II.G.3 Hybrid Sulfur Thermochemical Cycle

William A. Summers (Primary Contact),
John Steimke, Timothy Steeper, David Hobbs,
Hector Colon-Mercado, David Herman,
Mark Elvington, Maximilian Gorensek
Savannah River National Laboratory (SRNL)
Savannah River Site, Building 773-42A
Aiken, SC 29808
Phone: (803) 725-7766; Fax: (803) 725-8829
E-mail: william.summers@srnl.doe.gov

DOE Technology Development Manager:
Carl Sink
Phone: (301) 903-5131; Fax: (301) 903-0180
E-mail: carl.sink@nuclear.energy.gov

Subcontractor:
Giner Electrochemical Systems LLC, Newton, MA

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Objectives

- Develop the Hybrid Sulfur (HyS) thermochemical water-splitting process for hydrogen production using heat from advanced nuclear reactors.
- Optimize the cycle design and establish design requirements for key components.
- Design and demonstrate an SO_2-depolarized electrolyzer (SDE) capable of operating at low voltage (<600 mV) and high current density (>500 mA/cm^2).
- Characterize, analyze and select cell components, including proton exchange membrane.
- Conduct electrolyzer tests demonstrating successful operation without sulfur limitations.

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:

(H) System Efficiency

(U) High-Temperature Thermochemical Technology

(V) High-Temperature Robust Materials

Technical Targets

DOE's Office of Nuclear Energy has the lead responsibility for hydrogen production utilizing nuclear energy for high-temperature (700°-1,000°C) thermochemical water-splitting chemical cycles. The Office of Hydrogen, Fuel Cells and Infrastructure Technologies will collaborate with Nuclear Energy (NE) on the thermochemical hydrogen production research and development activities. This project addresses the goal of the Nuclear Hydrogen Initiative (NHI) [1] to demonstrate the economic, commercial-scale production of hydrogen using nuclear energy.

The project is conducting component development and unit testing for an SDE, which is the key component of the HyS thermochemical process. Insights gained from this work will be applied toward the design, scale up and demonstration testing of a complete HyS process meeting the NHI goals for interfacing with advanced nuclear reactors.

Accomplishments

- Established collaborations with leading proton exchange membrane (PEM) suppliers and characterized the ionic conductivity, SO_2 diffusion and chemical stability of over 15 advanced membranes.
- Organized and hosted an international workshop on SDE technology.
- Completed testing of 11 additional (37 total) single-cell electrolyzer configurations at temperature of 80°C and pressure to 700 kPa.
- Upgraded test facility to permit unattended 24/7 operation.
- Invented a new operating method to prevent sulfur build-up inside of the cell.
- Completed two 200+ hour tests of electrolyzer demonstrating operation without sulfur build-up limitations.
- Completed major conceptual design and cost study of HyS process demonstrating potential for >40% thermal efficiency and competitive cost of hydrogen when coupled with an advanced Generation IV gas-cooled nuclear reactor.

Introduction

High temperature (750-900°C) thermal energy can be utilized in thermochemical water-splitting cycles to produce hydrogen with no greenhouse gas emissions.

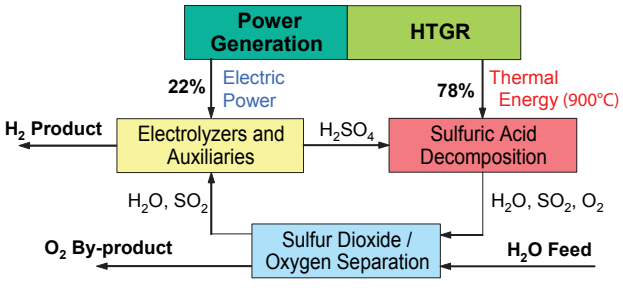
The HyS Process uses two linked chemical reactions to produce hydrogen in an electrochemical reaction and oxygen in a thermochemical reaction [2]. Sulfur dioxide is used to depolarize the anode in a water electrolyzer, creating sulfuric acid and releasing the hydrogen. Heat is used to thermally decompose the acid, regenerating the sulfur dioxide and releasing the oxygen. Central solar receivers or high temperature gas-cooled nuclear reactors can be used to supply the heat. The process has the potential for high efficiency, competitive cost of hydrogen, and it has been demonstrated at a laboratory scale to confirm performance characteristics. A simplified block schematic showing the major process steps is shown in Figure 1.

