IV.I.3 Low Temperature Electrolytic Hydrogen Production*

John W. Weidner, Ph.D.
Professor
University of South Carolina
Swearingen Engineering Center
Columbia, SC 29208
Phone: (803) 777-3207; Fax (803) 777-8265; E-mail: weidner@engr.sc.edu

DOE Technology Development Manager: Mark Paster
Phone: (202) 586-2821; Fax: (202) 586-9811; E-mail: Mark.Paster@ee.doe.gov

DOE Project Officer: Paul Bakke
Phone: (303) 275-4916; Fax: (303) 275-4753; E-mail: Paul.Bakke@go.doe.gov

Contract Number: DE-FC36-04GO14232

Subcontractors:
Savannah River National Laboratory, Aiken, SC
South Carolina State University, Orangeburg, SC

Start Date: June 1, 2004
Projected End Date: November 30, 2005

**Congressionally directed project*

Objective

To overcome many of the materials problems associated with high temperature thermochemical cycles, the following electrolytic systems will be investigated (1) the electrolytic decomposition of HBr for the calcium bromide thermochemical cycle; (2) the electrolytic decomposition of HCl for the reverse Deacon thermochemical cycle; and (3) the electrolytic decomposition of SO_2 for the hybrid sulfur thermochemical cycle.

Technical Barriers

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

- G. Capital Cost
- H. System Efficiency

Approach

- Generate hydrogen from an electrochemical reactor by electrolyzing HCl.
- Build a reactor to electrolyze HBr to produce H_2.
- Generate hydrogen from a proton exchange membrane (PEM) electrochemical reactor by electrolyzing HBr.
- Build a reactor to oxidize SO_2 electrochemically to produce H_2.
- Generate hydrogen by oxidizing SO_2 in a PEM electrochemical reactor.

Key Results

- Conversion of SO_2 to SO_3 in a PEM electrolyzer was accomplished. The cell voltage was lower by over 150 mV at 4.0 kA/m^2 compared to the liquid phase process (*i.e.,* Westinghouse process). This improved performance was achieved at one-tenth the Pt loading.
- The maximum current density achieved for the gas-phase HCl process was 10 kA/m^2 at cell voltages lower than 2 V. That's a five hold increase over the liquid-phase process (*i.e.,* Uhde process). At 4 kA/m^2, the cell voltage was 500 mV lower than the liquid-phase process.
- The maximum current density achieved for HBr reaction was 20 kA/m^2 at cell voltages lower than 2 V. At 4 kA/m^2, the cell voltage was 500 mV lower than the gas-phase HCl process (*i.e.,* 1.0 V lower than the liquid phase HCl process).

Future Directions

- Mathematical models will be developed to predict the operation of a PEM electrolyzer for the generation of hydrogen from HCl, HBr and SO_2.

Background

Thermochemical cycles produce hydrogen through a series of chemical reactions that result in the splitting of water at much lower temperatures (~800-1,000ºC) than direct thermal dissociation (>2,500ºC) [1,2]). All other chemical species in these reactions are recycled resulting in the consumption of only heat and water to produce hydrogen and oxygen. Since water rather than hydrocarbons are used as the source of hydrogen, no carbon dioxide emissions are produced and the hydrogen produced is highly pure.

Although there are hundreds of possible thermochemical cycles that can produce hydrogen from water, the two leading candidates are the sulfur-based cycles and the calcium-bromide-based cycles [3-5]. The sulfur-based processes all have the common oxygen generating, high-temperature step, which is the decomposition of sulfuric acid to sulfur dioxide and oxygen at temperatures in the 850-1,000ºC range. In the sulfur-iodine (SI) cycle, the SO_2 is converted back to H_2SO_4 and hydrogen is produced via a two-step process involving iodine. The distillation of hydrogen iodine (HI) from solution and concurrent decomposition to iodine is the most difficult process issue for the iodine containing portion of the cycle [4,5].

