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Disclaimer:

Hybrid Thermochemical Hydrogen Production

There exists a significant and growing need for clean, efficient, and large-scale hydrogen production. Using high temperature heat, thermochemical cycles can provide an energy-efficient route for hydrogen production. The Hybrid Sulfur process is a promising thermochemical water-splitting cycle with global-scale hydrogen production potential. The SO_2-depolarized electrolyzer is a critical component of the cycle. At the core of the electrolyzer is the membrane-electrode assembly, which consists of a solid electrolyte membrane sandwiched between two electrocatalyst layers. New electrocatalyst and membrane materials are being developed with the goals of improving the electrolyzer performance and extending the lifetime of the membrane-electrode assembly. A high-throughput methodology is being developed to screen potential candidates based on Pt and Au thin films prepared through physical vapor deposition. SO_2 oxidation reaction kinetics are being analyzed for the novel catalysts and compared to the state-of-the-art, Pt/C. In addition, advanced polymer electrolyte membranes of polybenzimidazole (PBI) will be utilized, which have shown superior performance in comparison to the state-of-the-art, Nafion®. These catalysts and membranes will be combined to produce high performance membrane-electrode assemblies.

Awards and Recognition

DOE-EERE CRADA awarded

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature **Date**

Hybrid Thermochemical Hydrogen Production

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Thrust Area:
Clean Energy

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The Hybrid Sulfur (HyS) process is a promising thermochemical water-splitting cycle with global scale hydrogen production potential. The SO_2-depolarized electrolyzer (SDE) is a critical component of the cycle. At the core of the SDE is the membrane-electrode assembly (MEA), which consists of a polymer electrolyte membrane (PEM) sandwiched between two electrocatalyst layers. New electrocatalyst and membrane materials are being developed with the goals of improving the electrolyzer performance and extending the lifetime of the MEA. A high-throughput methodology is being developed to screen potential candidates based on Pt and Au thin films prepared through physical vapor deposition. SO_2 oxidation reaction kinetics are being analyzed for the novel catalysts and compared to the state-of-the-art, Pt/C. In addition, advanced polymer electrolyte membranes of polybenzimidazole (PBI) will be utilized, which have shown superior performance in comparison to the state-of-the-art, Nafion®. These catalysts and membranes will be combined to produce high performance MEAs.

FY2018 Objectives

- Electrocatalyst Development
  - Develop High-throughput catalyst screening methodology
  - Develop carbon-supported catalysts
- Membrane Development
  - Develop optimized membranes
  - Membrane testing
- Electrolyzer Performance Evaluation
  - Membrane electrode assembly fabrication
  - Modification of test station
  - Evaluate material performance in electrolyzer

Introduction

There exists a significant and growing need for clean, efficient, and large-scale hydrogen production. Using high temperature heat, thermochemical cycles can provide an energy-efficient route for hydrogen production. The HyS process is a promising thermochemical water-splitting cycle with significant

scalability. The HyS process, one of the most researched thermochemical cycles, is a sulfur-based water-splitting cycle which contains a low temperature electrolysis step, and thus can be considered an electrochemical and thermochemical hybrid process. In the HyS process, H_2SO_4 is thermally decomposed at high temperature (> 600 °C), producing SO_2 [r1]. SO_2 and H_2O enter the SDE where SO_2 is oxidized to form H_2SO_4 and H^+ at the anode [r2], while at the cathode, H^+ is reduced to form H_2 [r3]. The overall electrochemical reaction consists of the production of H_2SO_4 and H_2 [r4], while the entire cycle produces H_2 and O_2 from H_2O with no side products [r5]. Figure 1 shows a simplified schematic of the overall process and the main chemical reactions taking place.

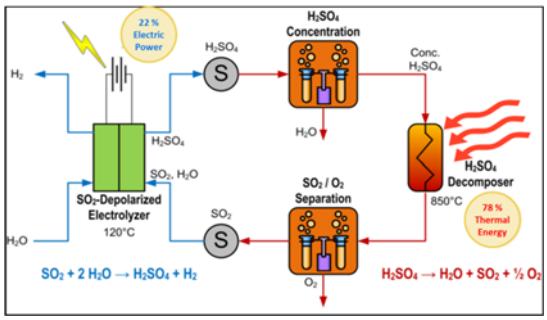

Figure 1. Simplified schematic of the HyS

$H_2SO_4 \rightarrow SO_2 + \frac{1}{2}O_2 + H_2O$ Thermochemical Step [r1]

