

Contract No:

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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 SO₂-depolarized electrolyzer (SDE) 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. SO₂ 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) are 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 publicly published in its current form.

SRNL Legal Signature

Signature

Date

Hybrid Thermochemical Hydrogen Production

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Subcontractors:

University of South Carolina (USC)
Savannah River Consulting, (SRC)

Thrust Area:

Secure Energy Manufacturing

Start Date: October 1, 2017

End Date: September 30, 2019

The Hybrid Sulfur (HyS) process is a promising thermochemical water-splitting cycle with global scale hydrogen production potential. The SO₂-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. SO₂ 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) are 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.

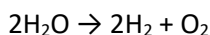
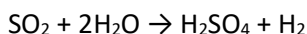
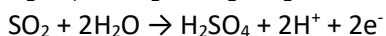
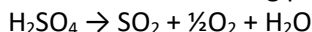
FY2019 Objectives

- 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
 - 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 ($> 600\text{ }^\circ\text{C}$), 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.



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 analyte 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.

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.

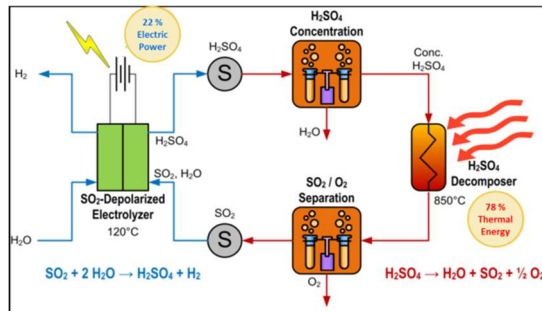


Figure 1. Simplified schematic of the HyS

Thermochemical Step	[r1]
Anode Electrochemical Step	[r2]
Cathode Electrochemical Step	[r3]
Overall Electrochemical Step	[r4]
Cycle Process Reaction	[r5]

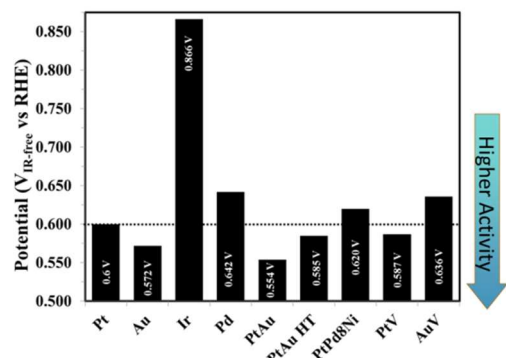


Figure 2. Initial catalyst screening results for the reaction [r2]. Chronopotentiometry test performed in 30 wt% H_2SO_4 saturated with SO_2 .

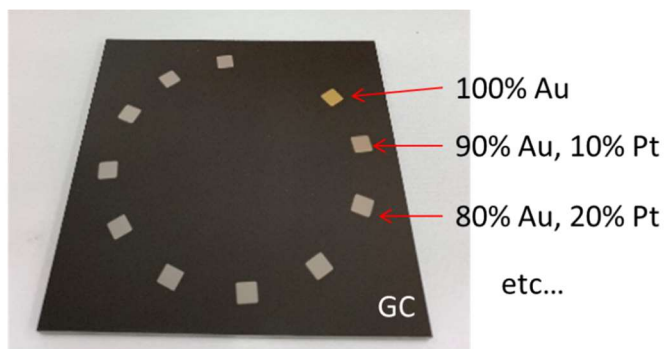
Task 2-Membrane Development: Nafion® has long been the PEM solid electrolyte material of choice due to its stability in highly corrosive solutions (30 wt% H₂SO₄ saturated with SO₂) and at high operating temperature (80 °C), while maintaining practical ionic conductivity. However, to meet H₂ cost targets, 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 thin-film evaluation

Combinatorial trimetallic catalyst films of Pt, Au, and V were prepared by sputtering a range of compositions onto glassy carbon plates (Figure 3). The catalyst films were 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. A scanning droplet system (SDS) was used in the SECM to study the electrochemical activity of the films. This system was used as it is more suitable for studying irreversible reactions such as SO₂ oxidation. Figure 4 shows the composition results from the analysis of Au and Pt thin films. Compositions were analyzed at 0.6 V and 0.1 V vs Ag/Ag₂SO₄. The low and high potentials were selected to view the reaction kinetics at the regions close to the thermodynamic limited potential (0.1 V) and at the kinetically limited region (0.6 V). As observed by the results from the pure AuPt samples, an increase of activity with increasing Au content is observed. The effects of V addition are currently being evaluated.



x6 sample plates w/ varying V content

Figure 3. Example of combinatorial bimetallic catalyst films of Pt and Au prepared by sputter depositing a range of compositions onto glassy carbon plates.