In the 1970s, Westinghouse Electric Corporation developed the hybrid sulfur process, which eliminated the use of iodine completely [6,7]. They electrochemically oxidized SO_2 to H_2SO_4 from a liquid-phase anode stream. Westinghouse demonstrated this process on a scale of 150 l/h of hydrogen in 1976, and a conceptual plant design has been developed.

The calcium-bromide-based cycles also have the potential of high efficiencies but with lower temperature requirements than the sulfur-based cycles (~750ºC). The common step in these cycles is the conversion of CaO and Br_2 to $CaBr_2$ and O_2 at approximately 550ºC, and the conversion of $CaBr_2$ back to CaO and HBr at 730ºC. The second recycle step, converting HBr to Br_2 and generating hydrogen, can be done thermally in a solid-gas, fixed bed reactor of iron oxide, which in turn needs to be regenerated [4,5]. The iron reaction beds can be eliminated in a modified Ca-Br cycle by converting HBr directly to Br_2 and H_2 in a single step. This direct conversion can be performed electrochemically [8-9] or in a plasma process [10].

Aqueous-phase electrolysis suffers from (1) low current densities due to liquid-phase mass-transfer limitations, and (2) difficult product separation due to dissolution of Br_2 in solution [8]. Gas-phase electrolysis has been attempted in phosphoric-acid [8,9] and molten-salt cells [10] to address these limitations. Although Br_2 dissolution was avoided in these cells, cell performance was poor.

Results and Discussion

The results of our work are summarized in Figure 1. In the PEM electrolyzer, SO_2 oxidation in the gas phase reduced the cell voltage by over 150 mV at 4.0 kA/m^2 compared to SO_2 oxidation in the liquid phase (*i.e.,* Westinghouse data). This improvement was achieved with one-tenth the Pt loading. The process started to become mass-transfer limited at 4.0 kA/m^2 due to limitations in transporting water across the membrane above these currents. Further improvements maybe be possible by using thinner membranes, a humidified SO_2 feed stream, and elevated pressures.

In the HCl electrolyzer, decreased voltage and improvements in current densities were achieved over previous liquid-phase HCl electrolysis (*i.e.*, Uhde process). At 4.0 kA/m^2, the voltage was decreased by approximately 500 mV. Current densities were increased by a factor of 5, from 4.0 kA/m^2 to 10 kA/m^2, with no evidence of mass-transfer limitations. Higher current could have been achieved, but we wanted to avoid the corrosive effects of oxygen evolution.

In the HBr electrolyzer, further decreases in voltage and improvements in current densities were achieved. At 4.0 kA/m^2, the voltage was decreased another 500 mV compared to the gas-phase HCl reaction. Due to these lower voltages, a current density of 20 kA/m^2 was achieved with no signs of oxygen evolution.

Conclusions

A PEM electrolyzer was developed for the electrochemical conversion of: (1) SO_2 to H_2SO_4 and H_2; (2) HCl to Cl_2 and H_2; and (3) HBr to Br_2 and H_2. We showed that carrying out the anode reactions in the gas phase of a PEM electrolyzer significantly improves the electrochemical step in these three hybrid processes. These results indicate that all three of the cycles should be studied further as potential candidates for large-scale production of hydrogen for the hydrogen economy.

From the results in Figure 1, the HBr cycle looks the most promising because of its wider operating window (*i.e.,* large current densities), lower cell voltage, less expensive catalyst (RuO_2 rather than Pt), and more stable operation. In contrast, HCl conversion has larger cell voltages (*i.e.,* lower efficiencies), and the SO_2 conversion uses Pt, which is costly and is degraded by sulfur poisoning. However, the overall cycle, not just the electrochemical step, needs to be considered before a final candidate is chosen. For example, the oxygen production step in the chlorine and bromine cycles occurs at a lower temperature, simplifying the nuclear reactor. For the hybrid sulfur process, the sulfuric acid decomposition step is further developed, and in theory the cell voltage could be lowered further and less expensive catalysts could be developed.