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$ Anode Electrochemical Step [r2]

$2H^+ + 2e^- \rightarrow H_2$ Cathode Electrochemical Step [r3]

$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$ Overall Electrochemical Step [r4]

$2H_2O \rightarrow 2H_2 + O_2$ Cycle Process Reaction [r5]

The electrolysis step must be maintained at the highest possible conversion fraction to minimize unreacted SO_2 and obtain high H_2SO_4 concentration. Unreacted SO_2 must be recycled, and water must be removed prior to the high temperature decomposition step. Both of these are energy intensive steps and must be minimized to keep process efficiency high. Operation of the electrolyzer at the target conditions, however, is unfeasible using the current state-of-the-art materials. Therefore, new materials will be required to achieve the electrolysis performance goals. This project is focused on the development of new electrocatalysts and membranes and their effect on process efficiency, with the goals of improving the electrolyzer performance and extending the lifetime of the MEA.

Approach

A collaborative effort between SRNL and USC was initiated to develop novel materials designed to operate under the HyS process conditions with superior performance compared to the state-of-the-art. SRNL is utilizing its expertise in catalyst development and screening, along with USC's expertise in membrane development and gas anolyte stream HyS operation, in order to achieve improvements in the HyS and meet DOE-EERE's hydrogen production goals. The work is being carried out in three main tasks.

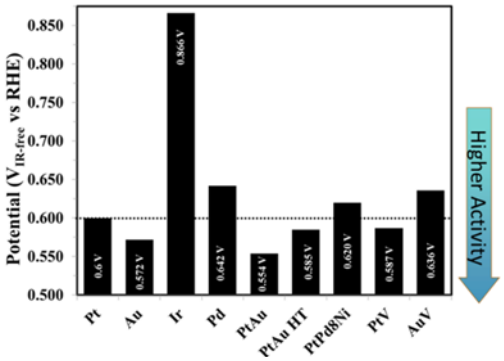

Figure 2. Initial catalyst screening results for the [r2]. Chronopotentiometry test performed in 30 wt% H_2SO_4 saturated with SO_2.

Task 1-Catalyst Development: Pt black and Pt/C have long been the state-of-the-art catalysts for PEM electrolyzers. Recently, as demonstrated in Figure 2, advances in catalyst design have demonstrated that Pt-M (M: V, Co, Fe, etc.), Au, and Au-based catalysts have improved kinetics for the SO_2 oxidation reaction [r2]. In order to design a catalyst for the conditions of the HyS, a high-throughput combinatorial methodology is under development that will aid in the catalyst selection. Once a catalyst composition has been identified, electrocatalyst materials will be produced in order to test them in-situ.

Task 2-Membrane Development: Nafion® has long been the PEM solid electrolyte material of choice due to its stability in highly corrosive solutions (30 wt% H_2SO_4 saturated with SO_2) and at high operating temperature (80 °C), while maintaining practical ionic conductivity. However, to meet H_2 cost targets, membrane materials capable of operating at higher temperatures and acid concentrations are needed. At higher temperatures (>80 °C) and acid concentrations, Nafion® and many other solid electrolyte membranes become dehydrated and consequently become more resistive to ion transport. Benicewicz and Weidner's research groups at USC are currently developing membrane materials specific for the HyS process. Not only are the membranes able to operate at higher temperatures than Nafion®, they can also operate at higher acid concentrations as they do not rely on water content for their H^+ conductivity. Membranes developed at USC will be evaluated at SRNL and combined with newly developed catalysts to meet HyS operational targets.

Task 3-Electrolyzer Performance Evaluation: SRNL modified its existing pressurized button cell test facility to evaluate the performance of new catalysts and s-PBI membranes. MEAs are being fabricated and tested for activity and stability according to SRNL's developed protocols.

Results/Discussion

Combinatorial Catalyst Development

An order with an external company was established in FY18 to produce combinatorial trimetallic catalyst films of Pt, Au, and V. The metals will be deposited by sputtering a range of compositions onto glassy carbon plates. These catalysts will be characterized by X-ray diffraction (XRD) and texture analysis via pole figure measurements. Literature research and discussions with partner universities are currently underway to develop an appropriate technique. XRD pole figure analysis will provide insight on whether the catalyst crystallites have a preferred orientation, how the orientation changes with composition, and how it affects reactivity.

