Hybrid Sulfur Thermochemical Process Development Annual Report

William A. Summers (Primary Contact), Melvin R. Buckner
Savannah River National Laboratory
SRS Building 773-42A
Aiken, SC 29808
803-725-7766 (phone); 803-725-8829 (fax); william.summers@srnl.doe.gov

DOE Technology Development Manager: David Henderson, NE-20
301-903-3097; david.henderson@hq.doe.gov

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Hybrid Sulfur Thermochemical Process Development

Objectives for FY2005

- Develop a conceptual design for the Hybrid Sulfur thermochemical hydrogen production system, including preliminary flowsheet analysis, estimated system performance, and projected hydrogen production costs
- Identify key technical issues and concerns, and prepare a development plan for a fully-integrated laboratory demonstration of the HyS Cycle
- Perform proof-of-principle demonstration testing of an SO_2 anode-depolarized electrolyzer using a single-cell PEM-type water electrolyzer under near-ambient conditions

Technical Barriers

This project addresses the following technical barriers of the Nuclear Hydrogen Initiative:

- Process realization: achieving reasonable performance of small-scale experiments
- Nuclear reactor & central hydrogen production facility costs

Approach

- Create a high-efficiency process design for the Hybrid Sulfur thermochemical water-splitting cycle
  - Update and improve original Westinghouse flowsheets
  - Use AspenPlus software to calculate mass and energy balances and to optimize system performance and hydrogen production cost
- Develop and test a high-performance PEM-based electrolyzer using SO_2 anode depolarization
  - Leverage PEM fuel cell and electrolyzer advancements to develop a low-cost H_2O/ SO_2 electrolyzer achieving cell voltages of <0.6 volts per cell
  - Perform small-scale proof-of-concept testing beginning with a modified PEM water electrolyzer
  - Characterize performance, materials integrity, sulfur crossover, and effects of operating conditions (temperature, pressure, acid concentration)

Accomplishments

- Improved the Hybrid Sulfur process design by optimizing each major subsystem (resulting in 3 patent disclosures). Increased overall process thermal efficiency (HHV-basis) from 42% to 48.8%. Identified further efficiency improvements.
- Identified key technical issues and established performance goal for SO_2-depolarized electrolyzer of <0.6 volts per cell at 500 mA/cm2 current density
- Performed cost analysis of complete N^{th}-of-a-Kind nuclear hydrogen plant capable of producing 580 tonnes per day of hydrogen and determined hydrogen production cost of $1.60/kg without O_2 credit
- Designed, constructed and commissioned SO_2-depolarized electrolyzer test facility
- Demonstrated SO_2-depolarized water electrolysis in small-scale cell at near ambient temperature and pressure. Preliminary measurements indicate cell voltages of less than 0.6 volts per cell at low current density. This is about one-third the voltage required for conventional water electrolysis, so the same amount of hydrogen can be produced for about one-third the electrical power requirement.

Future Directions

- Evaluate various improved electrolyzer components, including electrolyte membrane, electrocatalysts, MEA assembly, and electrode flow structures
- Develop analytical models and analyze electrolyzer design and performance
- Upgrade electrolyzer test facility to include additional online instrumentation and modified flow arrangements
- Conduct atmospheric testing of improved electrolyzer configurations
- Design and build a pressurized test facility
- Design and build a single-cell pressurized SO_2-depolarized electrolyzer
- Design and build a multi-cell pressurized SO_2-depolarized electrolyzer with hydrogen generation capacity of 1000 liters per hour
- Design, construct and test an integrated laboratory model of the Hybrid Sulfur Thermochemical Process with hydrogen generation capacity of 1000 liters per hour, including electrolyzer and acid decompositions sections

Discussion

Introduction

The Hybrid Sulfur (HyS) Thermochemical Process is a means of producing hydrogen via water-splitting through a combination of chemical reactions and electrochemistry. Energy is supplied to the system as high temperature heat (approximately 900°C) and electricity. Advanced nuclear reactors (Generation IV) or central solar receivers can be the source of the primary energy. Large-scale hydrogen production based on this process could be a major contributor to meeting the needs of a hydrogen economy. This project's objectives include optimization of the HyS process design, analysis of technical issues and concerns, creation of a development plan, and laboratory-scale proof-of-concept testing.