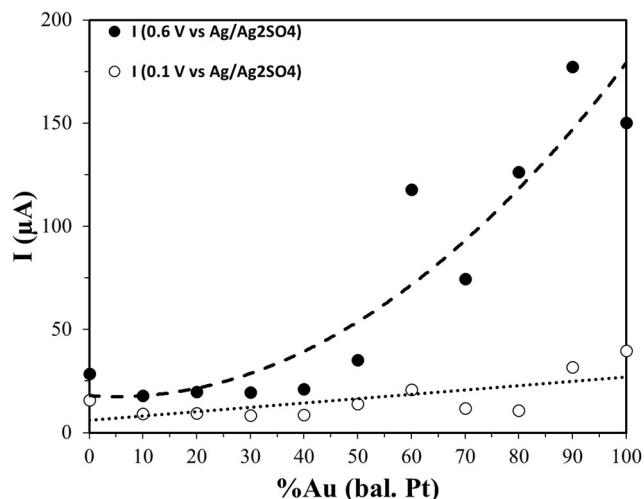


Figure 4. SDS-SECM combinatorial analysis of thin-film PtAu films on glassy carbon substrate.

Ex-situ catalyst evaluation

Prior literature reports have shown that acid electrolyte concentration can impact the catalysts' electrochemical activity by varying diffusion limitations. This observation was taken under consideration while evaluating the electrocatalysts via rotating disc electrode (RDE). Various concentrations of sulfuric acid solutions with 50mM sodium sulfite salt (Na_2SO_3) were used as well-defined surrogates instead of dissolved SO_2 . It is important to note that during electrolyzer testing with SO_2 , it is difficult to predict the local acid concentration at the electrode layer due to possible mass transport limitations. Therefore, understanding the effect of sulfuric acid concentration on RDE performance can help predict the environment at the catalyst layer in the electrolyzer. Once a thin layer of catalyst powder was loaded onto the RDE tip, we conducted sulfite oxidation in increasingly concentrated sulfuric acid solutions with a rotation speed of 400 rpm (Figure 5). The first noteworthy observation is that there is a significant difference in the limiting current that is dependent on the acid concentration. Although the sodium sulfite concentration is constant in all acid solutions, a continuous decrease in limiting currents is observed as the acid concentration increases. This effect is attributed to changes in the diffusion coefficient and kinematic viscosity. In the 3.5 M sulfuric acid solution, Au has a lower onset potential for the oxidation of sulfite to sulfate. The diffusion-limited currents observed for Au and Pt catalyst are similar. In 7 M sulfuric acid, Pt has a lower onset potential, but Au has a higher limiting current and outperforms Pt from about 0.57 V to approximately 1.1 V (vs. NHE). In 9 M sulfuric acid, Pt again has a slightly lower onset potential, but Au again exhibits higher limiting current and outperforms Pt from about 0.62 V until 1.0 V. Au has just one oxidation peak under all concentrations tested. Pt, however, has a second oxidation step that is observed in both 7 M and 9 M H_2SO_4 concentrations at approximately 0.95V. It is possible that the second oxidation step is influenced by the formation of a Pt oxide layer. This result, using metal nanoparticles deposited on carbon black, confirms the thin film combinatorial screening performed using SDS-SECM, where Au shows better activity than Pt.

In-situ material evaluation

The electrochemical performance of Pt/C and Au/C catalysts were also evaluated in an electrolysis cell. In the present experiments, the metal loading on the anode remained the same for both Pt and Au, but a lower loading ($0.1 \text{ mg}_M \text{ cm}^{-2}$) than typically observed in the literature ($\sim 1 \text{ mg}_M \text{ cm}^{-2}$) was used. The lower loadings were selected to facilitate evaluations of

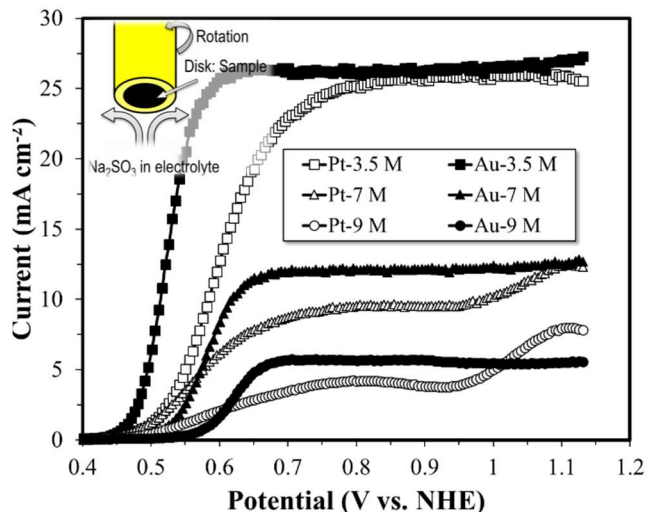


Figure 5. Linear sweep voltammetry measured at 400 RPM for 20% Au/C (solid symbols) and 40% Pt/C (open symbols) in 3.5M (squares), 7M (triangles), and 9M (circles) sulfuric acid, all with 50 mM sulfite measured at 50 mV/s. Insert shows the simplified schematic of the rotating disc experiment.