The catalyst films will be mapped by scanning electrochemical microscopy (SECM) in order to determine the most active catalyst composition. In order to develop this method, a SECM was set up and tested under various conditions. Cyclic voltammetry and approach curves were obtained for the ferrocyanide/ferricyanide redox couple in two different electrolytes (Figure 3), and were consistent with expected trends and literature data.[1] A catalyst mapping experiment was also performed on the same anolyte in KCl electrolyte with a gold electrode and showed catalyst activity that varied across the surface. This demonstrates that SECM can be used as a sensitive probe of surface reactivity, but experimental conditions need to be further optimized to eliminate streaks in the scanning direction. In addition to standard SECM techniques, a scanning droplet system (SDS) has been procured, which will be more suitable for studying irreversible reactions such as SO_2 oxidation.[2]

SDS-SECM system requires specific material surface properties for the system to scan the surface. Several tests were carried out to validate the materials that will be used in the high-throughput catalyst screening and compared to results using standard characterization techniques. The performance of metal nanoparticles supported on carbon black and that of metal thin films on glassy carbon was evaluated in two different electrolytes. As shown in Figure 4, a comparison between model solutions and SO_2 saturated sulfuric acid solutions yielded similar results for metal-doped carbon electrocatalysts and thin metal films, respectively. As confirmed by both tests, gold catalysts show higher performance than the state of the art catalysts, platinum on carbon.

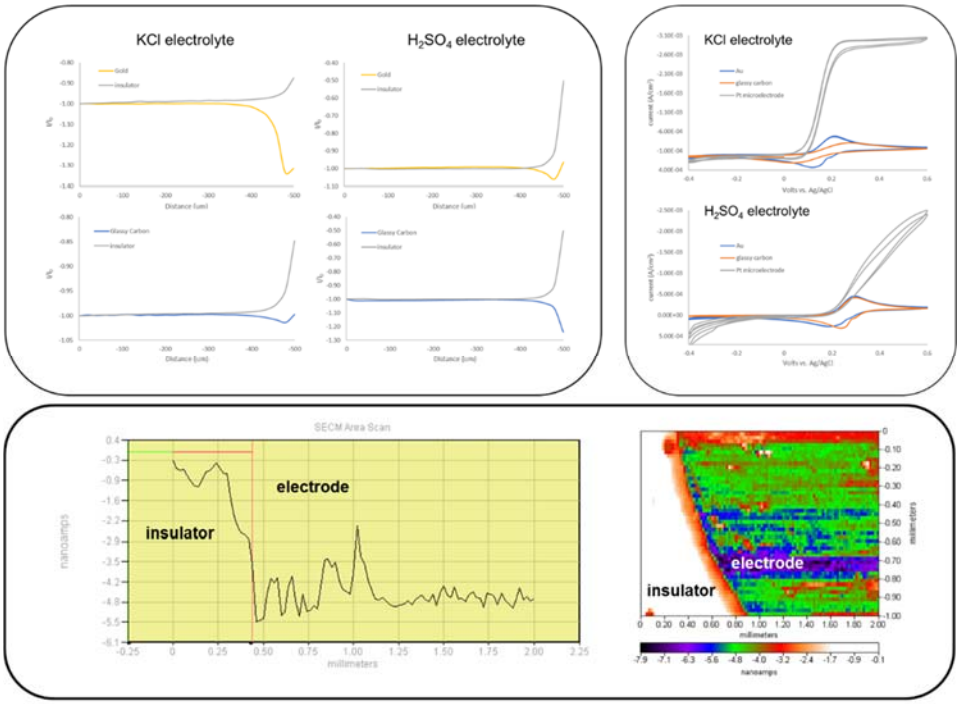

Figure 3. SECM approach curves (top left) and cyclic voltammograms (top right) for 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M electrolyte on gold and glassy carbon electrodes; line scan and surface map of a gold electrode in 5 mM $[Fe(CN)_6]^{3-/4-}$ anolyte and 0.1 M electrolyte