The key component of the HyS Process is the SO_2-depolarized electrolyzer (SDE). Studies were performed that showed that an electrolyzer operating in the range of 500-600 mV per cell can lead to an overall HyS cycle efficiency in excess of 50%, which is superior to all other currently proposed thermochemical cycles. Economic analysis indicated hydrogen production costs of approximately $1.60 per kilogram for a mature nuclear hydrogen production plant. However, in order to meet commercialization goals, the electrolyzer should be capable of operating at high current density, have a long operating lifetime, and have an acceptable capital cost. The use of proton-exchange-membrane (PEM) technology, which leverages work for the development of PEM fuel cells, was selected as the most promising route to meeting these goals. The major accomplishments of this project were the design and construction of a suitable electrolyzer test facility and the proof-of-concept testing of a PEM-based SDE.

Approach

The HyS Process was characterized by performing a complete process conceptual design, including flowsheet analysis, estimated system performance, and projected hydrogen production costs. Each major subsystem was analyzed and optimized. The AspenPlus software package was used to calculate mass and energy balances and to establish operating conditions for each major component, including the SO_2-depolarized electrolysis section.

A test facility was designed and constructed for testing SO_2-depolarized electrolyzers. An SDE based on commercially available PEM technology was procured and tested. A second custom-designed SDE was constructed using different materials and catalyst loadings. Proof-of-concept testing was performed at near-ambient pressure and room temperature. Test results were analyzed to determine performance trends, improvement needs, and long-term SDE potential. A detailed SDE development plan was prepared.

Results

A conceptual design for the Hybrid Sulfur Process (HyS) was prepared and modeled using the Aspen Plus™ software package [1]. A process flow diagram of the conceptual design was created, and material and energy balances computed. The HyS process is an all fluids cycle that involves a single thermochemical step and a single electrolytic step. As such, it is not a pure thermochemical cycle, but rather it is a hybrid thermochemical/electrochemical cycle. The HyS process (also known as the Westinghouse Sulfur Cycle) was originally developed by Westinghouse Electric in the 1970's and early 1980's [2,3]. The current work seeks to improve on the original process design, and to utilize modern proton-exchange-membrane (PEM) electrolysis cell technology.

The two-step HyS Cycle consists of the following two chemical reactions:

$H_2SO_4 \Leftrightarrow SO_2 + H_2O + \frac{1}{2} O_2$ Thermochemical, 800-900 °C

$2\ H_2O + SO_2 \Leftrightarrow H_2SO_4 + H_2$ Electrochemical, 100-120 °C

The presence of SO_2 at the anode of the electrolyzer greatly decreases the reversible cell potential for electrolysis. Whereas direct electrolysis of water has a reversible potential of 1.23 Volts at 25°C, the reversible cell potential for SO_2 anode-depolarized electrolysis is only 0.29 Volts in 50% sulfuric acid. When combined with the endothermic decomposition of H_2SO_4, the net thermal efficiency for water-splitting by the HyS process is significantly higher than that for a process consisting of all electric production followed by direct water electrolysis.

A block flow schematic for the HyS process is shown in Figure 1. The HyS process can be thought of as comprising three different sections. The first section includes the electrolyzers and their associated equipment. Next are the sulfuric acid concentration and decomposition operations, which produce water and gaseous mixtures of SO_2 and oxygen. Finally, the need to separate a clean O_2 product stream from the SO_2/O_2 mixture coming from sulfuric acid decomposition, and dissolve the remaining SO_2 in the anolyte, leads to a third flowsheet section where these tasks are accomplished.

The overall net thermal efficiency for the HyS cycle was calculated as 48.8%. The efficiency was based on the higher heating value (HHV) of the hydrogen product divided by the total thermal energy requirements, including the thermal energy used to generate electricity with a 50% heat-to-electric conversion efficiency. The impact of cell potential and SO2 conversion per pass is shown in Figure 2. Higher thermal efficiencies, exceeding 50% HHV-basis, are deemed feasible for plants utilizing increased nuclear reactor outlet temperatures and based on further optimized process flowsheets.

