

II.H.2 Hybrid Sulfur Thermochemical Process Development

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Subcontractor:

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Technical Targets

This project is aimed at the development and demonstration of nuclear hydrogen production technologies necessary to produce hydrogen at a cost competitive with other alternative transportation fuels. The focus is on the HyS thermochemical cycle that can be powered by heat from high temperature gas reactors. While specific quantitative technical targets have not been defined for the Nuclear Hydrogen Initiative, if successful this project is expected to address the following DOE technical target as outlined in the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

TABLE 1. DOE Targets for Hydrogen Production

By 2017, develop high-temperature thermochemical cycles driven by concentrated solar energy to produce hydrogen with a projected cost of \$3.00/gge at the plant gate (\$4.00/gge delivered) and verify the potential for this technology to be competitive in the long term.

Objectives

- Develop and demonstrate a thermochemical hydrogen production system based on the Hybrid Sulfur (HyS) process that can be powered by heat from nuclear high temperature gas reactors.
- Prepare improved process flowsheets for the HyS process and establish design requirements for the electrochemical section.
- Develop and test an SO₂-depolarized electrolyzer capable of operation at 600 mV cell voltage at 500 mA/cm² current density.
- Characterize, analyze and select cell components.
- Conduct single cell electrolyzer testing.
- Characterize performance for a multi-cell electrolyzer stack capable of 100 lph hydrogen production.

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

Accomplishments

- Conducted 100-hour longevity test for single-cell electrolyzer with nominal 60 cm² active cell area.
- Completed construction of multi-cell stack with rated capacity of 100 lph hydrogen.
- Prepared improved HyS process design capable of achieving >40% higher heating value (HHV) efficiency and producing 2 kg/s hydrogen output based on a 500 MWt high temperature gas reactor.
- Identified and characterized key components for SO₂-depolarized electrolyzer, including measurement of SO₂ diffusion through membranes, electrocatalyst activity and membrane electrode assembly (MEA) performance in a small-scale (2 cm²) test facility.
- Conducted single cell electrolyzer testing on 16 new MEA configurations.
- Completed characterization testing of a multi-cell SO₂ electrolyzer achieving a hydrogen production rate of 80 lph.
- Demonstrated feasibility of using a gas diffusion electrode and gap cell design for conducting the SO₂ electrolysis with significant reduction in sulfur crossover.



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. A schematic showing the two major chemical reactions for the HyS process is shown in Figure 1.

A major challenge for the HyS process is 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 for hydrogen production 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, which also releases the co-product oxygen. An overall thermal efficiency for converting heat to hydrogen with this process of 40-50% (HHV-basis) is deemed possible based on detailed flowsheet analysis.

This project focuses on the development of the SDE. A companion project under the DOE-NE Nuclear Hydrogen Initiative involves the development of the high temperature acid decomposition system. Upon establishment of these two technologies, an integrated lab-scale experiment will be conducted to demonstrate

closed-loop operation. If successful, the process will be scaled-up for demonstration with DOE's Next Generation Nuclear Plant.

Approach

In contrast to previous efforts to develop an SDE, SRNL has based its work on the use of proton exchange membrane (PEM) technology. The advantages of this design concept include high electrochemical efficiency, small footprint, and potential for competitive capital cost, all 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.

The baseline electrolyzer design approach involves operation with liquid anolyte feed comprised of sulfuric acid containing dissolved sulfur dioxide. Hydrogen gas is evolved at the cathode. Due to the corrosive nature of the acid, all wetted components must be constructed of carbon or polymeric 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 nominal 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 Systems, LLC) and a larger, multi-cell electrolyzer was designed, constructed and tested. Future development will include the design and construction of an integrated lab-scale experiment (ILS) that will demonstrate operation of a complete closed-cycle HyS process.

