II.B.5 Electrolyzer Development for the HyS Thermochemical Cycle

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

Overall Objectives

- Identify and quantify anode electrocatalysts and advanced proton-exchange membranes to improve the performance and lower the capital and operating costs for the electrolysis step of the Hybrid Sulfur (HyS) thermochemical water-splitting process
- Demonstrate electrolyzer operation at elevated temperature and pressure up to 140°C and 2 MPa
- Improve electrolyzer efficiency to achieve 600 mV cell potential at high current density

Fiscal Year (FY) 2013 Objectives

- Complete integration of major components into the Pressurized Button Cell Test Facility
- Identify and screen electrocatalysts with the potential to reduce oxidation overpotential by >20 mV versus the state-of-the-art platinum catalyst
- Characterize three or more anode catalysts in conditions of sulfur dioxide saturated solutions of 30-50 wt% H_2SO_4

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 (RD&D) Plan:

(T) Coupling Concentrated Solar Energy and Thermochemical Cycles

(W) Materials and Catalysts Development

(X) Chemical Reactor Development and Capital Costs

Technical Targets

This project is conducting studies to improve the performance and lower the capital and operating costs for the electrolysis step of the HyS thermochemical cycle. Insights gained from these studies will be applied toward the design and demonstration of a solar-driven HyS thermochemical cycle that meets the following DOE 2020 hydrogen production targets for high-temperature, solar-driven, thermochemical processes as given in Table 3.1.7 of the Multi-Year RD&D Plan:

- Hydrogen Cost: $3.70/kg
- Solar to Hydrogen Energy Conversion Ratio: 20%

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APPROACH

The DOE is supporting research to verify the potential for solar thermochemical (STCH) cycles for hydrogen production to be competitive in the long-term and by 2020 to develop this technology to produce hydrogen with a projected cost of $3.70/gasoline gallon equivalent at the plant gate. The HyS process is a promising sulfur-based STCH cycle that depends on a simple, two-step chemical process with all fluid reactants. It contains a low-energy electrolysis step, making it a thermo/electrochemical hybrid process. In this process, sulfuric acid (H_2SO_4) is thermally decomposed by solar energy at high temperature (>800°C), producing SO_2, O_2, and steam. Sulfuric acid saturated with SO_2 is then pumped into a sulfur dioxide-depolarized electrolyzer (SDE) that electrochemically oxidizes sulfur dioxide with water to form sulfuric acid at the anode and reduces protons to form hydrogen at the cathode. The reversible cell potential for this electrochemical process is -0.158 V (standard hydrogen electrode) versus -1.229 V (standard hydrogen electrode) for low-temperature water electrolysis [1]. The overall electrochemical reaction consists of the production of H_2SO_4 and H_2, while the entire cycle produces H_2 and O_2 from H_2O with no side products.

The SDE is the major developmental technology in this cycle, and the objective of the research is to identify, develop, and demonstrate new SDE components to improve the efficiency and lower the costs of this key step. The focus of the research is on the anode electrocatalyst and the proton exchange membrane. New research has shown that Pt alloys with transition metals, gold, and gold alloys can decrease the overpotential for the SO_2 oxidation reaction [2]. Another major goal of the research is to develop membranes that can operate at elevated temperature and pressure (140°C and 2 MPa) for extended periods without degradation of

performance. Higher-temperature operation is expected to reduce kinetic polarization losses at the anode and permit the use of advanced membranes (versus Nafion®). Previous low-temperature results indicate that the advanced membranes can also reduce the crossover of SO_2 through the membrane to the cathode, thereby eliminating or minimizing elemental sulfur formation that can reduce cell performance and operating lifetime.

ACCOMPLISHMENTS

This project was initiated in June 2013. Accomplishments to date include:

- Identified tantalum-coated parts as a more cost-effective alternative instead of custom-made zirconium fittings for construction of the metal parts of the Pressurized Button Cell Test Facility.
- Began modification of the original piping and instrumentation diagram from earlier large-scale testing to accommodate the changes in size and type of parts to be used in the Pressurized Button Cell Test Facility and to permit operating conditions up to 130°C and 1 MPa.
- Identified candidate anode electrocatalysts, including Pt, Au, PtAu, PtAg, PtPd, AuPd, AuAg, PtCr, and AuCr, that have potential to reduce anode polarization by greater than 100 mV versus state-of-art Pt catalyst. All chemicals and materials were purchased and received.

FUTURE DIRECTIONS

- Complete design, procurement of parts, and construction of Pressurized Button Cell Test Facility
- Integrate all major components into the Pressurized Button Cell Test Facility with the capability to increase operating conditions up to 130°C and 1 MPa
- Initiate testing of advanced, high-temperature membrane electrode assemblies
- Prepare and sputter catalysts on substrates and test activity on model solutions

REFERENCES

1. Gorensek, M.B.; Staser, J.A.; Stanford, T.G.; Weidner, J.W., A thermodynamic analysis of the SO2/H2SO4 system in SO2-depolarized electrolysis. *International Journal of Hydrogen Energy* **2009,** *34* (15), 6089-6095.

2. O'Brien, J.A.; Chemistry, U. o. N. S. o., *Solar Hydrogen: A Fundamental and Applied Electrochemical Investigation of the Hybrid Sulfur Cycle Electrolyser*. University of Newcastle: 2011.