Preliminary estimates for the capital cost and the hydrogen production cost (including O&M requirements, nuclear fuel costs and capital carrying charges) for an Nth-of-a-kind nuclear hydrogen production plant using the HyS process were prepared. The nuclear heat source design and cost prepared for a recent DOE-NE NERI study [4] using General Atomics Modular Helium Reactors and the SI thermochemical cycle were used as a cost comparison basis. Capital costs for the SO_2-depolarized electrolysis subsystem were based on comparisons with comparable PEM systems, and a total subsystem cost of $2000 per square meter of active cell area was used as the baseline. The cost of hydrogen production for the HyS process nuclear hydrogen production plant was determined to be $1.60 per kilogram at the plant gate for the baseline case. The inclusion of by-product credits for oxygen production lowered the hydrogen production cost to $1.31 per kilogram. These costs are less than comparable cost estimates given in Reference 3 for a nuclear plant with an SI thermochemical water-splitting process.

A test facility for testing SO_2-depolarized electrolyzer (SDE) was designed and constructed. The facility was located in a large chemical hood as shown in Figure 3. A 100 lb. cylinder of sulfur dioxide is shown on the left. To the right of it is the SO_2 Absorber. In the upper middle of the picture is the electrolyzer cell. Below it is the anolyte flowmeter, and below that is the anolyte pump. Further to the right is the hydrogen collector. Air flow was maintained whenever hydrogen or sulfur dioxide was present in the hood. The hood was effective, no sulfur dioxide odor leaked out.

The cathode side of the electrolyzer being tested was connected to the hydrogen handling side of the facility. For safety, a pressure relief valve was connected to the hydrogen outlet of the electrolyzer. Downstream of the relief valve was a Backpressure Regulator to demonstrate the ability of the electrolyzer to generate hydrogen at elevated pressures. This is an important capability because this would reduce the cost of compressing the product hydrogen in a production plant. Downstream of the Backpressure Regulator is a three way valve that can direct product hydrogen either directly outside the building or to the Hydrogen Collector for flow measurement. The inner cylinder of the Hydrogen Collection Cylinder was made from glass; an outer cylinder made from acrylic protected the glass cylinder.

Two slightly different SDE's were designed, procured and tested. The first electrolyzer was based on a commercially available PEM water electrolyzer manufactured by Proton Energy Systems, Inc. (PES). The PES electrolyzer, shown in Figure 4, was built with Hastelloy B and Teflon wetted parts, a PEM electrolyte, and porous titanium electrodes. It had an active cell area of 86 cm^2, and a Pt catalyst loading of 4 mg/cm^2. The second electrolyzer was assembled for SRNL by the University of South Carolina (USC). It was constructed with platinized carbon cloth electrodes, a Nafion 115 PEM electrolyte, carbon paper flow fields, and solid graphite back plates. The USC electrolyzer had an active cell area of 40 cm^2 and a Pt catalyst loading of 0.5 mg/cm^2.

Test data under various operating conditions are plotted on polarization curves for both the PES and USC SDE's in Figure 5 and 6, respectively. The project achieved a major accomplishment by demonstrating sulfur dioxide depolarized electrolysis operation in both cells. SDE is evidenced by hydrogen production at the cathode and sulfuric acid production at the anode (witnessed by the absence of oxygen generation) and with cell voltages substantially less than the theoretical reversible voltage for straight water electrolysis (1.23 V). The test results showed cell voltages of less than 0.6 VDC at low current densities at room temperature and near-ambient pressure. The ability to utilize a PEM cell to perform SDE is a major step toward the goal of developing a cost-effective HyS hydrogen production system.

The PES cell was designed for liquid water feed, and it had relatively low fluid flow resistance and good mass transfer characteristics. However, the PES cell failed after a short period of operation due to internal corrosion of the titanium electrodes in the presence of sulfuric acid. The USC cell was constructed of carbon-based components and had excellent corrosion resistance. However, it was a modified design originally based on gaseous reactants, and it had poor mass transfer characteristics when using liquid sulfuric acid feed with dissolved SO_2. This resulted in substantially increased polarization losses at higher current densities. Future work will focus on improved cell designs and operation at higher temperature and pressure. The membranes in both cells permitted the passage of some sulfur dioxide from the anode to the cathode, which reacted with hydrogen gas to form elemental sulfur. However, the sulfur did not appear to poison the cathode electrocatalyst, and it was easily washed out of the cells. Future designs should eliminate of minimize SO_2 crossover, or should be designed to mitigate its effects on long-term cell performance.