A major challenge for the HyS cycle is the development of an efficient, cost-effective electrochemical reactor, or SDE. The use of SO_2-depolarization reduces the standard cell potential from 1.23 V for conventional water electrolysis to 0.158 V, dramatically reducing the electricity required per unit of hydrogen production. This project focuses on the development of the SDE. The SDE must be capable of operation at low voltage (<600 mV), high current density (>500 mA/cm^2), long-life (>40,000 hours) and competitive capital cost. A companion project under the DOE-NE NHI [3] involves the development of the high temperature acid decomposition system, which is required to close the cycle. 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 (NGNP), which is scheduled to be built at the Idaho National Laboratory by year 2021 [4].

Approach

In contrast to past efforts by others to develop an SDE, Savannah River National Laboratory (SRNL) has based its work on the use of 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 automotive fuel cells and direct methanol 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.

To achieve the project objectives, a component development project to identify, characterize and select the best PEM electrolyte, electrocatalysts, and associated cell components is being conducted. Button cell testing is used to verify promising alternatives. Advanced membranes that have lower water content and can operate at higher temperature (120 to 140°C) appear the most promising. Single cell electrolyzers of approximately 60 cm^2 active cell area are then used to conduct proof-of-concept tests and determine performance and lifetime. Post-test examinations using scanning electron microscopy (SEM) are used to examine the PEMs to determine if sulfur deposits have accumulated inside. Avoidance of sulfur build-up is a key requirement for long-term cell operation. Successful configurations will then be assembled into multi-cell stacks, as well as being scaled up to larger cell sizes. The SDE can then be combined with an acid decomposition system and balance of system components to demonstrate integrated HyS Process operation.



HTGR - high-temperature gas-cooled reactor

FIGURE 1. Simplified Block Schematic of Hybrid Sulfur Thermochemical Cycle

Results

In the past year, the main focus has been on the exploration of high temperature membranes and SDE operation without sulfur limitations. Collaborations were established with leading researchers and membrane developers from industry, academia and national laboratories. During the selection process of commercially available and experimental membranes, an array of thicknesses, equivalent weights, chemistry, and reinforcements were considered. Commercial membranes include perfluorinated sulfonic acid (PFSA) membranes, such as DuPont Nafion®, which was chosen as the benchmark for comparing membrane performance. Many of the experimental membranes were prepared exclusively to reduce the transport of inert species, such as dissolved SO_2. A number of these membranes were already under development for use in direct methanol fuel cells, which have a similar crossover problem involving methanol. SRNL hosted an information exchange and workshop in 2009 to discuss SDE membranes and related research areas. It was attended by many of the leading PEM experts in the country, as well as representatives from five countries. The presentations and workshop results can be assessed on the SRNL Web site [5]. A list of the some of the

membranes selected and characterized by SRNL in the past year is given in Table 1.

TABLE 1. Membranes Selected and Characterized by SRNL

Membrane Type	Supplier
Perfluorinated sulfonic acid (PFSA)	DuPont
Polybenzimidizole (PBI)	BASF (Germany)
Sulfonated Diels-Alder polyphenylenes (SDAPP)	Sandia National Laboratories
Stretched recast PFSA	Case Western Reserve University
Nafion®/fluorinated ethylene propylene (FEP) blends	Case Western Reserve University
Treated PFSA	Giner Electrochemical Systems LLC
Perfluorocyclobutane-biphenyl vinyl ether (BPVE)	Clemson University
Perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene (BPVE-6F)	Clemson University

An ideal membrane has high proton conductivity and low SO_2 transport. These parameters were evaluated using a custom-made permeation cell; a schematic of the cell is shown in Figure 2. The cell consists of two glass chambers joined by a Teflon® bridge where the membrane is secured. During measurements both chambers were filled with the concentrated acid of interest (typically 30 wt% H_2SO_4) and purged of oxygen by flowing nitrogen. A constant potential is applied and the SO_2 transport through the membrane is determined by measurement of the current as a function of time. The test unit was also modified to perform as a small electrolyzer in order to compare the performance of various membranes and electrocatalysts. Membrane electrode assemblies (MEAs) were fabricated and installed in the apparatus, which was then operated as a button-cell electrolyzer. A two electrode system was used with a potential of 1.1 V applied across the cell. Testing was limited to atmospheric pressure, and typically operated at 60-80°C. Each membrane was also tested for through-plane ionic conductivity using electrochemical impedance spectroscopy. The results are shown in Figure 3.

