

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

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Technical Barriers

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

- (S) High-Temperature Robust Material
- (T) Coupling Concentrated Solar Energy and Thermochemical Cycles
- (U) Concentrated Solar Energy Capital Cost
- (W) Materials and Catalysts Development
- (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 and Renewable Energy's (EERE) Solar Program. Electrolyzer performance projections represent current estimates of performance based on extrapolations to cell operation at 130°C. Heliostat capital cost and solar-to-electric conversion efficiency are consistent with the current viewpoint of the EERE Solar Program.

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

Characteristic	Units	2015 Target	SRNL 2015 Projections	2020 Targets	SRNL 2020 Projections
Solar-Driven Hydrogen Cost	\$/kg	14.80	7.58	3.70	3.52
Solar-to-Hydrogen (STH) Energy Conversion Ratio	%	10	15.6	20	19.1
Heliostat Capital Cost	\$/m ²	140	140	75	75
Solar-to-Electric Efficiency	%	---	20.6	---	25

Overall Objectives

- Develop highly efficient process designs for coupling the Hybrid Sulfur (HyS) thermochemical process with a concentrated solar energy system capable of achieving a hydrogen cost at the plant gate of <\$2 per kilogram of H₂.
- Demonstrate SO₂-depolarized electrolysis (SDE) using improved electrocatalysts and high temperature proton exchange membranes (PEMs) that permit high efficiency hydrogen production.

Fiscal Year (FY) 2016 Objectives

- Analyze and select a baseline plant design that utilizes high-temperature solar heating, energy storage and permits 24-hour hydrogen production.
- Develop Aspen Plus™ process flowsheet models, calculate plant performance and efficiency.
- Estimate capital and operating and maintenance (O&M) costs for a commercial plant and utilize the H2A analysis tool to determine projected hydrogen production costs for 2015 and 2020 design concepts.
- Utilize the Pressurized Button Cell Test Facility (PBCTF) to test candidate high-temperature PEMs and demonstrate SDE performance improvements of 80 mV over performance with the baseline Nafion® PEM.

FY 2016 Accomplishments

- Conducted flowsheet analyses and tradeoff studies to identify preferred solar-driven HyS system design configurations and selected a baseline solar HyS plant design.
- Completed full Aspen Plus flowsheet and overall process efficiency determination including pinch point analysis and design of heat exchange network.
- Utilized DOE H2A analysis tool to estimate hydrogen production cost for solar-driven HyS process for current status (2015) and projected Calendar Year (CY) 2020 conditions.
- Identified several high temperature PEMs and characterized them in the PBCTF.
- Achieved FY 2015 go/no-go criteria of >50 mV improvement in SDE voltage versus baseline Nafion membranes.



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. Hybrid thermochemical cycles have an electrochemical step in the process, and therefore require some electricity input in addition to the thermal input. 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, much of the previous development work was based on the idea that the heat would be provided from a high temperature nuclear reactor operating continuously. Therefore, new designs are necessary to accommodate the use of solar energy, which requires either intermittent operation or a means of energy storage. 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 (SO₂) and oxygen. In the second step the SO₂ 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 H₂ and O₂. The electrolyzer, known as the SDE, requires only about one-third as much electricity as a conventional water electrolyzer.

APPROACH

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. Task 2 involves experimental work relating to the development of the SDE, the key reaction step in the process. The focus of the research is to improve performance by developing better electrocatalysts and PEMs while increasing the cell's operating temperature from the 70–90°C range to 120–130°C. A new PBCTF was built in 2015 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
- Direct or indirect heating of the acid decomposer
- Integrated or separate operation of process sections (electrolysis and acid decomposition)

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

- Falling particle receiver (FPR) (uses heated “sand” for thermal energy storage)
- Cavity receiver to heat helium (requires chemical energy storage)
- Direct solar-heated acid vaporizer and decomposer (requires chemical energy storage)

Tradeoff studies resulted in the selection of a baseline conceptual design consisting of a liquid-fed electrolyzer, an indirectly heated acid decomposition reactor, thermal energy storage, and a solar receiver based on the FPR concept being developed by Sandia National Laboratories. The use of heated sand to provide high temperature thermal energy storage permits continuous, 24-hour operation of the complete HyS plant. A diagram of the FPR is shown in Figure 1.

Aspen Plus flowsheets were completed and mass and energy balances were calculated in order to determine the process efficiency. The performance of the solar portion of the plant was based on assumptions from the EERE Solar Program. The overall solar-to-hydrogen (STH) conversion ratio for the CY 2020 design was estimated to be 19.1%.

