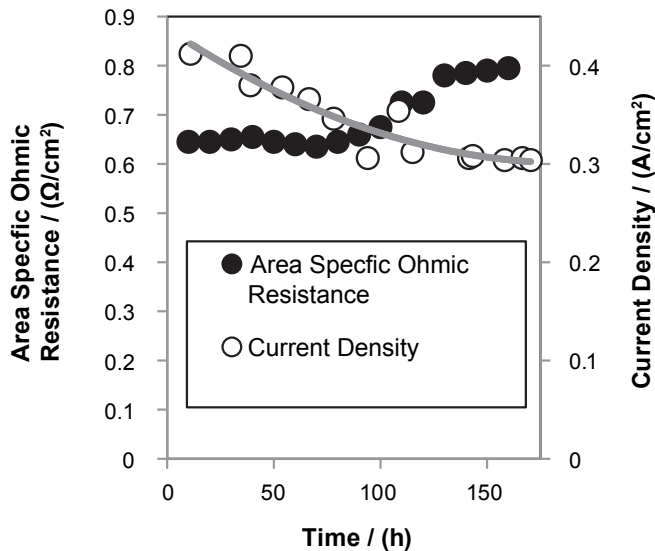
Effect of increasing temperature. Details of the chemistry, the electrolyzer system and changes made to accommodate operation at 100°C are described elsewhere [3]. The results of the tests at 40-100°C are shown in Figure 1. At 0.7 V, there was a 15% increase in current density as the temperature was increased from 80°C to 100°C. EIS measurements showed that the increase in current density was due to decreases in internal ohmic and charge transfer resistances.

Long-term tests. The results of the 168-hour test at 80°C are shown in Figure 2. The current density decreased from an initial value near 0.5 A/cm² to about 0.3 A/cm² (the milestone value) at the end of the test. The cell was operational for 168 hours while the membrane was contacted by the solution for over 400 hours. The hydrogen production efficiency was measured and found to be ≥95% of the theoretical value predicted by Faraday's Law. EIS was used to characterize the electrolyzer processes. Analysis of the EIS data is ongoing but preliminary results indicated that the internal ohmic resistance increased with time, which suggests membrane degradation.



Conditions: Single Pressed Nafion[®] 117, Pt loading 0.8 mg/cm² on each electrode, 2 M CuCl in 7 M HCl, anolyte, 7 M HCl catholyte, 230 mL/min flow rate, 1-1.3 bar and 40-100°C

FIGURE 1. Polarization Curves for Four Temperatures



Conditions: Single pressed Nafion® 117, 20% Pt loading 0.8 mg/cm² on each electrode, 1-2 M CuCl in 6-7 M HCl anolyte, 7 M HCl catholyte, 230 mL/min flow rate, 80°C and 1 bar

FIGURE 2. Current Density (right) and Internal Ohmic Resistance (left) during the 168-Hour Test vs. Cell Potential

Pt loading studies. SEM images of painted electrode surfaces showed a dense catalyst deposit suggesting inactive Pt within the catalyst layer. An airbrush method was tested as a means to apply a thinner deposit. SEM images in Figure 3 show the very different surfaces. When the airbrushed Pt loadings were reduced to 0.1 and 0.4 mg/cm² on the anode and cathode, respectively, the current density was 0.55 A/cm² at 0.7 V. Past tests used 0.8 mg/cm² on both electrodes. GTI's tests with a 6.45-cm² electrolyzer showed that the current density was nearly independent of the Pt loading on the anode when the Pt loading on the cathode was 0.5 mg/cm². Atomic Energy of Canada Limited uses none on the anode but has not reported Pt loading on the cathode.

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Scale up. Testing of the one full-size 300-cm² cell showed a current density of 0.55 A/cm² at 0.7 V and 60°C. A stack with two 300-cm² cells was then fabricated and tested to ensure that the mass flow distribution was even and that there were no shunt currents. At 0.7 V, the current density was 0.36 A/cm² and H₂ production efficiency was 98% of the theoretical value. Conversion of Cu(I) to Cu(II) was 65% when the flow rate was 210 mL/min.