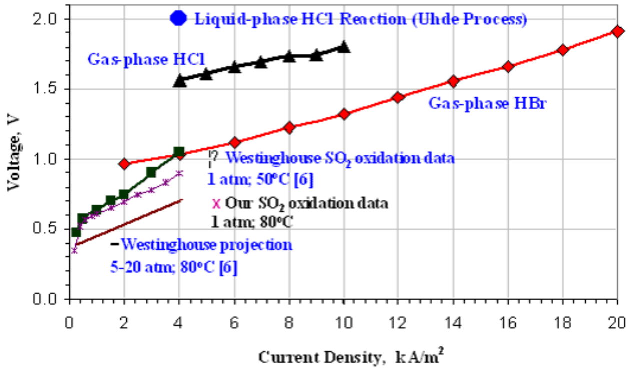

Figure 1. The current-voltage response for SO_2, HCl, and HBr electrolysis in a PEM electrolyzer. Our gas-phase SO_2 results were achieved with a Pt loading one-tenth that of Westinghouse's liquid phased process.

FY 2005 Publications and Presentations:

1. P. Sivasubramanian, Ramaraja P. Ramasamy, Charles E. Holland, F. Freire, and J.W. Weidner, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," The American Institute of Chemical Engineers Spring Meeting, Atlanta, GA, April, 2005.
2. Weidner, J.W., P. Sivasubramanian, and F. Freire, "Electrochemical Recovery of Cl_2 from Anhydrous HCl Using a Polymer Electrolyte Membrane Reactor," The Electrochemical Society, Honolulu, HI, October, 2004.
3. Weidner, J.W., P. Sivasubramanian, and F. Freire, "Electrochemical Conversion of Anhydrous HBr to Br_2 for Hydrogen Production," The Electrochemical Society, Honolulu, HI, October, 2004.
4. Gomadam, P. and J. W. Weidner, "Modeling Volume Expansion in Lithium-Ion Batteries," The Electrochemical Society, Honolulu, HI, October, 2004.

5. P. Sivasubramanian, R. P. Ramasamy, F. J. Freire, C. E. Holland and J. W. Weidner, “Electrochemical Hydrogen Production from Thermochemical Cycles using a Proton Exchange Membrane Electrolyzer”, Manuscript submitted for publication in the *International Journal of Hydrogen Energy*, 2005.

References

1. M. A. Rosen, *Int. J. Hydrogen Energy,* 20, 7, 547 (1995).
2. National Academy of Engineering, “The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs,” Chapter 8 (2004).
3. M. A. Rosen, *Int. J. Hydrogen Energy,* 21, 5, 349 (1996).
4. Nuclear Hydrogen R&D Plan DRAFT; Department Of Energy, Office of Nuclear Energy, Science and Technology, 2004.
5. Nuclear Hydrogen Initiative: Ten Year Program Plan, Office of Advanced Nuclear Research, DOE Office of Nuclear Energy, Science and Technology, March 2005.
6. P. W. Lu, E. R. Garcia and R. L. Ammon, *J. Appl. Electrochem.*, 11, 347 (1981).
7. P. W. Lu and R. L. Ammon, *J. Electrochem. Soc.,* 127, 2610 (1980).
8. W. Kondo, S. Mizuta, Y. Oosawa, T. Kumagai, and K. Fujii, “Decomposition of Hydrogen Bromide or Iodide by Gas Phase Electrolysis”; *Bull. Chem. Soc. Jpn.*, 56, p. 2504 (1983).
9. Y. Shimizu, N. Miura and N. Yamazoe, *Int. J. Hydrogen Energy*, 13(6), 345 (1988).
10. C. N. Wauters, and J. Winnick, *AIChE Journal*, 44(10), 2144-2148 (1998).