

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

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Project End Date: Project continuation and direction determined annually by DOE

- (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%

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 current density of 500 mA/cm² or higher

Fiscal Year (FY) 2014 Objectives

- Complete integration of major components into the Pressurized Button Cell Test Facility (PBCTF) that will ultimately allow testing of catalysts and membranes at pressures up to 1 MPa and temperatures of 130°C. Major components include anolyte tank, electrolyzer cell, hydrogen storage tank, and anolyte pump.
- 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% H₂SO₄.

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:

FY 2014 Accomplishments

- Identified and purchased tantalum-coated parts as a more cost-effective alternative instead of custom-made zirconium fittings for construction of the metal parts of the PBCTF.
- Finished modification of the original piping and instrumentation diagram as well as finished construction of the set-up from earlier large-scale testing to accommodate the changes in size and type of parts to be used in the PBCTF.
- Finished construction and integration of all components.
- Tested thin-film electrodes as candidate anode electrocatalysts, including Pt, Pd, Ir, Au, PtAu, and PtV. Au, PtAu and PtV showed 28 mV, 46 mV, and 13 mV reduction, respectively, on the anode polarization versus state-of-the-art Pt catalyst.



INTRODUCTION

Solar thermochemical hydrogen (STCH) cycles have the potential to produce hydrogen at competitive costs. The DOE is supporting research on STCH cycles for hydrogen production that can be competitive in the long-term and by 2020 be developed 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 ($>800^\circ\text{C}$), 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, SHE) versus -1.229 V (SHE) 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 high-temperature 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.

APPROACH

There are two main approaches that were studied for performance improvements on the SDE: anode electrocatalysts and expanded operating conditions (operating temperatures up to 130°C and pressures up to 1 MPa). Electrocatalyst anode materials that can provide higher activity for the SO_2 oxidation were investigated. Materials are expected to provide similar amount of corrosion resistance as state-of-the-art Pt electrocatalysts, while increasing the kinetic current at comparable operating potentials. This approach will not only improve the overall performance of the PBCTF system, but will also reduce the amount of precious metals used in the SDE.

Operation at expanded operating conditions will allow the system to operate at a higher efficiency by reducing kinetic and ionic/mass transfer losses. The system is being redesigned for operation at higher temperatures and pressures in order to get baseline performance of state-of-the-art materials (i.e., catalysts consisting of Pt/C and

Nafion[®] membranes) at different operating conditions. This information will be useful for establishing and making performance comparisons when using next-generation membranes and electrocatalysts.

RESULTS

Depending on the operating conditions, around 70% of the losses in efficiency in the electrolyzer arise from the kinetic losses associated with the anode electrode. Improvements in anode performance are being sought as a way to improve overall electrochemical performance of the electrolyzer. Over the past, the SDE research has been focused on Pt electrocatalysts. However, new research has shown that Pt alloys with transition metals, Au, and Au alloys can decrease the overpotential for the SO_2 oxidation reaction [2]. Catalytic thin films were prepared by sputter deposition on corrosion-resistant coupons for the materials of interest (Pt, Au, Pd, Ir, etc.) and were evaluated in sulfur-dioxide-saturated sulfuric acid solutions. Figure 1 shows the typical Tafel plots for the electrolysis of SO_2 by Pt. As observed in Figure 1, the performance consists of two curved lines coming together to form a point. The top curved line gives an indication of the reaction rate far from equilibrium potentials. This top curved line is representative of the current region where the electrolyzer will be operated. In other words, a shift to the lower right side of the plot will indicate significant improvement in the electrocatalyst performance that will translate to higher plant efficiency. The shaded area under the dashed lines indicates the milestone target of $\geq 20\text{ mV}$ performance improvement over un-modified Pt catalysts. The performance of the catalysts tested away from equilibrium conditions is plotted in Figure 2 at the current

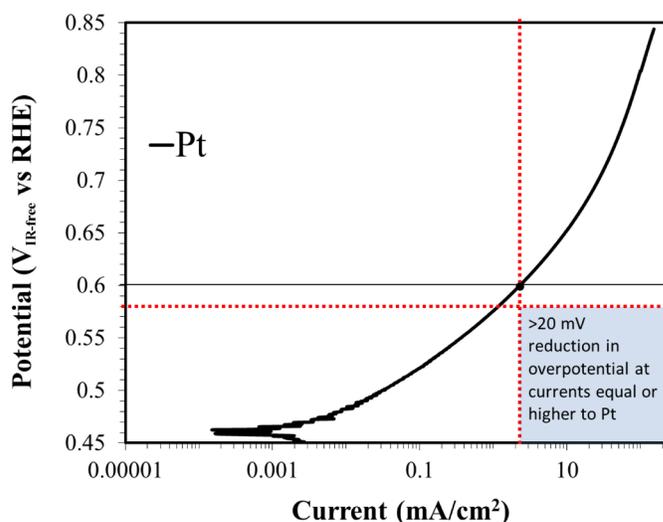


FIGURE 1. Typical consecutive Tafel plots for the electrolysis of SO_2 by Pt. Test performed in SO_2 saturated with 30 wt% sulfuric acid at room temperature. Shaded area indicates FY 2013 milestone performance target.

