II.C.3 Electrolyzer Component Development for the HyS Thermochemical Cycle

William A. Summers (Primary Contact), Héctor Colón-Mercado, Maximilian Gorensek, Claudio Corgnale, Mark Elvington
Savannah River National Laboratory (SRNL)
SRS, Building 999-2W
Aiken, SC 29808
Phone: (803) 617-8590
Email: bill.summers@src.energy

DOE Manager
Eric Miller
Phone: (202) 287-5829
Email: Eric.Miller@ee.doe.gov

Subcontractor
Savannah River Consultants, Aiken, SC

Project Start Date: June 1, 2013
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop highly efficient process designs for coupling the hybrid sulfur (HyS) thermochemical process with a concentrated solar energy system
- Demonstrate sulfur dioxide (SO_2)-depolarized electrolysis (SDE) using improved electrocatalysts and high temperature proton exchange membranes that permit high efficiency hydrogen production

Fiscal Year (FY) 2015 Objectives

- Identify and optimize design options for a solar-heated HyS process, including consideration of both thermal energy storage and chemical energy storage
- Perform system design and analysis, develop Aspen Plus™ process flowsheet models, material and energy balances and calculated plant performance and efficiency
- Estimate capital costs for a commercial plant and utilize the Hydrogen Analysis (H2A) tool to determine projected hydrogen production costs for various design and operating scenarios
- Construct and operate a pressurized button cell test facility (PBCTF) capable of testing advanced SDE designs at temperatures up to 120°C and pressures up to 5 bar
- Develop technical solutions to improving the performance, lifetime and cost effectiveness of the SDE, including identification of improved electrocatalysts and characterization of at least three candidate high temperature proton exchange membranes
- Demonstrate high temperature, high pressure SDE operation using advanced membranes with at least a 50 mV improvement over performance with the baseline Nafion® proton exchange membrane

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(T) Coupling Concentrated Solar Energy and Thermochemical Cycles

(W) Materials and Catalyst Development

(X) Chemical Reactor Development and Capital Costs

(AB) Chemical and Thermal Storage

(AC) Solar Receiver and Reactor Interface Development

Technical Targets

This project is conducting system design studies and electrolyzer development and testing in order to improve the performance and lower the capital and operating costs for the HyS thermochemical cycle. Detailed flowsheet analysis and mass and energy balances are used to estimate potential overall system efficiency. Capital cost estimates used in the H2A analysis for hydrogen production costs are based on previous work funded by the DOE Office of Nuclear Energy combined with solar system cost estimates based on goals for the Office of Energy Efficiency & Renewable Energy Solar Program. Electrolyzer performance represents current low temperature (<90°C) operation; higher temperature electrolyzer operation is a goal of the program and is expected to significantly improve electrolyzer efficiency. Table 1 shows how this project contributes to the technical targets of the DOE Fuel Cell Technologies Office for solar-driven high temperature thermochemical hydrogen production.

FY 2015 Accomplishments

Accomplishments during the current project period include:

TABLE 1. Progress towards Meeting Technical Targets for Solar-Driven High Temperature Thermochemical Hydrogen Production

Characteristic	Units	2015 Target	2020 Target	SRNL Status (July 2015)	SRNL 2020 Projections
Solar-Driven Hydrogen Cost	$/kg	14.80	3.70	8.01	3.61
Solar-to-Hydrogen (STH) Energy Conversion Ratio	%	10	20	10.5	19.5
SDE Operating Temperature	°C	120	120	90	120
SDE Voltage at 500 mA/cm^2	mV	720	600	770	600

- Conducted flowsheet analyses and tradeoff studies to identify preferred solar-driven HyS system design configuration
- Completed full Aspen Plus™ flowsheet and overall process efficiency determination for baseline solar-driven HyS process design
- Constructed and commissioned new PBCTF to permit testing of membrane electrode assemblies (MEAs) using advanced high temperature membranes and improved electrocatalysts
- Redesigned and fabricated improved anode flow field for small-scale PBCTF to improve flow distribution and more closely match interdigitated design used in previous larger single cell test facility
- Characterized performance of baseline MEAs with Nafion® membranes
- Utilized DOE H2A tool to estimate hydrogen production cost for solar-driven HyS process for current status (2015) and projected calendar year 2020 conditions

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INTRODUCTION

Thermochemical water splitting processes produce hydrogen by using heat to drive a series of linked chemical reactions that result in water being split into separate hydrogen and oxygen streams with all the intermediate chemicals being recycled. Therefore, the inputs are simply water and heat, and the products are hydrogen and oxygen plus waste heat. Most thermochemical processes use relatively high temperature heat (in excess of 900°C), which can be generated by either high temperature nuclear reactors or concentrated solar energy.