The lowest SO_2 transport coefficient was measured for membranes of the DuPont bilayer and high equivalent weight PFSA, but these also showed unacceptably low ionic conductivity. The best combined performance (low SO_2 transport and high conductivity) was observed for PBI, BPVE, and Case Nafion®-FEP blend. These test results were determined at 67°C and atmospheric pressure. Several of the more promising membranes, such as the Clemson BPVE and Sandia SDAPP, are expected to perform better at higher temperature (120-140°C). This requires pressurization in order to maintain an adequate concentration of SO_2 in the anolyte. A new pressurized button cell test facility is being constructed to permit testing at up to 150°C and 2 MPa in order to fully explore the higher temperature membranes. Giner Electrochemical Systems LLC is supporting SRNL in this work, including construction of a major portion of the pressurized button-cell test facility and construction of multi-cell SDE stacks. This helps to leverage Giner's experience in manufacturing commercial PEM water electrolyzers.

A major goal of the past year's HyS research project was to demonstrate operation of an SDE without sulfur layer build-up inside of the MEA. PEM electrolytes require hydration for efficient operation, which can permit neutral species, such as sulfur dioxide, to pass through the membrane. In the SDE, sulfur dioxide that diffuses through the membrane from the anode to the cathode can be reduced to elemental sulfur, which is an

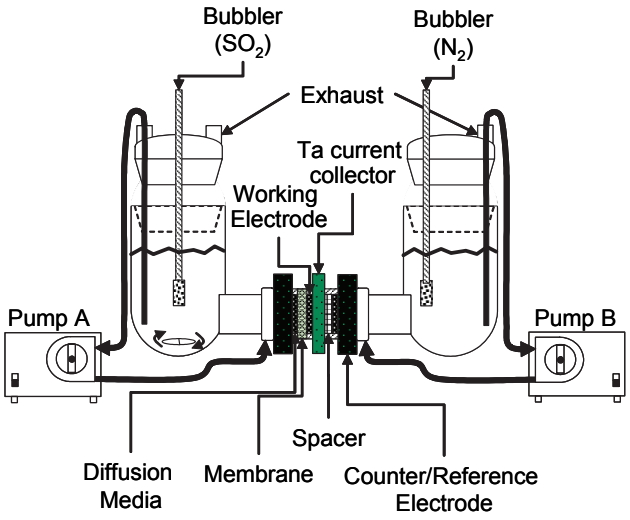


FIGURE 2. Simplified Schematic of the SO_2 Transport Characterization Cell

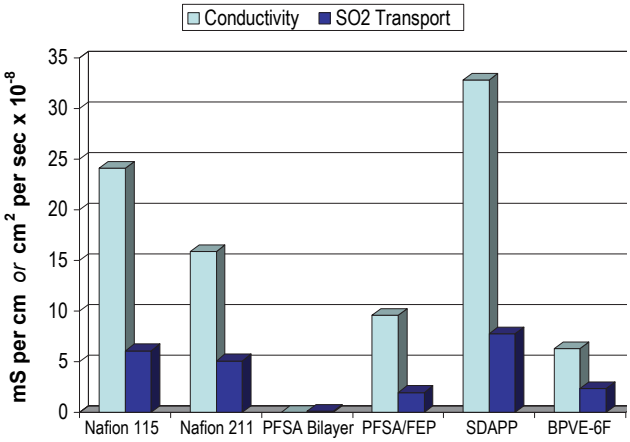


FIGURE 3. SO_2 Diffusion and Conductivity Results for SDE Membranes

unwanted side reaction. Most of the prior SDE tests at SRNL resulted in sulfur build-up inside of the cell's MEA, a phenomenon that reduces performance and limits operating lifetime. Figure 4 is an SEM micrograph showing the result of sulfur layer formation.