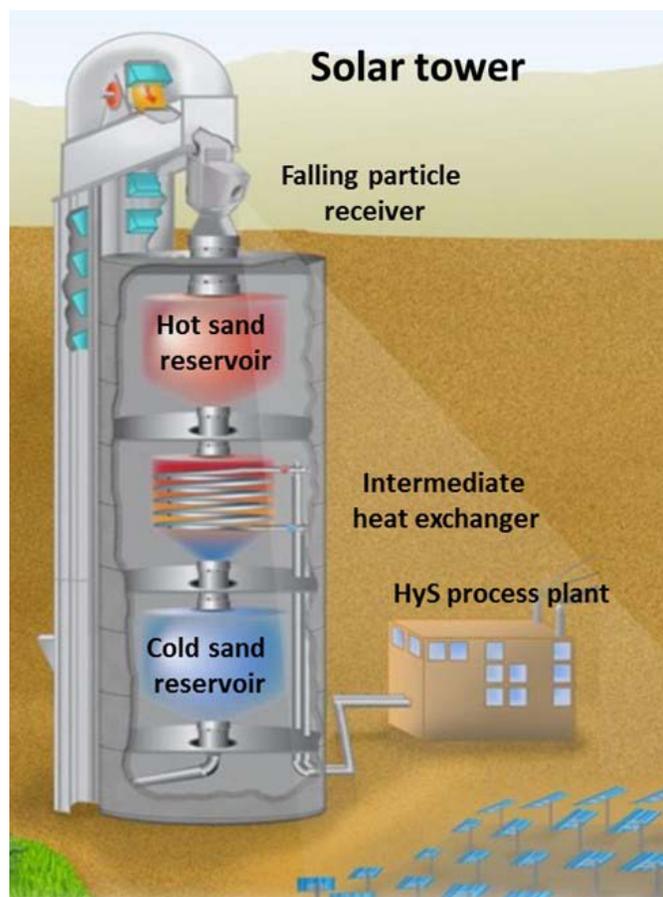


FIGURE 1. Diagram of the falling particle receiver

Hydrogen production cost estimates using the DOE H2A program resulted in a projected cost for CY 2020 of \$3.52/kg, exceeding DOE goals. A breakdown of the production cost estimate is shown in Figure 2. Electricity costs assumed solar-generated electricity at 6¢/kWhr.

Electrolyzer development included the fabrication and testing of membrane electrode assemblies (MEAs) in the PBCTF. MEAs consisting of a Nafion 115 PEM, with Tanaka Kikinzoku Kogyo platinumized carbon electrocatalyst for both the anode and cathode, were used to determine the baseline SDE performance. Tests were performed at temperatures between 60°C and 90°C in water and in 30 wt% sulfuric acid. As expected, it was observed that the performance improves as a function of temperature, primarily as a result of increased reaction rate and a corresponding reduction in the kinetic overpotential at the anode. This result is paramount in utilizing advanced high temperature membranes, since operating at elevated temperature necessitates the use of non-Nafion based PEMs. Several alternative high temperature membranes were selected for potential application in the HyS electrolyzer. These membranes are required to have a combination of good chemical stability (resistant to H₂SO₄ corrosion), high ionic conductivity at high temperature

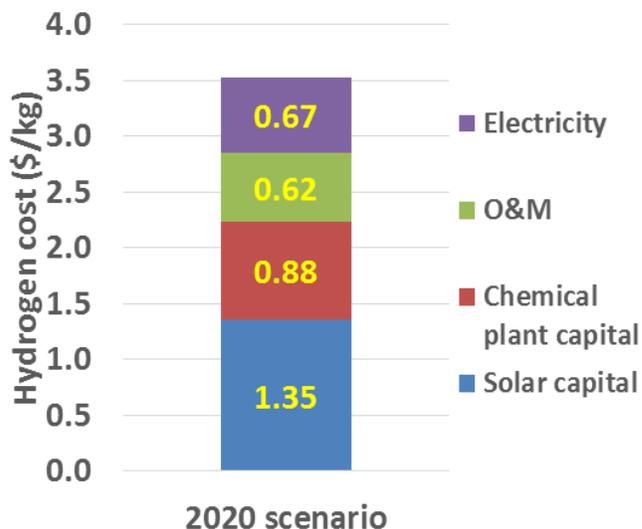


FIGURE 2. Cost breakdown for the 2020 solar HyS plant

(>120°C), and low SO₂ flux. Tests were conducted using a sulfonated-diels-alder-poly-phenylene membrane from Sandia National Laboratories. Testing at 91°C showed a 50 mV improvement over the baseline Nafion MEA, which met the project's FY 2015 go/no-go criteria. Deconvolution of the data indicated the potential for >150 mV improvement at 130°C. High temperature testing to verify this result is ongoing. The goal is to demonstrate stable SDE performance of 600 mV at a current density of 500 mA/cm².

CONCLUSIONS AND FUTURE DIRECTIONS

Work this year has resulted in the following conclusions:

- A solar HyS design, based on detailed modeling and equipment sizing and costing, has the potential to meet DOE's goals for hydrogen production cost and STH conversion ratio.
- The baseline system design consists of the FPR, thermal energy storage, an indirectly heated acid decomposer, a liquid-fed SDE and continuous (24/7) hydrogen production.
- SDE performance improves with increasing temperature; new high temperature PEMs are necessary for tests above 90°C; operation at ≥130°C is projected to meet SDE performance targets.

Future work (not currently funded) should include the following:

- Updating the process design and H2A analysis for an ultimate plant design meeting the DOE hydrogen production cost goal of <\$2/kg H₂.
- Modelling and testing of the "bayonet" acid decomposition reactor.

- Fabrication of MEAs with high temperature membranes and various electrocatalyst compositions and testing in the PBCTF at >130°C for up to 1,000 hr.
- Construction and testing of an integrated HyS process at laboratory scale.
- Integrated testing of the acid decomposition system with a FPR.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. William A. Summers, Maximilian Gorenssek, Hector Colon-Mercado, Claudio Corgnale and Mark Elvington, "Electrolyzer Component Development for the HyS Thermochemical Cycle, Project PD096," DOE EERE Fuel Cell Technologies Office, 2016 Annual Merit Review and Peer Evaluation, Washington, D.C., June 8, 2016.