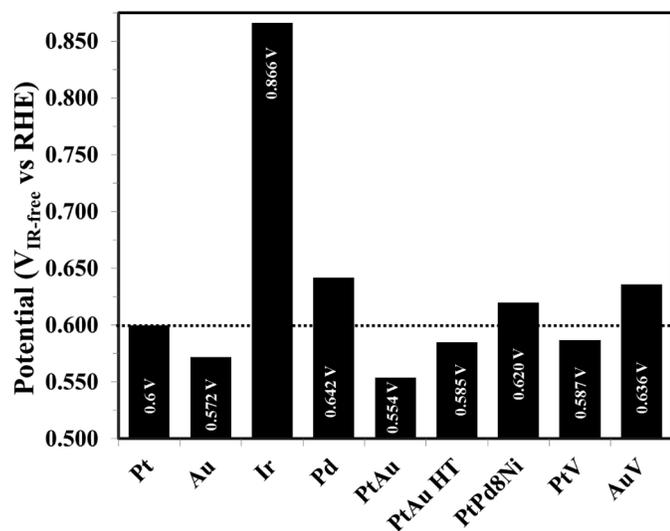


FIGURE 2. Operation Potential of the Different Catalysts Working at the Current Density of Pt Operated at 600 mV

density 2.3 mA/cm^2 . The use of Au or the addition of Au or V to the Pt catalysts decreases the operational voltage (better performance). The catalysts with performance better than Pt (0.6 V or lower voltage): are observed by PtAu alloy (0.554 V) > Au (0.572 V) > PtAu-HT (0.587 V) > PtV (0.587 V).

In addition to improvements in catalyst activity, operation of the electrolyzer at higher temperatures and pressures will facilitate the kinetics and mass transfer and allow the use of high-temperature membranes, and, therefore, will improve overall performance. Fabrication of the PBCTF will facilitate the testing of anode electrocatalysts and high-temperature membranes at improved SDE-relevant conditions. Because of the corrosive nature of the sulfuric acid, specialty instruments and materials need to be used. Previous experience has indicated that metals such as zirconium and tantalum can provide both mechanical and chemical resistance. Polymer use is limited to uses such as liners due to the operating temperatures and pressures. Design, procurement, and fabrication were completed. Major fabrication items include the SO_2 acid anolyte tank and the electrochemical cell. All metal-wetted parts of the anolyte tank are made of Zircalloy, while the wetted parts of the electrochemical cell are made of graphite and fluoro-polymers. To integrate all the different components, tantalum-wetted fittings were used. Figure 3 shows the complete integration of all the components. With the setup completed, baseline performance of state-of-the-art materials, such as Nafion[®] and platinumized carbon, will be assessed followed by testing of the advanced materials.

CONCLUSIONS AND FUTURE DIRECTIONS

- Identified and procured tantalum-coated parts as a more cost-effective alternative instead of custom-made

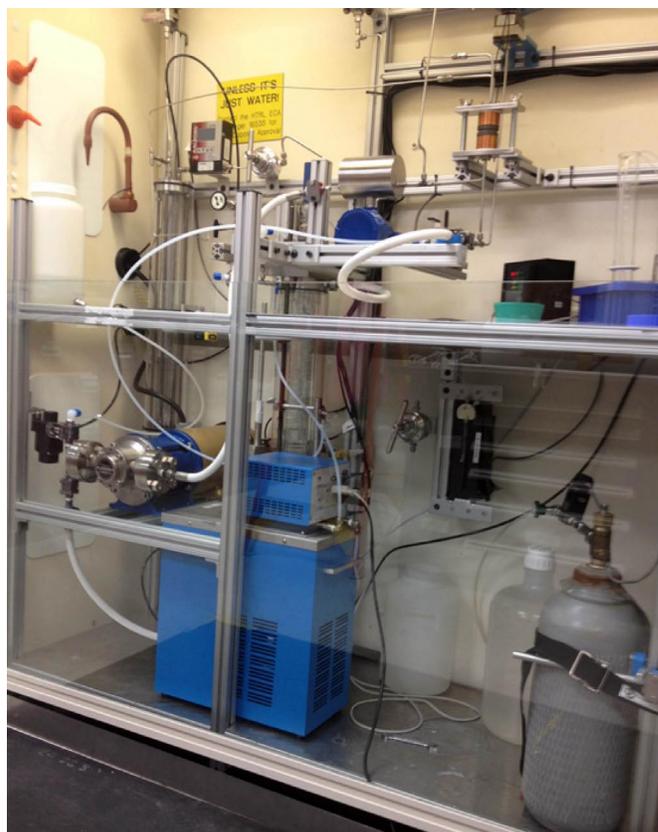


FIGURE 3. Photograph of Completed System

zirconium fittings for construction of the metal parts of the PBCTF.

- Finished modification of the original piping and instrumentation diagram as well as finished fabrication of parts to be used in the PBCTF.
- Finished construction and integration of all components.
- Tested thin-film electrodes as candidate anode electrocatalysts, including Pt, Pd, Ir, Au, PtAu, and PtV. Au, PtAu, and PtV showed 28 mV, 46 mV, and 13 mV reduction on the anode polarization, respectively, versus state-of-the-art Pt catalyst.
- Future work will establish baseline performance of state-of-the-art materials and start studying the performance of new high-temperature membranes.

REFERENCES

- Gorensek, M.B.; Staser, J.A.; Stanford, T.G.; Weidner, J.W., A thermodynamic analysis of the $\text{SO}_2/\text{H}_2\text{SO}_4$ system in SO_2 -depolarized electrolysis. *International Journal of Hydrogen Energy* 2009, 34 (15), 6089-6095.
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