In response to this technology challenge, SRNL devised a new operating method (patent applied for) that significantly reduces the amount of sulfur dioxide available to diffuse through the membrane. The small amount of SO_2 that does reach the cathode is converted into hydrogen sulfide gas, rather than elemental sulfur, and it exits the cell along with the hydrogen, thus avoiding the life-limiting build-up of sulfur inside of the MEA. This is a major breakthrough in permitting PEM cells to be used in the SDE mode. The new sulfur-limiting operating method was successfully demonstrated in a series of single cell electrolyzer tests, using a Nafion® membrane with a 54 cm^2 active cell area. A 50-hour and two 212-hour longevity tests were conducted. Physical observations during testing indicated a noticeable reduction in sulfur presence, and post-test visual examinations of the SDE indicated good cell integrity and no appearance of sulfur on the MEA. The final test run was conducted continuously for 212 hours prior to a controlled shutdown. The cell voltage was extremely stable throughout, as shown in Figure 5. Operating conditions included a cell temperature and pressure of 80°C and 172 kPa, respectively. The current density was maintained at 500 mA per cm^2, which is the commercial design goal. Measurement of hydrogen production closely matched the theoretical value, indicating very good current efficiency. The cell voltage was approximately 760 mV, which is above the commercial goal of 600 mV. However, operation

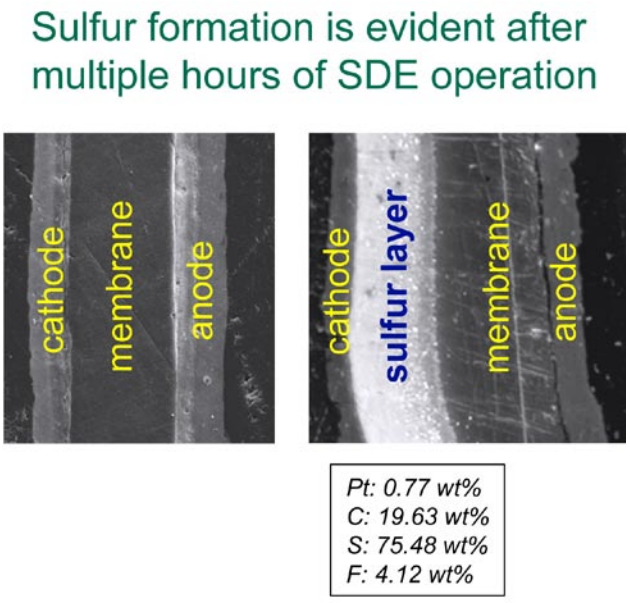


FIGURE 4. SEM Micrographs Depicting Sulfur Formation Inside MEA

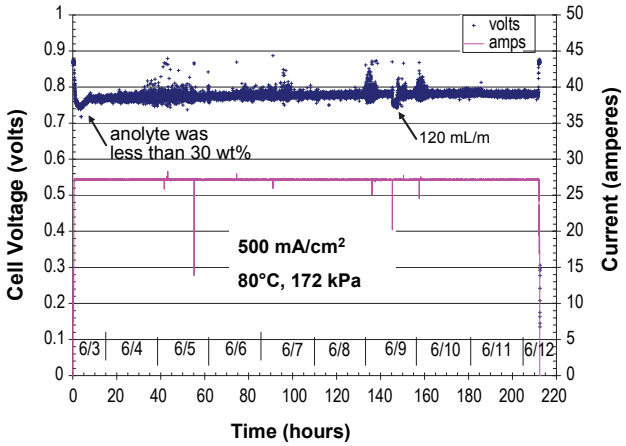


FIGURE 5. Voltage vs. Time for MEA No. 37

at higher temperature and pressure and the use of advanced membranes are expected to reduce the voltage in future configurations.

The MEAs from each of the tests were examined by various analytical methods to verify the absence of sulfur build-up. SEM and energy dispersive X-ray analysis were used to examine multiple locations on each layer of the MEAs. Results showed no localized concentration of sulfur and no evidence of a precursor stage to a sulfur-rich build-up layer. These results confirm that operation of the SDE using the sulfur-limiting method successfully prevents sulfur accumulation inside of the cell.

In addition to the experimental work on the SDE, a comprehensive conceptual design and cost study was performed in conjunction with industry partners for an integrated nuclear hydrogen plant employing the HyS Process and a Generation IV advanced nuclear reactor. The HyS flowsheet was optimized, and the overall plant configuration was modified to permit substantially more hydrogen production per nuclear reactor than the previous concept. The overall thermal efficiency and cost of hydrogen from the nuclear hydrogen plant were deemed attractive as a future greenhouse gas-free hydrogen production option, especially for delivering hydrogen to large industrial users, such as chemical, oil refining and synthetic fuel plants.

