II.J.2 Hybrid Sulfur Thermochemical Process Development

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Objectives

- Establish process design requirements for Hybrid Sulfur (HyS) process electrolyzers.
- Develop and test an SO_2-depolarized electrolyzer.
- Characterize, analyze and select cell components.
- Demonstrate single cell electrolyzer test for 100 hours continuous operation.

Technical Barriers

This project addresses the following technical barriers from section 4.3 of the Nuclear Hydrogen Initiative Ten Year Research and Development and Program Plan:

(A) Efficiency
(B) Materials
(C) Conditions
(D) Process Uncertainties
(E) Process Simulation and Evaluation
(F) Integrated Demonstration

Contribution to Achievement of DOE Nuclear Hydrogen Initiative Milestones

This project will contribute to the achievement of the following DOE Nuclear Hydrogen production milestones from the Thermochemical Technology section of the Nuclear Hydrogen Initiative Ten Year Research and Development and Progam Plan:

- Milestone 2, FY 2006: Complete characterization tests for single-cell electrolyzer. (4Q, 2006)
- Milestone 6, FY 2007: Complete characterization testing for hybrid S membranes. (4Q, 2007)
- Milestone 7, FY 2007: Complete final design of lab-scale electrolyzer. (4Q, 2007)
- Milestone 2, FY 2008: Construct Hybrid Sulfur ILS experiment. (4Q, 2008)

Accomplishments

- Prepared improved HyS process design and modeled flowsheet performance with AspenPlus®. Achieved overall process efficiency of 54% (higher heating value [HHV]).
- Identified and characterized key components for SO_2-depolarized electrolyzer.
- Designed, built and operated an electrolyzer test facility capable of operation with concentrated sulfuric acid anolyte at 80°C and 6 atmospheres.
- Designed, built and tested a single cell electrolyzer (nominally 60 cm^2 active area) using 13 different membrane electrode assembly (MEA) designs.
- Completed a 100 hours continuous longevity test of a single-cell SO_2 electrolyzer.
- Designed and constructed a multi-cell electrolyzer of 100 lph hydrogen capacity.

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Introduction

High temperature thermal energy, derived from central solar receivers or advanced high-temperature nuclear reactors, can be utilized to produce hydrogen through the dissociation of water molecules in processes known as thermochemical water-splitting cycles. Pure thermochemical cycles require heat only to drive a series of connected chemical reactions, whereas hybrid cycles employ at least one electrochemical step. The HyS process is a leading candidate among the hybrid thermochemical cycles. It has the potential for high efficiency, competitive cost of hydrogen, and it has been demonstrated at a laboratory scale to confirm performance characteristics.

The major challenges for the development of the HyS process are associated with the development of an efficient, cost-effective electrochemical reactor, known as a sulfur dioxide-depolarized water electrolyzer (SDE). The use of SO_2-depolarization reduces the theoretical cell voltage to 0.158 V, in contrast to the 1.23 V theoretical voltage required for conventional water electrolysis. In order to complete the HyS cycle, the product sulfuric acid from the electrolyzer must be decomposed to regenerate the SO_2 in a high temperature acid decomposition system. An overall thermal efficiency for converting heat to hydrogen with this process of greater than 50% (HHV) is deemed possible.

In contrast to previous efforts to develop an SDE, SRNL has based its work on the use of modern proton exchange membrane (PEM) technology. The advantages of this design concept include high electrochemical efficiency and small footprint, both of which are crucial for successful implementation on a commercial scale. Since PEM technology is also the subject of intense development efforts for use in water electrolyzers and automotive fuel cells, there is the opportunity for leveraging that work for improving the SDE. The application is challenging, however, since the SDE must react sulfur dioxide with water to produce hydrogen in the presence of strong sulfuric acid under elevated temperature and pressure.