The HyS process is one of the most advanced of the thermochemical water-splitting cycles; each of the major reaction steps has been experimentally validated and detailed system designs have been created. However, further process design work is necessary for use with solar energy, and key technical barriers remain to be overcome. HyS is the only practical two-step thermochemical cycle with all fluid reactants. In the first step sulfuric acid is thermally decomposed at high temperature (>800°C) to produce sulfur dioxide (SO_2) and oxygen. In the second step the SO_2 is used to depolarize the anode of a water electrolyzer, resulting in the production of hydrogen at the cathode and sulfuric acid (which is sent to the decomposer) at the anode. The overall reaction is the splitting of water into H_2 and O_2. The electrolyzer, known as the SDE, requires only about one-third as much electricity as a conventional water electrolyzer.

APPROACH

Much of the previous system design work on the HyS process was based on the use of heat from nuclear reactors, while the current work focuses on the use of solar energy. The key experimental work relates to development of the SDE. SRNL's approach is to build on prior experience gained through development of the nuclear-driven HyS process and to leverage in-house expertise in hydrogen technology and electrochemistry to verify and improve the SDE. The project is divided into two main tasks: (1) System Design and Analysis and (2) Electrolyzer Development and Testing. The goals of Task 1 are to utilize modelling and flowsheet analyses to develop efficient and cost effective HyS plant designs based on the use of concentrated solar power. Both direct and indirect solar heating of the high temperature acid decomposition step will be analyzed in addition to the use of both thermal energy storage and chemical energy storage. The focus of the research on the SDE is to improve performance by developing better electrocatalysts and increasing the cell's operating temperature from the 70–90°C range to 120–130°C. The higher temperature requires replacing the baseline Nafion® proton exchange membrane with new high temperature membranes. A new PBCTF will be built to permit the higher temperature testing and to facilitate rapid characterization of membrane candidates.

RESULTS

Several alternative configurations for the solar HyS flowsheet were studied. These included the following options:

- Gaseous-fed or liquid-fed electrolyzer
- Continuous or diurnal operation
- Thermal versus chemical energy storage
- Use of a secondary heat transfer fluid for the acid decomposer
- Integrated or separate operation of process sections (electrolysis and acid decomposition).

In addition, three different design options were selected for the solar receiver as follows:

- Falling particle receiver
  - Uses heated “sand” for thermal energy storage
  - Allows for continuous 24 h acid decomposition operation
- Cavity receiver with tubular heat exchanger
  - Secondary heat transfer fluid (e.g., He) heated in receiver
  - Daytime acid system operation combined with chemical energy storage
- Direct solar-heated acid vaporizer and decomposer
  - Daytime acid system operation combined with chemical energy storage.

The SO_2-depolarized electrolyzer can be operated with anode feed consisting of either vapor (SO_2 and H_2O) or liquid (SO_2 dissolved in sulfuric acid); both result in liquid H_2SO_4 anode product. Previous testing showed similar SDE performance for the two options, but they require different flowsheet designs to close the cycle and integrate the SDE with the solar acid decomposer. Extensive flowsheet analysis and trade studies were conducted to evaluate the two approaches, resulting in the conclusion that the liquid feed SDE approach is preferred.

An Aspen Plus™ flowsheet for the baseline system design using the Falling Particle Receiver, thermal energy storage and a liquid-fed electrolyzer was completed. Mass and energy balances were calculated and utilized to determine process efficiency. The overall STH conversion ratio for near-term design conditions was 10.5%; the 2020 STH was 19.5%. Efficiency assumptions are shown in Table 2. Additional improvements in the process flowsheet and the SDE performance are expected to result in the long-term STH exceeding the DOE goal of 20.0%. Hydrogen production cost estimates using the DOE H2A program resulted in near-term (2015) costs of $8.01 per kilogram and year 2020 costs of $3.61 per kilogram, exceeding DOE goals.

TABLE 2. Baseline Solar HyS Performance Summary

Plant Section	2015 Status	2020 Projections
Heliostat Field Efficiency	45%	55%
Solar Receiver Efficiency	85%	90%
Thermal Energy Storage Efficiency	95%	95%
Solar Electric Generation Efficiency	15%	22%
SDE Electrolyzer Voltage	770 mV	600 mV
Thermal Input to Acid Decomposition (from Aspen Plus™ Flowsheet)	477 kJ/mol	342 kJ/mol
Solar Input to Field for Heat	1,247 kJ/mol	691 kJ/mol
Solar Input for Electricity	1,049 kJ/mol	548 kJ/mol
Solar-to-Hydrogen Conversion Ratio	**10.5%**	**19.5%**

Accomplishments for Task 2, Electrolyzer Development and Testing, included the final assembly and commissioning of the PBCTF, fabrication and testing of MEAs, procurement of samples of several high temperature membranes, and redesign of the PBCTF electrolyzer, including a new flow field. Figure 1 shows the completed PBCTF. Membrane electrode assemblies for initial testing in the PBCTF were prepared using a Nafion® 115 proton exchange membrane,

FIGURE 1. Photograph of pressurized button cell test facility

with Tanaka Kikinzoku Kogyo Company (TKK) platinized carbon electrocatalyst for both the anode and cathode. These MEAs were used to determine the baseline SDE performance, with temperatures up to 90°C, the limit of both the Nafion® membrane and the current anolyte feed pump. A new anolyte pump, capable of operation up to 130°C and 10 bar, was received and will be installed for later high temperature cell testing.