Conclusions and Future Directions

The HyS Process is one of the most promising candidates for thermochemical hydrogen production using heat for advanced nuclear reactors or solar central receivers.

- In 2009, a major breakthrough in SDE development was achieved by demonstrating a method of operation that permits the use of PEMs without the limitation of sulfur layer build-up inside of the MEA.

- Collaborations were established with leading PEM developers; several promising high temperature membranes were identified, indicating high probability of meeting the commercial performance goals previously established for the SDE.
- Design and cost studies performed in collaboration with industry indicate that an integrated advanced nuclear reactor and HyS hydrogen plant could be an attractive greenhouse gas-free hydrogen production option.

The DOE-NE NHI will be concluded at the end of Fiscal Year 2009, with responsibility for hydrogen process development assumed by the NGNP program. If HyS is selected, the next activities may include testing of high temperature membranes, scale up to larger SDE cell sizes, construction of a multi-cell stack, and demonstration of an integrated lab-scale experiment of a complete HyS Process, including the SDE and acid decomposition steps.

Special Recognitions & Awards/Patents Issued

1. Program met a DOE-NE Level 1 Milestone by demonstrating SDE operation without sulfur build-up limitations using an innovative operating method. A patent has been applied for.

FY 2009 Publications/Presentations

1. W.A. Summers, "Hybrid Sulfur Thermochemical Cycle," 2009 DOE Hydrogen Program Review, Presentation PD#13, Arlington, VA, May, 2009.

2. D. Hobbs, "Challenges and Progress in the Development of a Sulfur-Dioxide Depolarized Electrolyzer for Efficient Hydrogen Production," 2009 Pittsburgh Conference, Salt Lake City, UT, March 9, 2009.

3. W.A. Summers, "Development Status of the Hybrid Sulfur Thermochemical Production Process," OECD/NEA Fourth Information Exchange Meeting on Nuclear Production of Hydrogen, Oakbrook, IL, April 14, 2009.

4. W.A. Summers and M. Gorensek, "Hybrid Sulfur Flowsheets using PEM Electrolysis and a Bayonet Decomposition Reactor," *International Journal of Hydrogen Energy*, Volume 34, Issue 9, May 2009, pg 4097- 4114.

5. W.A. Summers, M. Gorensek and C. Corgnale, "Conceptual Design and Cost Estimate for a Solar-Powered Hybrid Sulfur Hydrogen Production Process," Proceedings of AIChE 2008 Annual Meeting, Philiadelphia, PA, November 19, 2008.

6. W.A. Summers, J. Steimke, D. Hobbs, H. Colon-Mercado and M. Gorensek, "Development of a Sulfur Dioxide Depolarized Electrolyzer for the Hybrid Sulfur Thermochemical Process," HTR 2008 4th International Topical Meeting on High Temperature Reactor Technology, Washington, D.C., September 30, 2008.

7. H.R. Colon-Mercado, M.C. Elvington, D.T. Hobbs, "Component Development Needs for the Hybrid Sulfur Electrolyzer", WSRC-STI-2008-00291, DOE-NE Nuclear Hydrogen Initiative Work Package, N-SR07TC0301, May, 2008.

8. M. Gorensek et al., "Hybrid Sulfur Process Reference Design and Cost Analysis," DOE Information, www.osti.gov/bridge/ ID: 956960 (2009).

9. M. Gorensek, J. Staser, T. Stanford, J. Weidner, "A Thermodyamic Analysis of the the SO2/H2SO4 System in SO2-depolarized Electrolysis," *International Journal of Hydrogen Energy*, Article in Press, Available online at www.sciencedirect.com (2009).

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2. W. Summers, M. Gorensek, M. Buckner and Z. Qureshi, "Conceptual Design for a Hybrid Sulfur Thermochemical Hydrogen Production Process," *ANS Transactions*, **92**, 101 (2005).

3. P. Pickard, "Sulfur-Iodine Thermochemical Cycle," DOE Hydrogen Program, 2008 Annual Progress Report, November, 2008, pg. 226-228.

4. Department of Energy's Next Generation Nuclear Plant, http://www.nextgenerationnuclearplant.com/.

5. "Hybrid Sulfur Electrolyzer Workshop and Information Exchange", Savannah River National Laboratory, Aiken, SC, April 20-21, 2009, http://srnl.doe.gov/hse_workshop/index.htm.