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Recent Advances in the Development of the Hybrid Sulfur Process for Hydrogen Production

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Abstract

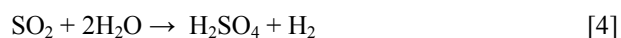
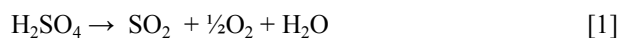
Thermochemical processes are being developed to provide global-scale quantities of hydrogen. A variant on sulfur-based thermochemical cycles is the Hybrid Sulfur (HyS) Process, which uses a sulfur dioxide depolarized electrolyzer (SDE) to produce the hydrogen. In the HyS Process, sulfur dioxide is oxidized in the presence of water at the electrolyzer anode to produce sulfuric acid and protons. The protons are transported through a cation-exchange membrane electrolyte to the cathode and are reduced to form hydrogen. In the second stage of the process, the sulfuric acid by-product from the electrolyzer is thermally decomposed at high temperature to produce sulfur dioxide and oxygen. The two gases are separated and the sulfur dioxide recycled to the electrolyzer for oxidation. The Savannah River National Laboratory (SRNL) has been exploring a fuel-cell design concept for the SDE using an anolyte feed comprised of concentrated sulfuric acid saturated with sulfur dioxide. The advantages of this design concept include high electrochemical efficiency and small footprint compared to a parallel-plate electrolyzer design. This paper will provide a summary of recent advances in the development of the SDE for the HyS process.

Introduction

Alternative energy generation and storage systems are the subject of increased interest and innovative research to meet continually increasing energy demands in the face of a diminishing supply of nonrenewable fossil fuels. Hydrogen is an attractive energy carrier since it contains the highest energy per mass ratio of any conventional fuel. Transitioning to a hydrogen-based energy system will require significant scale-up compared to existing capabilities. These global-scale demands can be met by water electrolysis or through thermochemical water-splitting cycles. Water electrolysis offers several advantages over other production methods, however, the technology required and energy input can make hydrogen produced by this method expensive. Thermochemical water splitting cycles offer an alternative highly efficient route for hydrogen production.^[1] Among the many possible thermochemical cycles for the production of hydrogen, the sulfur-based cycles lead in overall energy efficiency.

The Hybrid Sulfur (HyS) Process is a sulfur-based two-step thermochemical-electrochemical hybrid cycle. In this process sulfuric acid is thermally decomposed at high temperature (900 °C) producing SO_2 [eqn 1]. H_2SO_4 saturated with SO_2 is then pumped into a SDE. The SDE electrochemically oxidizes sulfur dioxide to form sulfuric acid at the anode [eqn 2] and reduces protons to form hydrogen at the cathode [eqn 3]. The overall electrochemical

reaction consists of the production of H_2SO_4 and H_2 [eqn 4], while the entire cycle produces H_2 and O_2 from H_2O with no side products [eqn 5].



Sulfur dioxide oxidation has a reversible half-cell potential of -0.158 V (SHE), while low temperature water electrolysis has a reversible half cell potential of -1.23 V (SHE), thus the HyS process requires lower electrical energy input. Due to ohmic, kinetic, and mass transport overpotential losses, an operating cell potential of 0.6 V has been targeted for HyS electrolyzer operation at a current density of 500 mA cm^{-2} . This operating condition would result in an estimated overall process efficiency of 41% with approximately 30% of the energy input powering the electrolyzer.

The development of a liquid-fed HyS electrolyzer began in the late 1970s and continued until the early 1980s. At this stage of development, the SDE featured a parallel-plate filter-press type design with a separator/membrane to keep the anolyte and catholyte compartments separate.^[4] Approximately five years ago

renewed interest in the HyS process initiated a review of the SDE design concept, since significant advances have occurred in electrochemical technology over the last 30 years, particularly in the development of hydrogen fuel cells. From this review, SRNL adopted a fuel cell design concept for the SDE as shown in Figure 1.^[3,5,6] The heart of the fuel cell is the membrane electrode assembly or MEA, which consists of the anode, cation-exchange membrane and cathode (see Figure 1). To optimize the performance of the SDE, we have investigated key properties of electrocatalysts and cation-ion exchange membranes. This paper presents a summary of these findings as well as results of work to identify operating conditions that limit the formation of an undesired sulfur-rich layer between the cathode and membrane.