Initial MEA testing indicated a problem with the introduction of anolyte feed (SO_2 saturated sulfuric acid) into the small (2 cm^2) circular button cell, resulting in a large pressure drop and poor flow distribution. Extensive SDE testing had been performed previously using larger (60 cm^2) rectangular MEAs with a linear interdigitated flow field. A new flow field was designed and fabricated for the PBCTF, resulting in improved performance similar to that of the larger, rectangular electrolysis cell. Test results are shown in Figure 2. The tests were performed in water and in 30 wt% sulfuric acid. The data was collected at temperatures between 60ºC and 90ºC. As it can be observed, the performance improves as a function of temperature. This result is expected since the kinetic overpotential loss is reduced as temperature (and the resulting reaction rate) is increased. This result is paramount in utilizing advanced high temperature membranes, since operating at elevated temperature necessitates the use of non-Nafion®-based proton exchange membranes. At temperatures above 80°C, Nafion® begins to dehydrate and its mechanical properties are reduced. This significantly lowers the ionic conductivity, rendering it impractical for efficient SDE use. Therefore, alternative high temperature membranes have been selected for potential application in the HyS electrolyzer. These membranes are required to have a combination of good chemical stability

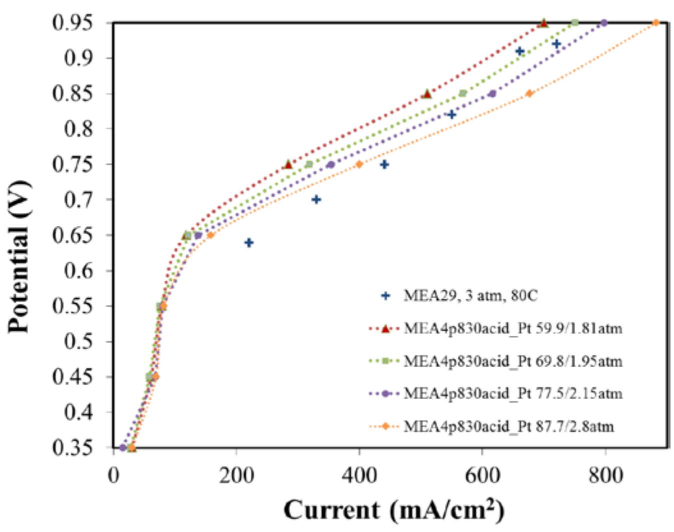

FIGURE 2. Electrolyzer performance for MEAs with Nafion® membranes in 30 wt% acid at various temperatures. MEA29 corresponds to previous large-scale test performance.

(resistant to H_2SO_4 corrosion), high ionic conductivity at high temperature (>120°C), and low SO_2 flux. Advanced membranes for testing include: sulfonated-diels-alder-poly-phenylene Sandia National Laboratories, sulfonated perfluorocyclobutyl aryl ether block copolymer (BPVE-6F, Clemson University), and a new generation of H_2SO_4-doped polybenzimidazole University of South Carolina and BASF. Future work will include testing these next generation MEAs at temperatures up to 130ºC.

CONCLUSIONS AND FUTURE DIRECTIONS

Work this year has resulted in the following conclusions:

- The baseline solar HyS design meets DOE's goals for hydrogen production cost and solar-to-hydrogen conversion ratio.
- The baseline system design consists of the falling particle receiver, thermal energy storage, a liquid-fed SDE, and continuous (24/7) hydrogen production.
- The PBCTF with the modified flow field provides performance consistent with previous larger-scale tests and can be used to establish the baseline Nafion® performance.
- SDE performance improves with increasing temperature; new high temperature proton exchange membranes are necessary for tests above 90°C.

Future work will include the following:

- Completion of trade studies for the remaining receiver designs and process design options
- Updating of capital and operating costs for the baseline system design and preparation of a final hydrogen production cost estimate using the H2A program
- Modelling of the acid decomposition reactor based on the "bayonet" design concept
- Fabrication and testing of MEAs with at least three high temperature membranes and various electrocatalyst compositions in the PBCTF at 70–90°C
- Upgrading the PBCTF with the installation of the high temperature anolyte pump, followed by MEA testing at temperatures of 120–130°C
- Demonstration of MEA performance that exceeds the Nafion® baseline performance by ≥50 mV at a current density of 500 mA/cm^2.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. William A. Summers, Maximilian Gorensek, and Hector Colon-Mercado, "Electrolyzer Component Development for the HyS Thermochemical Cycle, Project PD096," DOE EERE Fuel Cell Technologies Office, 2015 Annual Merit Review and Peer Evaluation, Arlington, VA, June 8–15, 2015.