Results

An improved process flowsheet for the HyS process was developed under a collaborative agreement with industry partner Westinghouse Electric. Optimization of the integration of the process with a 500 MWh Pebble Bed Modular Reactor resulted in a

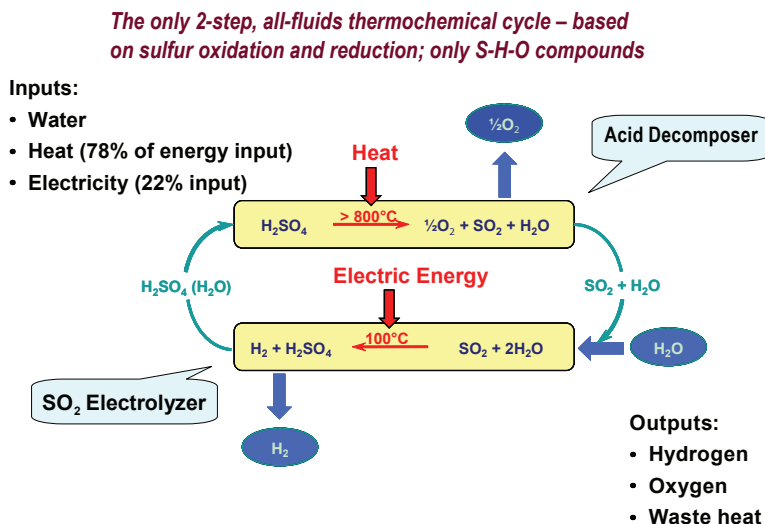


FIGURE 1. Hybrid Sulfur Process Schematic

hydrogen output of approximately 2 kg/sec, which was a significant improvement over the previous design. Work was conducted to prepare a capital cost estimate and to determine the hydrogen production costs. Results will be reported at the conclusion of this study.

Studies in electrolyzer component development focused on three main areas: 1) the characterization of MEAs after performance tests in the single cell electrolyzer, 2) evaluation of electrocatalysts and membranes using a small scale electrolyzer, and 3) empirical analysis to evaluate the contribution of individual cell components to the overall electrochemical performance. Scanning electron microscopic studies of samples taken from MEAs tested in the SRNL single-cell electrolyzer test station indicated a sulfur-rich layer forms between the cathode catalyst layer and the membrane. Based on a review of operating conditions for each of the MEAs evaluated, it was concluded that the formation of the layer results from the reduction of sulfur dioxide as it passes through the MEA and reaches the catalyst layer at the cathode-membrane interface. Formation of the sulfur rich layer results in partial delamination of the cathode catalyst layer leading to diminished performance. It is postulated that operating the electrolyzer at elevated pressure significantly increases the rate of sulfur formation due to increased adsorption of hydrogen on the internal catalyst surface. Thus, identification of a membrane that exhibits much lower transport of sulfur dioxide is needed to reduce the quantity of sulfur dioxide that reaches the cathode catalyst and is reduced to produce the sulfur-rich layer. Three candidate membranes are currently being evaluated that have shown promise from preliminary studies, (1) modified Nafion®, (2) polybenzimidazole (PBI), and (3) sulfonated Diels Alder polyphenylene (SDAPP). Efforts in conjunction with Giner Electrochemical Systems, LLC were also conducted to develop a modified cell design consisting of a gap cell with a gas diffusion electrode. Successful development of this approach may provide an alternative means of increasing cell performance and minimizing sulfur crossover.

Electrocatalyst development included testing of platinum (Pt) and platinum-alloy catalysts in 30 wt% sulfuric acid solution to examine their activity for the sulfur dioxide oxidation. Linear sweep voltammetry showed an increase in activity for catalysts containing Pt alloyed with non-noble transition metals such as cobalt and chromium. However, when Pt was alloyed with noble metals, such as iridium or ruthenium, the kinetic activity decreased. Further testing is recommended to determine if these binary alloys will provide the increased reaction kinetic needed to meet the design targets. We also plan to test the performance of these catalyst materials for both proton and sulfur dioxide reduction. The latter may provide another parameter by which we can control the reduction of sulfur dioxide

upon transport to the cathode catalyst surface. A small-scale electrolyzer (2 cm² active area) was fabricated, successfully installed and utilized as an additional tool to evaluate the effect of different operating conditions on electrolyzer and MEA performance. Currently this electrolyzer is limited to testing at temperatures up to 80°C and at atmospheric pressure.

Selected electrochemical performance data from the single-cell SDE testing were analyzed with the aid of an empirical equation which takes into account the overpotential of each of the components comprising overall cell voltage. By using the empirical equation, the performance data was broken down into its components and a comparison of the potential losses was made. A comparison of the test data and the model predictions is shown in Figure 2. The empirical results are shown in Table 2.