Conclusions

- HyS process is a viable thermochemical cycle which can achieve high thermal efficiency and low hydrogen production costs when combined with an advanced nuclear reactor
- SO_2-depolarized electrolysis is the key step in developing the HyS process
- Water electrolysis using PEM-type cell designs has been demonstrated under SO_2-depolarized conditions at low cell voltages (<0.6 VDC)
- Further electrolyzer development is required to improve performance at high current densities by minimizing mass transfer resistance and limiting SO_2 crossover to the cathode
- An integrated laboratory model of the complete HyS cycle, including the electrolyzer and the acid decomposition system, is required to establish closed loop operation

References

1. M.R. Buckner et al., “Conceptual Design for a Hybrid Sulfur Hydrogen Production Plant,” Savannah River National Laboratory Report WSRC-TR-2004-00460, prepared for U.S. Department of Energy under appropriation AF38, National Hydrogen Initiative, April 1, 2005.
2. G.H. Farbman, “The conceptual design of an integrated nuclear-hydrogen production plant using the sulfur cycle water decomposition system”, NASA Contractor Report, NASA-CR-134976, Washington, D.C., April, 1976.
3. G.H. Parker, “Solar thermal hydrogen production process”, Final Report, December, 1982, to US DOE, DOE/ET/20608-1, Westinghouse Electric Corp., Pittsburgh, Pennsylvania, January 21, 1983.
4. W.A. Summers, et al., “Centralized Hydrogen Production from Nuclear Power: Infrastructure Analysis and Test-case Design Study, Interim Report”, NERI Project 02-160, WSRC-TR-2004-00318, Savannah River National Laboratory, July 31, 2004.

FY 2005 Publications/Presentations

1. W. A. Summers, “Hybrid Sulfur Thermochemical Process”, DOE Office of Nuclear Energy, Science and Technology, Semi-annual Program Review, Washington, DC, September 21, 2004 (presentation).
2. M. R. Buckner, “Hybrid Sulfur Thermochemical Process”, DOE Office of Nuclear Energy, Science and Technology, Semi-annual Program Review, Washington, DC, March 10, 2005 (presentation).
3. M. R. Buckner et al, “Conceptual Design for a Hybrid Sulfur Hydrogen Production Plant”, prepared for DOE Office of Nuclear Energy, Science and Technology under appropriation AF38, Nuclear Hydrogen Initiative, Savannah River National Laboratory Report No. WSRC-TR-2004-00460, April 1, 2005.
4. M. B. Gorensek, W. A. Summers and Mr. R. Buckner, “Conceptual Design for a Hybrid Sulfur Thermochemical Hydrogen Process Plant”, AIChE Spring 2005 National Meeting, Atlanta, GA, April 13, 2005.
5. W.A. Summers and M. R. Buckner, “Hybrid Sulfur Thermochemical Process Development – Project PDP45,” proceedings of 2005 DOE Hydrogen Program Review, http://www.hydrogen.energy.gov/, Washington, DC, May 23, 2005.

Special Recognitions & Awards/Patents Issued

1. No patents filed. Three patent disclosures in progress.

Acronyms

DOE	Department of Energy
HHV	Higher heating value
HyS	Hybrid Sulfur Process
MEA	Membrane electrode assembly
NERI	Nuclear Energy Research Initiative
PEM	Proton-exchange-membrane
PES	Proton Energy Systems, Inc.
SDE	SO_2-depolarized electrolyzer
SI	Sulfur Iodine process
SRNL	Savannah River National Laboratory
USC	University of South Carolina

Figure Captions

Figure 1. Block Schematic of Hybrid Sulfur Thermochemical Process
Figure 2. Process Efficiency versus Cell Voltage for HyS Process
Figure 3. SO_2-depolarized Electrolyzer Test Facility
Figure 4. Photograph of PES test electrolyzer (80 cm^2 active cell area)
Figure 5. Polarization curve test results for PES electrolyzer
Figure 6. Polarization curve test results for USC electrolyzer

Figure 1.