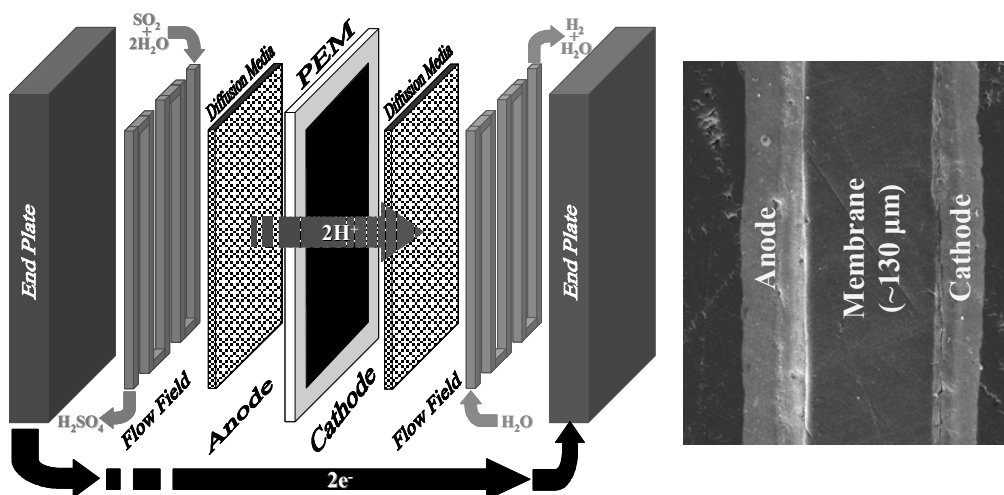


Figure 1. Schematic diagram of SDE (left) and scanning electron micrograph showing the anode (Pt/C), membrane (Nafion[®]) and cathode (Pt/C) regions of the membrane electrode assembly, MEA (right).

Experimental

All membranes were hydrated prior to testing by immersing in deionized water. Commercially available membranes included perfluorinated sulfonic acid (PFSA) membranes^[7] from DuPont and polybenzimidazole (PBI)^[8] membranes from BASF. Experimental membranes included the following; (1) sulfonated Diels-Alder polyphenylenes (SDAPP)^[9] from Sandia National Laboratories (SNL), (2) PFSA/fluorinated ethylene propylene (FEP) blends from Case Western Reserve University, and (3) perfluorocyclobutane-biphenyl vinyl ether (BPVE) and perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene (BPVE-6F) polymer blends from Clemson University.^[10]

The chemical stability of the membranes was determined by immersing the membrane into a 9.2 M (60 wt%) H_2SO_4 at 80 °C for 24 hours. Following acid exposure, the membranes were rinsed and stored in deionized water. Each membrane was inspected for visible signs of chemical attack. Fourier transform infrared spectroscopy (FTIR) was used with the attenuated total reflectance (ATR) sampling technique to determine if chemical attack occurred. FTIR spectra were measured with a Jasco FT/IR-6300 instrument before and after exposure to the hot, concentrated sulfuric acid solution.

Membrane transport of SO_2 was evaluated under non-polarized conditions using a permeation cell consisting of two glass chambers joined by a Teflon™ bridge where the membrane is secured. The bridge consists of a diffusion layer in the left chamber where acid saturated with SO_2 is pumped into the anolyte-membrane interface. Additionally, the diffusion media presses the membrane to the working electrode, which is supported by a perforated tantalum plate that provides electrical connection to the working electrode. Finally, a non-conductive diffusion media separates the tantalum support from the counter electrode in order to allow the flow of fresh acid pumped to the counter electrode without short circuiting the cell. Further details on the SO_2 transport

measurement method as well as that for ionic conductivity and resistivity are provided in reference 11.