The results indicate that for the testing condition examined the major overpotential contribution (~70% of all losses) arises from the slow reaction rate of oxidation of sulfur dioxide at the anode. Therefore, identification of a means to increase reaction kinetics at the anode

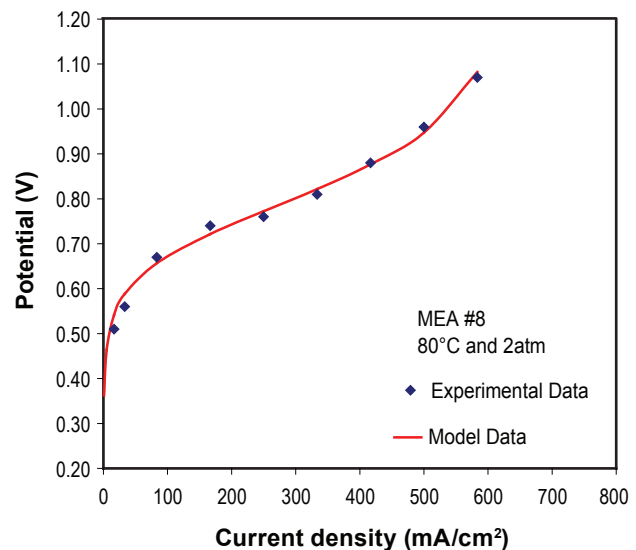


FIGURE 2. Comparison of Test Data and Empirical Prediction for Cell Potential Components

TABLE 2. Contribution of Overpotential Terms for SO₂ Electrolyzer: MEA #8 at a Current Density of 500 mA/cm² at 80°C and 30 wt% Sulfuric Acid

Pressure (atm)	Kinetic Loss (%)	Ohmic Loss (%)	Mass Transport Loss (%)
2	74	10	16
3	78	14	8
4	81	15	4

will provide the largest source of improvement in cell performance. This might be accomplished through a combination of operation at a higher temperature (which may require a new membrane) and development of a better catalyst for sulfur dioxide oxidation.

The electrolyzer test facility and the single-cell SDE constructed previously were used to conduct performance tests for various MEA configurations and to determine the effects of varying cell temperature, pressure and sulfuric acid concentration. 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 tested in order to optimize performance. A total of 27 MEA configurations have been tested to date (16 within the last year). 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.

A multi-cell SDE stack was designed and constructed in collaboration with industrial partner Giner Electrochemical Systems, LLC. The approach was to leverage PEM water electrolyzer technology and to maximize the use of existing components and hardware. The stack consists of three cells with an active cell area of 160 cm² each, for a total of 480 cm². (This compares to the single-cell electrolyzer that has a single-cell active area of 60 cm²). The rated hydrogen output for the three-cell stack is 100 liters per hour at a current density of 500 mA per cm². The MEA consists of a Pt-carbon anode, Nafion® 117 electrolyte membrane, and a Pt-carbon cathode. The stack construction is a modification of a standard Giner water electrolyzer design, although all wetted parts have been changed to carbon or polymer materials. An SRNL-designed graphite flowfield is used to distribute anolyte across the MEA. Anolyte feed consists of sulfuric acid containing dissolved sulfur dioxide. A drawing of the multi-cell stack assembly is shown in Figure 3. A photograph of the multi-cell stack installed in the SDE test facility at SRNL is shown in Figure 4.

The test facility was originally designed for the single-cell electrolyzer with a maximum hydrogen output of approximately 20 lph. It was modified for the larger stack testing with the goal of achieving as high a hydrogen output as possible within the constraints of the test facility. Characterization tests were conducted over a range of temperature, pressure and acid concentration. A maximum hydrogen output of 80 lph was achieved. The test facility was not automated for continuous, unattended testing, so the stack was started

and shutdown daily. During a 14-hour continuous run at fixed conditions the cell voltages showed no measurable degradation. Upon completion of characterization testing with the original MEAs, a second set of tests were conducted with MEAs using a different electrocatalyst. Similar results were obtained. Post-test examinations of both sets of MEAs indicated the formation of a sulfur layer inside the cell caused by SO₂ reduction. Advanced, higher temperature membranes identified in the component development tasks will be used to reduce this effect.