Approach

We are developing a PEM-type electrolyzer to operate with liquid anolyte feed comprised of sulfuric acid containing dissolved sulfur dioxide. Due to the corrosive nature of the acid, all wetted components must be constructed of carbon or Teflon materials. A test facility, capable of testing SDEs at elevated temperature and pressure in the presence of sulfur dioxide and sulfuric acid was constructed. Candidate PEM electrolytes were obtained and characterized by testing for proton conductivity and sulfur dioxide transport. Testing was also conducted to determine the performance of various electrocatalysts. The most promising membranes and electrocatalysts were assembled into MEAs for introduction into a test electrolyzer. A robust, versatile PEM-type SDE with a 60 cm^2 active area was designed and constructed. Testing was performed for various cell components and configurations. A collaboration was established with an industrial electrolyzer manufacturer (Giner Electrochemical) and a larger, multi-cell electrolyzer was designed and constructed.

Results

Component characterization tests were conducted on both commercial and experimental proton-conducting membranes that serve as the cell's electrolyte. Characterization testing was also done to select the electrocatalyst for the anode and cathode. Several different types of commercially-available membranes were analyzed for ionic resistivity and sulfur dioxide transport as a function of acid strength including perfluorinated sulfonic acid (PFSA), sulfonated poly-etherketone-ketone (SPEK), and poly-benzimidazole (PBI) membranes. Experimental membranes from the sulfonated diels-alder polyphenylenes (SDAPP) and platinum-treated PFSA were evaluated for ionic resistance and SO_2 transport as well. These membranes exhibited reduced transport coefficient for SO_2 transport without an increase in ionic resistivity. A graph showing the combined results of ionic conductivity and SO_2 transport for various candidate membranes is shown in Figure 1. The E750 membrane (SPEK polymer) had excellent performance, but it has been shown to be unstable under electrolyzer conditions.

Based on results to date, we recommend that Nafion® membranes with an equivalent weight of 1,100 serve as the baseline material for the SDE. Furthermore, we recommend continued evaluation of SDAPP, PBI and platinum-treated PFSA membranes. These membranes have shown improved sulfur dioxide transport characteristics, which may allow up to 100 times lower sulfur dioxide transport while decreasing catalyst layer delamination and membrane ionic resistivity.

Photographs of the electrolyzer test facility and the single cell SDE installed in the facility are shown in Figures 2 and 3. Tests were performed at acid concentrations from 30 to 50 wt% at temperatures ranging from ambient to 80°C and pressures up to 6 atmospheres. Several variations for flow fields and diffusion layers were tried, and a total of 13 different MEAs were tested. Typical test results are shown in Figure 4. A 100-hour continuous longevity test was successfully completed for the single cell electrolyzer using a Nafion® 115 membrane. A voltage increase of approximately 5% was observed over the duration of the test, and post-test examination showed some delamination of the cathode layer caused by sulfur formation.