Evaluation of catalyst performance featured cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using a Bioanalytical Systems (BAS) B/W electrochemical analyzer. Sulfuric acid solutions were prepared by diluting reagent grade sulfuric acid (Fisher Scientific) with deionized, distilled water. Prior to the measurements all solutions were purged of oxygen by bubbling nitrogen. For tests evaluating the oxidation of SO_2 , we continuously bubbled gaseous SO_2 (Scott Specialty Gases) through the sulfuric acid solution. CVs were performed at a scan rate of 50 mV/sec and in a potential window between 1004 mV and -100 mV vs. Ag/AgCl (3M NaCl). LSVs were performed in the potential window between 804 mV and 104 mV vs. Ag/AgCl at a scan rate of 5 mV/sec. The experiments were carried out at temperatures ranging from 30 °C up to 70 °C and sulfuric acid concentrations of 30 – 70 wt%. The curves were repeated until a stable performance was obtained. Both CV and LSV measurements were performed starting from the anodic potential and going in the cathodic direction.

Electrolyzer performance of membranes and catalysts was evaluated by fabricating a MEA of appropriate size and installing the MEA in a SDE. Figure

2 provides photographs of the two experimental electrolyzers used in the performance testing. The larger SDE features a working area of 54.8 cm^2 and can be operated at temperatures of between 30 and $80 \text{ }^\circ\text{C}$ and pressures of $1 - 6$ atmospheres. The smaller SDE has a working area of 2.5 cm^2 and can be operated at temperatures of between 30 and $80 \text{ }^\circ\text{C}$ at atmospheric pressure.

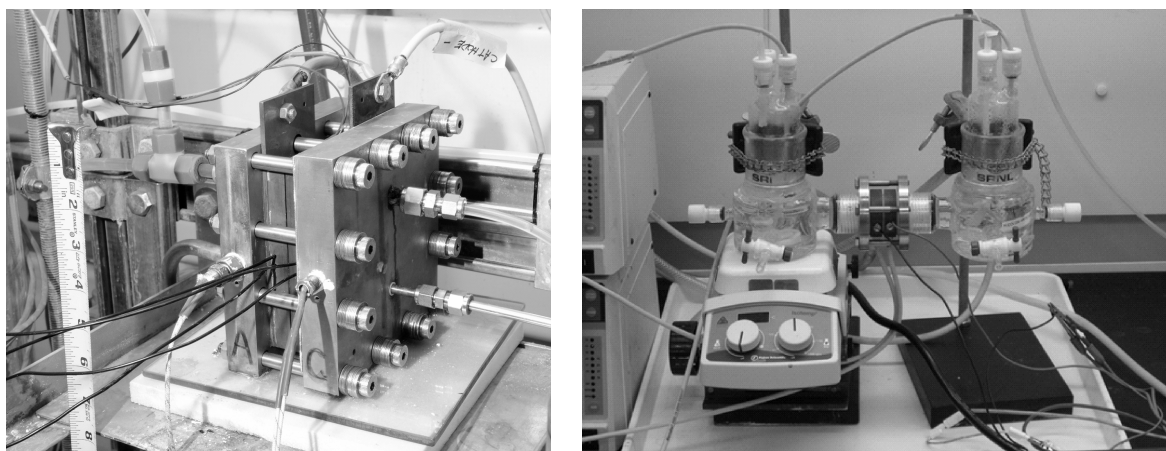


Figure 2. Photograph of single-cell electrolyzers with working area of 54.8 cm^2 (left) and 2.5 cm^2 (right).

Results and Discussion

The SRNL concept for the SDE features a fuel cell design as shown schematically in Figure 2. Concentrated sulfuric acid containing dissolved SO_2 is pumped into the anolyte compartment and transported to the anode on the surface of the MEA. Protons produced at the anode transport across the cation-exchange membrane, reach the cathode and are reduced to form hydrogen.

Hydrogen transports into the catholyte and exits the cell. Key components of the SDE include the anode, cathode and cation exchange membrane, which comprise the MEA for the cell (see Fig. 2), as well as current collector and flow fields for liquids and gases.

Flow fields for the anolyte and catholyte compartments used in the electrolyzer testing consisted of grooved graphite carbon pieces that are inserted into the thicker graphite carbon blocks along with either carbon paper (anode side) or carbon cloth (cathode side) placed between the carbon blocks and the MEA (see Figure 1). Stainless steel plates that are electrically isolated from the carbon blocks serve as endplates. These parts are sandwiched together in a filter-press arrangement and fastened with bolts. Heating elements are inserted into the endplates to provide auxiliary heating for higher temperature experiments.