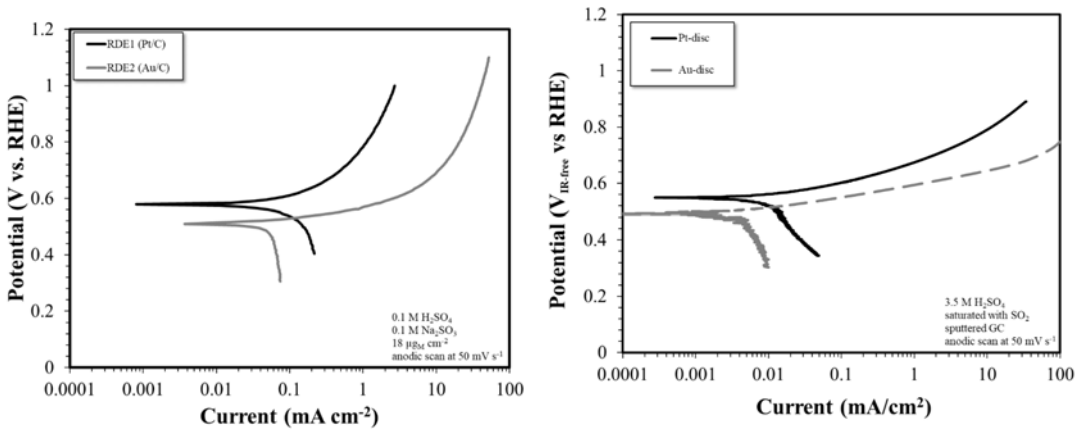

Figure 4. The use of model solutions (left) for the implementation in high throughput screening shows similar behavior to thin films tested in SO_2 saturated sulfuric acid solutions (right). As observed by our initial screening, Au/C shows better performance than Pt/C.

Electrolysis test station modification and validation

The MEA button cell test facility has been modified for gas-phase SO_2 testing. Various improvements were made during modification, such as elimination of dead volume and leak points, making the system more efficient and increasing throughput. The new gas-phase system has been successfully set up and tested. Figure 5 shows that the performance is comparable to liquid-phase at low current densities. At higher current densities, a discrepancy is observed, attributed to low pressure operation.

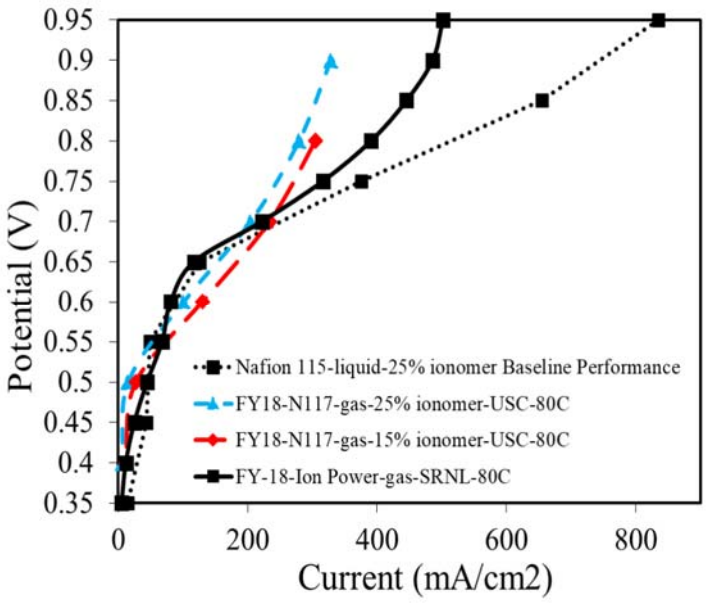

Figure 5. Performance curves for the operation of the gas fed button cell test facility compared to the liquid fed test results.

FY2018 Accomplishments

- Goal: Find better catalysts and membranes for the Hybrid Sulfur (HyS) process for hydrogen production from water
- Approach: Improve catalyst activity, improve membrane ionic conductivity, and improve catalyst/membrane stability for operation at higher temperature and higher acid concentration (faster kinetics and efficiency)
- Progress: Found promising new mixed-metal catalysts and better membranes for further exploration, developed new capabilities/techniques for high-throughput catalyst synthesis/testing, established new partnerships and external funding

Future Directions

- Initiate high throughput catalyst screening
- Develop, characterize and test metal supported on carbon anode catalysts
- Test sulfonated polybenzimidazole membrane electrode assemblies

References

1. Rock, P.A. *J. Phys. Chem.* **1966**, 70, 576-580
2. Gorensek, M.B. *Int. J. Hydrogen Energy* **2009**, 34, 6089-6095

Acronyms

DOE-EERE	Department of Energy-Office of Energy Efficiency and Renewable Energy
HyS	Hybrid Sulfur
MEA	membrane electrode assembly
PBI	polybenzimidazole

PEM	polymer electrolyte membrane
SDE	SO_2-depolarized electrolyzer
SDS	Scanning droplet system
SECM	Scanning electrochemical microscopy
SRC	Savannah River Consulting
SRNL	Savannah River National Laboratory
USC	University of South Carolina

Total Number of Post-Doctoral Researchers

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