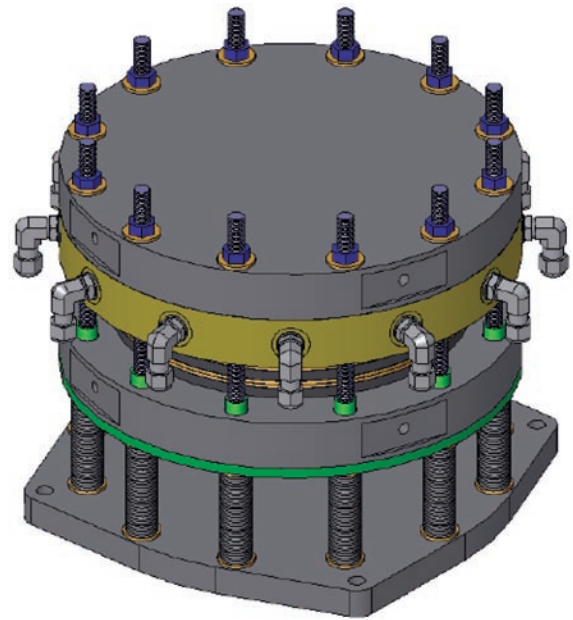


FIGURE 3. Artist's Drawing of Multi-Cell SDE Stack



FIGURE 4. Photograph of Multi-Cell SDE Stack Installed in Test Facility

Conclusions and Future Directions

We have demonstrated that PEM-type electrochemical cells can be successfully used in the SO₂-depolarized mode to generate hydrogen at low voltage. Conclusions and recommendations from research to date include:

- HyS process thermal efficiency (nuclear heat to hydrogen, HHV) of over 40% has been demonstrated in a complete flowsheet based on realistic conditions.
- Further work is required to reduce cell voltage and to minimize sulfur formation at the cathode caused by SO₂ transport through the membrane.
- Several promising experimental membranes have been identified and should be further investigated, including (1) modified Nafion[®], (2) PBI, and (3) SDAPP.
- The gap cell design being pursued with Giner appears promising and should be continued.
- Platinum alloyed with non-noble transition metals are attractive electrocatalysts.
- Kinetic overpotential at the anode is the largest source of voltage loss; higher temperatures and improved catalysts should be investigated.
- Single-cell tests are a useful means to qualify components and to measure electrolyzer performance; longer term testing should be implemented.
- The multi-cell stack tests were successful; the technology is ready to be implemented into an ILS experiment.
- Scale-up to both larger cell sizes (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. Proof of concept of the gas diffusion electrode gas cell design development will be completed and incorporated into the single-cell testing if successful. The test facility will be automated to permit unattended, longer duration testing. Efforts will be initiated leading to the design, construction and operation of an ILS of the entire HyS process, including both the electrochemical step and the high temperature acid decomposition.

FY 2008 Publications/Presentations

1. “Hybrid Sulfur Thermochemical Process Development”, proceedings of DOE Hydrogen Program 2007 Annual Merit Review, Arlington, VA, May, 2007.
2. “Catalyst Evaluation for a Sulfur Dioxide-Depolarized Electrolyzer”, *Electrochemistry Communications*, Volume 9, Issue 11, November 2007, Pages 2649-2653, Hèctor R. Còlon-Mercado and David T. Hobbs.
3. “Hybrid Sulfur Electrolyzer Development – FY08 First Quarter Report”, WSRC-STI-2007-00716, October 1, 2007 - December 31, 2008; Project Quarterly Report for DOE-NE Nuclear Hydrogen Initiative (NHI) Work Package, N-SR07TC0301, W.A. Summers.
4. “Hybrid Sulfur Electrolyzer Development – FY08 Second Quarter Report”, WSRC-STI-2008-00157, January 1, 2008 – March 31, 2008; Project Quarterly Report for DOE-NE Nuclear Hydrogen Initiative (NHI) Work Package, N-SR07TC0301, W.A. Summers.
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6. “Improved Process Flowsheet for the Hybrid Sulfur Process for Hydrogen Production”, proceedings AIChE Annual Meeting, Salt Lake City, Utah, November 6, 2007.
7. “Hybrid Sulfur Thermochemical Process Development”, proceedings of DOE Hydrogen Program 2008 Annual Merit Review, Arlington, VA, June 12, 2008.
8. “Component Development Needs for the Hybrid Sulfur Electrolyzer”, WSRC-STI-2008-00291, DOE-NE Nuclear Hydrogen Initiative (NHI) Work Package, N-SR07TC0301, H.R. Colon-Mercado, M.C. Elvington, D.T. Hobbs, May, 2008.