Catalyst Testing

The anode and cathode materials are key components of the SDE to ensure that the electrolyzer operates at maximum energy efficiency with long lifetimes. Compared to the cathode, the kinetics of the electrochemical oxidation of SO_2 at the anode are very slow. Consequently, most of the inefficiencies of the electrolyzer arise from the anode reaction kinetics. Thus, to date we have

focused on identifying materials that feature excellent catalytic activity and chemical stability for the oxidation of sulfur dioxide.

Fuel cells today feature electrodes comprised on fine metal powders supported on a carbon substrate. These types of materials can exhibit much different catalytic activity compared to the bulk metal powders that were used in the early development effort for the Hybrid Sulfur electrolyzer. The early testing featured a number of metals including platinum, palladium and other noble and transition metals.^[12] Of these, platinum received the most attention, although palladium was reported to be an excellent catalyst for the oxidation of sulfur dioxide. Thus, we investigated the performance of platinum and palladium supported on carbon as well as binary and ternary alloys of noble metals and transition metals.

Linear sweep voltammetry indicated the catalytic activity of both platinum deposited on carbon black (Pt/C) and palladium deposited on carbon black (Pd/C) changes with sulfuric acid concentration, temperature and with the number of cycles.^[13] A potential window of 0.30 V to 1.00 V vs. SHE was selected to avoid the reduction of SO₂ to S, which could passivate the catalyst surface, and avoid the dissolution of the metal catalysts at higher potentials.^[14] The open circuit voltage increased as the acid strength increases. For example, potentials for Pt/C measured 0.50 V, 0.56 V and 0.63 V vs. SHE in 3.5 M (30 wt%), 6.5 M (50 wt%) and 10.5 M (70 wt%) H₂SO₄ solutions, respectively. For

Pd/C, the potentials measured 0.59 V, 0.66 V and 0.73 V vs. SHE, in the 3.5 M, 6.5 M and 10.4 M H₂SO₄ solutions, respectively. In addition to a lower open circuit voltage, Pt/C exhibited higher exchange currents than Pd/C over all H₂SO₄ solution concentrations. In general, the activation energy for sulfur dioxide on Pt/C was less than half of that measured for Pd/C.^[13]

Cyclic voltammetry of Pt/C and Pd/C in concentrated H₂SO₄ solutions revealed that platinum became activated and palladium became deactivated with increasing number of cycles. Figure 3 presents the measured current as a function of cycle number for the oxidation of sulfur dioxide in 3.5 M H₂SO₄ solution at 30 °C. Pt/C shows a modest current initially, which more than doubles with cycle number up to a maximum value of about 30 A/mg Pt after 12 cycles. After reaching a maximum value, the current remained constant with additional cycles. In contrast to Pt/C, Pd/C exhibits a much higher initial current (31.9 A/mg Pd), which rapidly diminishes with each cycle and falls by more than 98% after 35 cycles.

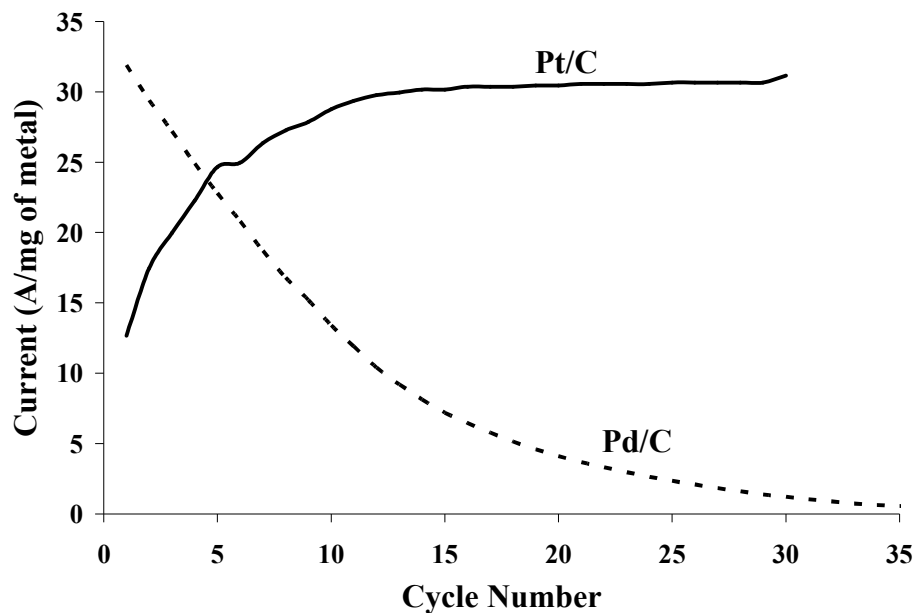


Figure 3. SO₂ Oxidation Current versus Cycle Number in 3.5 M H₂SO₄ solution at 30 °C.