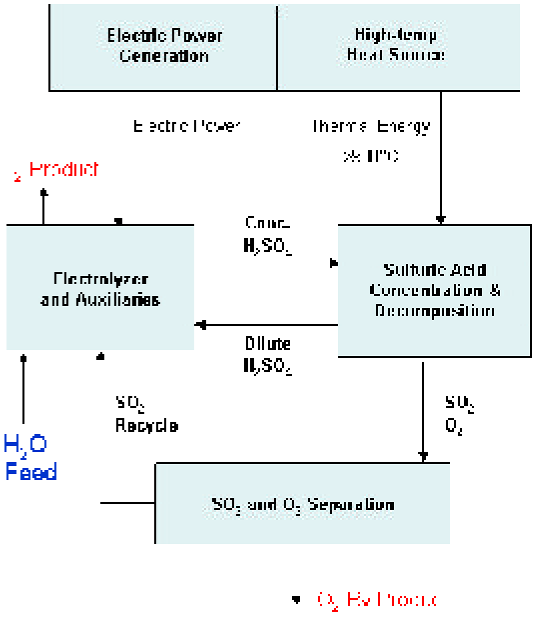

Figure 2.

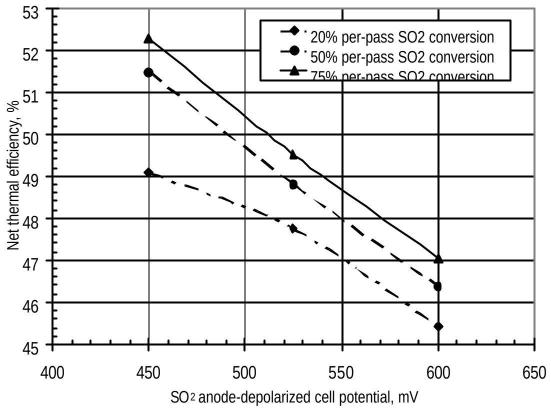

Figure 3.

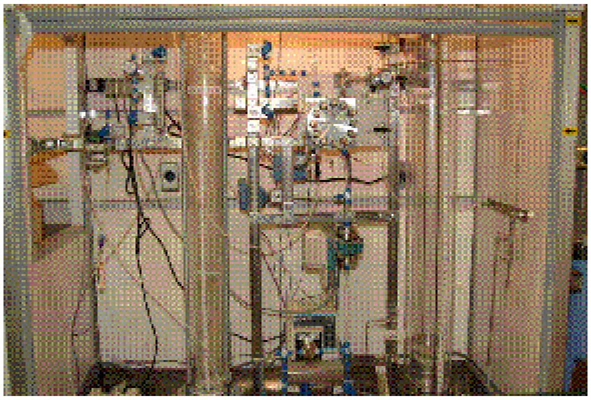

Figure 4.

Figure 5.

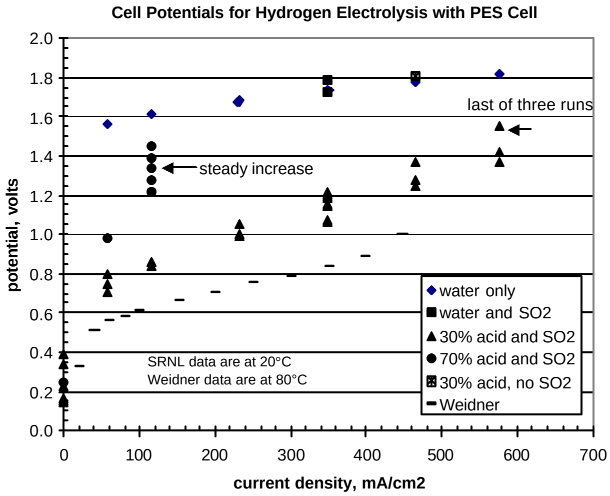

Figure 6.