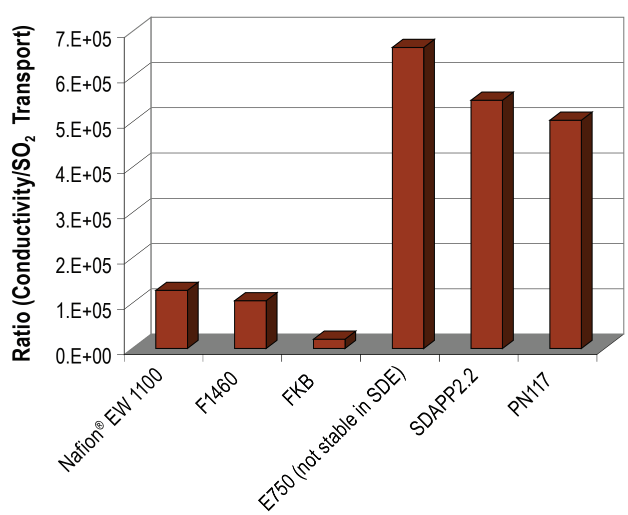

FIGURE 1. Characterization Results for Candidate Electrolyzer Membranes

FIGURE 2. Sulfur Dioxide Depolarized Electrolyzer Test Faciltiy

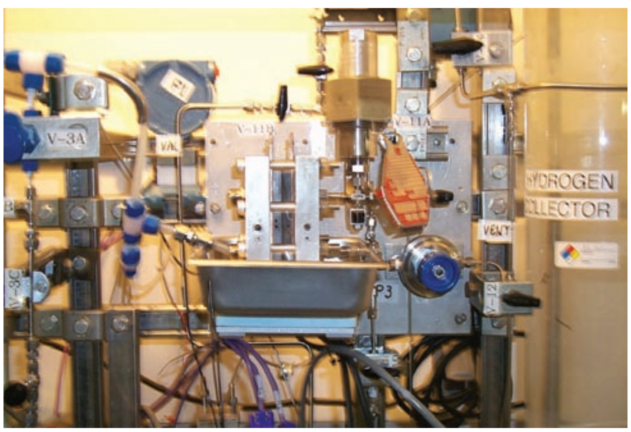

FIGURE 3. Photograph of Single Cell Electrolyzer Installed in Test Facility

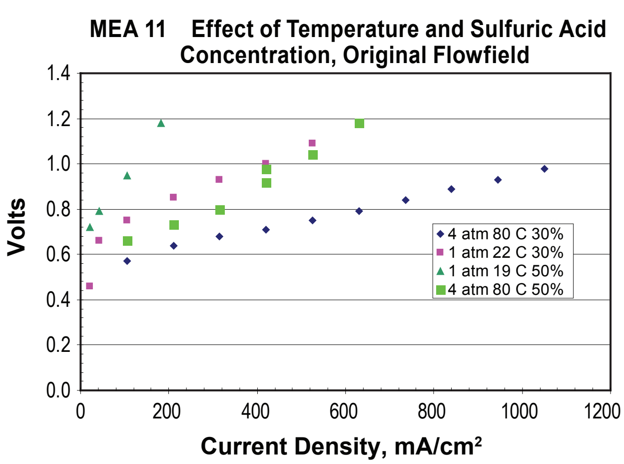

FIGURE 4. Representative Polarization Curves for SO_2-depolarized Electrolyzers

A multi-cell SDE design was completed and construction of a 3-cell stack was initiated in collaboration with industrial partner Giner Electrochemical. The approach was to leverage PEM water electrolyzer technology and to maximize the use of existing components and hardware. A drawing of the electrolyzer is shown in Figure 5. The stack is designed to produce 100 liters per hour of hydrogen under SO_2-depolarized conditions. It will be tested during FY 2008.

Conclusions and Future Directions

We have demonstrated that PEM-type electrochemical cells can be successfully used in the SO_2-depolarized mode to generate hydrogen at low voltage. Further work is required to reduce cell voltage and minimize sulfur formation at the cathode caused by SO_2 transport through the membrane. Several promising experimental membranes have been identified. Longevity testing is an important element in establishing lifetime issues, performance changes over time, and material concerns. Scale-up to both larger cell sizes