Preliminary tests with the 5-cell 300-cm² cell stack showed a large drop off in current within 20 minutes of the start of the test, indicating much of the Cu(I) was consumed. Two major changes in the ancillary equipment were therefore necessary, i.e., a higher capacity pump to provide greater flow rates and a redesigned recycle system with a larger capacity. After these system changes, the 5-cell stack was placed in

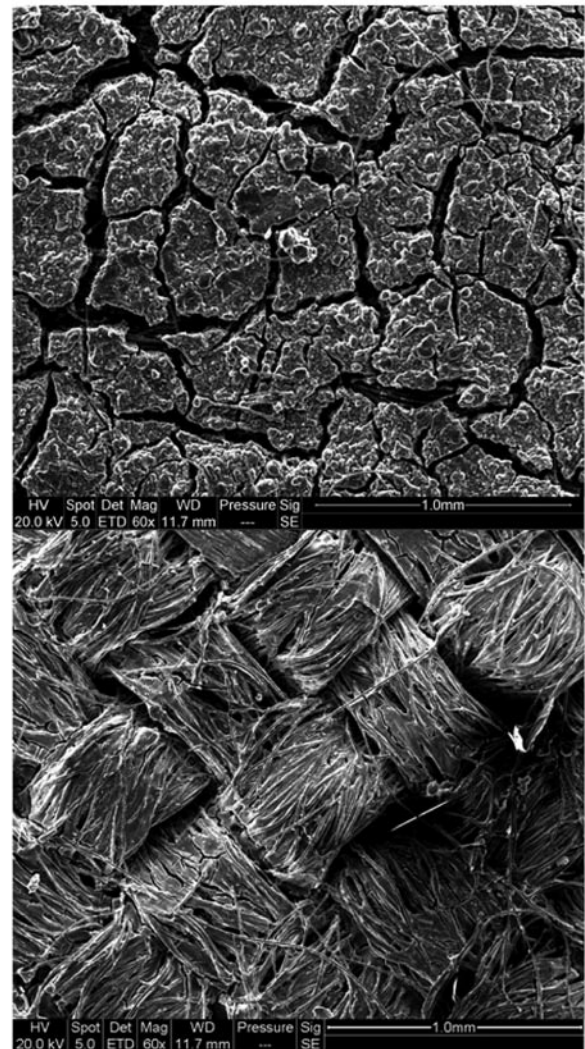
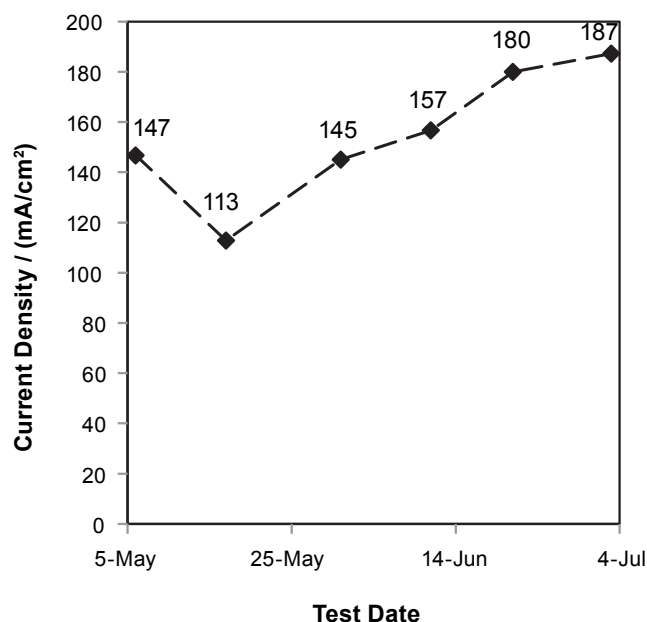


FIGURE 3. Two SEM Images Comparing Catalyst Application Differences between Painted (left) and Airbrushed (right) Electrodes (Pt loadings were 0.8 mg/cm² on both)

the testing facility. The current densities at several voltages were measured for each cell and the resulting polarization curves for each of the five cells overlapped each other. Figure 4 shows the results of the second set of tests with the 5-cell stack. The current density at 0.7 V varied between 0.11-0.15 A/cm², significantly lower than those for the one cell and the 2-cell stacks. Increases in the current densities, up to 0.19 A/cm², were obtained when the recycle time for the spent anolyte was increased and when the cathodic flow rate was increased from 600 to 800 mL/min. Tests at PSU also confirmed that cathodic and anodic flow rates affected current densities. Possible reasons for the lower current densities for the 2- and 5-cell full-size 300-cm² stacks compared to the single 300-cm² cell are under investigation. Preliminary data suggest that high back pressure due to the large amount of H₂ generated is limiting hydrogen release and reducing the flow rate of the solutions.