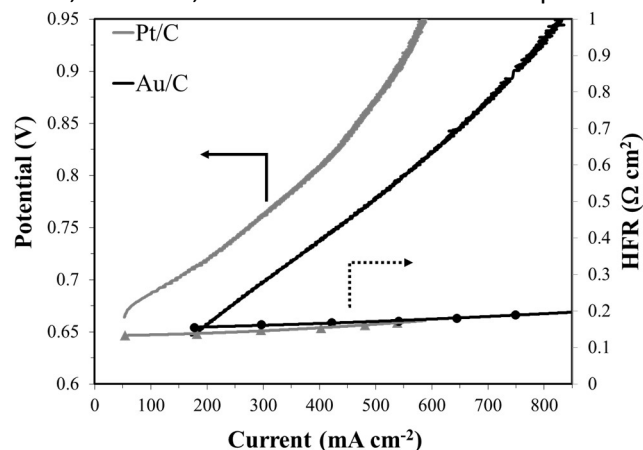


Figure 6. SO_2 performance curve for anodes with Pt/C (grey trace) and Au/C (black trace) tested at 90 °C. Metal loading is 0.1 mg cm^{-2} for all cases. Nafion® 115 was used for the test.

the kinetic limited regions of the electrolyzer performance. As observed in Figure 6, the SO_2 electrooxidation performance of the gold catalyst is superior to that of the Pt catalyst, confirming the RDE results. In addition, the high frequency resistance (HFR) is very similar for cells employing Pt/C and Au/C, indicating that the difference in performance is entirely due to the catalyst. The HFR increase as a function of current can be correlated to a local increase in acid concentration at the catalyst/membrane interface. The electrolyzer was not operated at potentials lower than 0.6 V to limit unreacted SO_2 crossover to the cathode.

High temperature operation was also evaluated with the use of sulfuric acid doped polybenzimidazole membrane (S-PBI). This membrane was prepared to meet the operation requirements in the SDE, which includes high temperature operation, high acid concentration, and low SO_2 crossover. Results from the testing are shown in Figure 7. As observed in the figure, S-PBI MEA shows around 150 mV improvements in the electrolyzer performance. Additionally, the high frequency resistance is much lower than that of the Nafion[®] based MEA. It is expected that further gains will be obtained by incorporation of the Au/C catalyst on the MEA.

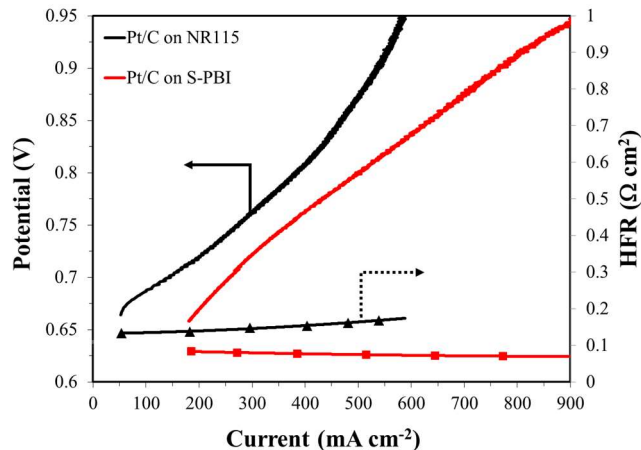


Figure 7. SO_2 performance curve for MEAs based on S-PBI and Nafion[®] 115. Anodes consist of Pt supported on carbon. Nafion[®] MEA tested at 90 °C and S-PBI tested at 110 °C.

FY2019 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, improved performance through the use of high temperature membranes

Future Directions

- Continue high throughput catalyst screening with ternary compositions
- Develop, characterize and test additional metal supported on carbon anode catalysts
- Continue optimization of sulfonated polybenzimidazole based membrane electrode assemblies

FY 2019 Publications/Presentations

BH. Meekins, V. Gopal, BA. Tavakoli Mehrabadi, MC. Elvington, P. Ganesan, JC. Weiss, JW. Weidner, HR. Colón-Mercado, "In-situ and ex-situ comparison of the electrochemical oxidation of SO_2 on carbon supported Pt and Au catalysts." Manuscript submitted to *International Journal of Hydrogen Energy*.

Acronyms

DOE-EERE Department of Energy-Office of Energy Efficiency and Renewable Energy

LDRD-2018-00021

LDRD Report

HyS	Hybrid Sulfur
MEA	membrane electrode assembly
S-PBI	sulfuric acid doped 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

B. Tavakoli (Post-doctoral student, USC)

L. Murdock (Graduate student, USC)

Total Number of Student Researchers

J. Weiss (under-graduate, USC)

V. Gopal (under-graduate, USC)