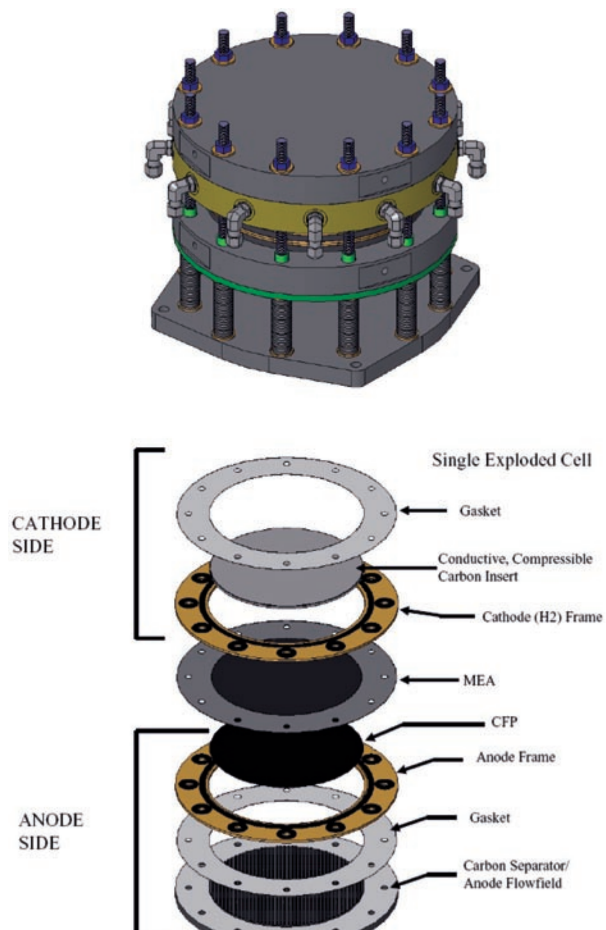

FIGURE 5. Drawing of Multi-Cell Electrolyzer with 100 lph Hydrogen Capacity

(greater cell active area) and larger stacks (more cells in series) are required to reach commercial sizes.

Future work will consist of continuing to characterize and incorporate advanced membranes and design concepts to improve cell performance. The larger multi-cell stack will be installed in the test facility and characterized. Testing will be expanded to more severe conditions, including stronger acid concentrations, higher temperature (>100°C) and pressures up to 20 atmospheres. The test facility will be automated to permit unattended, longer duration testing. Efforts will be initiated in FY 2008 leading to the design, construction and operation of an integrated lab-scale experiment of the entire Hybrid Sulfur process, including both the electrochemical step and the high temperature acid decomposition.

FY 2007 Publications/Presentations

1. H.R. Colon-Mercado, D.T. Hobbs, D.B. Coleman and A.A. Ekechukwu, "Initial Component Test Results and Analysis for an SO2-depolarized Electrolyzer Cell Design", WSRC-STI-2006-00064, Rev. 0, DOE-NE Nuclear Hydrogen Initiative research report, Work Package SR16TC21, August 1, 2006.

2. M.B. Gorensek, W.A. Summers and J. Eargle, "Expected Performance of Hybrid Sulfur Process Based on SO2-Depolarized Electrolyzer Technology", WSRC-STI-2006-00136, Rev. 0, DOE-NE Nuclear Hydrogen Initiative research report, Work Package SR16TC21, August 30, 2006.

3. J.L. Steimke and T.J. Steeper, "Characterization Testing and Analysis of Single Cell SO2 Depolarized Electrolyzer", WSRC-STI-2006-00120, Rev. 1, DOE-NE Nuclear Hydrogen Initiative research report, Work Package SR16TC21, September 15, 2006.

4. W.A. Summers, "Nuclear Hydrogen Production Based on the Hybrid Sulfur Thermochemical Process", WSRC-STI-2006-00200, Rev. 0, Proceedings of Third International Topical Meeting on High Temperature Reactor Technology (HTR2006), Sandton, South Africa, October 1–4, 2006.

5. J.L. Steimke and T.J. Steeper, "Generation of Hydrogen Using Hybrid Sulfur Process Electrolyzer", Proceedings of 2006 Southeastern Regional Meeting of the American Chemical Society, Augusta, Georgia, November 2, 2006.

6. H.R. Colon-Mercado, A.A. Ekechukwu and D.T. Hobbs, "Electrolyzer Component Testing for Hybrid Sulfur Process", Proceedings of 2006 Southeastern Regional Meeting of the American Chemical Society, Augusta, Georgia, November 2, 2006.

7. J.L. Steimke and T.J. Steeper, "Generation of Hydrogen Using Electrolyzer with Sulfur Dioxide Depolarized Anode", Proceedings of 2006 AIChE Annual Meeting, Orlando, Florida, November 13, 2006.

8. J.L. Steimke, "Design and Performance Objectives of the Single Cell Test System for SO2 Depolarized Electrolyzer Development", WSRC-STI-2007-00002, Rev. 0, DOE-NE Nuclear Hydrogen Initiative research report, Work Package N-SR07TC0301, January 15, 2007.

9. H.R. Colon-Mercado and D.T. Hobbs, "Baseline Membrane Selection and Characterization for an SDE", WSRC-STI-2007-00172, Rev. 0, DOE-NE Nuclear Hydrogen Initiative research report, Work Package N-SR07TC0301, April 15, 2007.

10. W.A. Summers, "Hybrid Sulfur Thermochemical Process Development", Project PD21, DOE Hydrogen Program Peer Review, May 16, 2007.