Conditions: Nafion[®] 112, Pt loading 0.5 mg/cm² on each electrode, 1 M CuCl in 7 M HCl anolyte, 7 M HCl catholyte, 600 mL/min flow rate, 60°C, 1 bar

FIGURE 4. Five-Cell Stack Performance at 0.7 V

Collaborations

Atomic Energy of Canada Limited and five Canadian universities are also working on the development of the CuCl cycle. Collaboration between the U.S. and Canada consists of an informal information exchange via biannual meetings wherein the latest results from each group are reported. For example, Atomic Energy Canada Limited has a new membrane and cell design that suppressed all copper crossover during a test of 1,600 hours at 45°C. The five Canadian universities led by the University of Ontario Institute of Technology are investigating materials of construction, hydrolysis reactor designs, new membrane materials, sensible heat recovery from the molten salt and the overall design of an integrated demonstration planned for the future. Summaries of the work in Canada are reported annually [4].

CONCLUSIONS

- PSU: Pt loadings were successfully reduced to less than half of the original value (0.8 mg/cm² on both electrodes to 0.4 mg/cm² on the cathode and 0.1 mg/cm² on the anode).
- PSU: Current density increased with increasing temperature.
- PSU: Degradation occurred due to an increase in internal ohmic resistance, possibly due to membrane degradation, in a 168-hour test.

- GTI: Tests with the 2- and 5-cell full-size 300-cm² stacks showed that mass flow was evenly distributed, shunt currents were absent and seals were durable between the cells. Further improvement is needed in the design to obtain higher current densities.
- GTI and PSU: Current density depended on cathodic and anodic flow rates.

FUTURE DIRECTIONS

- PSU: Identify degradation mechanisms observed in longer duration tests and determine methods to minimize these mechanisms.
- PSU: Design a laboratory-scale electrolyzer for operation above 100°C and pressures up to 24 bar (80°C tests are run at 1 bar, 100°C tests at 1.2-1.3 bar).
- GTI: Optimize system integration by studying flow rates, manifold hole size, pump head pressure, and possibly other variables to increase current densities in the 5-cell stack.
- All: Continue studies of methods to reduce Pt loading, study electrocatalytic properties of new catalysts, investigate other membranes that limit Cu crossover and have high durability.
- All: Continue collaboration with staff at Atomic Energy of Canada Limited and Canadian universities.

FY 2013 PUBLICATION/PRESENTATIONS

1. R. Schatz, S. Kim, S. Khurana, M.V. Fedkin, and S.N. Lvov, High Efficiency CuCl electrolyzer for Cu-Cl Thermochemical Cycle, ECS Transactions, 45(19), 2013, 153-164.
2. S. Khurana, D. Hall, R. Schatz, and S. N. Lvov, Diagnosis and Modeling of the CuCl Electrolyzer Using Electrochemical Impedance Spectroscopy, ECS Transactions, 2013 (in press).
3. D. M. Hall, R. S. Schatz, E. G. LaRow, S. N. Lvov, CuCl/HCl Electrolyzer Kinetics for Hydrogen Production via Cu-Cl Thermochemical Cycle, ECS Transactions, 2013 (submitted).
4. S. Ahmed and D. Tatterson, Electrolyzer Developments in the Cu-Cl Cycle, Ontario Research Foundation Workshop, Chalk River, Ontario, Canada, April 22, 2013 (oral presentation).
5. S.N. Lvov, R. Schatz, S. Kim, S. Khurana, A. Morse, M. Chung, and M. Fedkin, Hydrogen Production via Electrolysis in Cu-Cl Thermochemical Cycle, Pacific Rim Meeting on Electrochemical and Solid State Science, Honolulu, Hawaii, October 7–12, 2012 (an oral presentation).

REFERENCES

1. S. Dillich, Hydrogen Production and Delivery, presented at the 2013 Annual Merit Review and Peer Evaluation Meeting, Crystal City, VA, May 13, 2013.

2. M. Kromer et al., Support for Cost Analyses on Solar-Driven High Temperature Thermochemical Water-Splitting Cycles, DE-DT0000951 (Department of Energy report by TIAX LLC), 2011.
3. S.N. Lvov, R. Schatz, S. Kim, S. Khurana, A. Morse, M. Chung, and M. Fedkin, Hydrogen Production via Electrolysis in Cu-Cl Thermochemical Cycle, Pacific Rim Meeting on Electrochemical and Solid State Science, Honolulu, Hawaii, October 7–12, 2012 (an oral presentation).
4. G.F. Naterer et al., International Program on Hydrogen Production with the Copper-Chlorine Cycle, 2013, to be submitted to the International Journal of Hydrogen Energy.