The enhancement of electrocatalytic activity for Pt/C during the cyclic voltammetry experiment likely reflects reduction of SO₂ to S or partially reduced SO₂ onto the catalysis surface. Sulfur-containing deposits are well known to change the electrode reactivity by altering the binding characteristics of surface sites.^[15] For Pd/C, loss of activity likely reflects attack of the palladium leading to sintering of the particles and overall deactivation. In view of these results and the greater stability of the Pt/C catalyst, we conclude that Pt/C is a superior electrocatalyst to Pd/C for SO₂ oxidation in concentrated H₂SO₄ solutions.

Note however, Pt/C shows evidence of deterioration when polarized in 70 wt% H₂SO₄ solution at 50 °C or higher. Operating conditions targeted for the SDE include H₂SO₄ concentrations as high as 70 wt% and temperatures of 120 – 140 °C. Thus, further development of the anode electrocatalyst is needed to provide a material that can successfully perform in concentrated H₂SO₄ solutions at elevated temperatures.

To this end we have more recently initiated studies of binary and ternary metal alloy powders as anode catalyst materials. Figure 4 provides Tafel plots for the baseline Pt/C material as well as a binary alloys, Pt/Co/C and Pt/Ru/C, and ternary alloys, Pt/Co/Cr/C, Pt/Co/Ni/C and Pt/Co/Ir/C. Under the test condition, the Pt/C baseline material exhibited an open-circuit potential of 0.507 V (vs. SHE). Three of the experimental catalyst materials exhibited lower open-circuit potential and exchange currents equal to that of Pt/C indicating higher catalytic activity. These alloys included Pt/Co/Cr/C (open-circuit potential = 0.485 V vs. SHE), Pt/Co/C (0.488 V) and Pt/Co/Ni/C (0.501 V). Testing is in progress to determine the stability and catalytic properties of these promising materials at higher H₂SO₄ concentrations and temperatures.

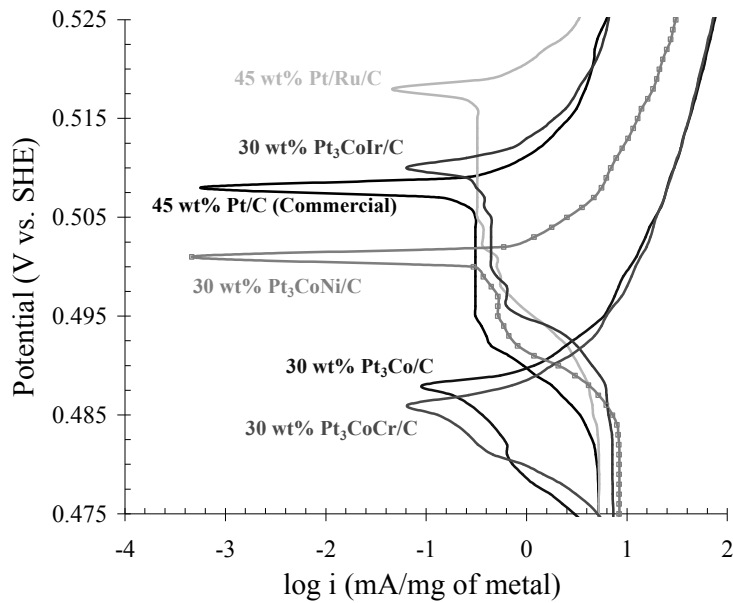


Figure 4. Tafel plots for Pt/C as well as binary and ternary alloys of Pt and other noble and transition metals

Ion-Exchange Membrane Testing

The ion-exchange membrane is a key component of the electrolyzer as it provides a physical and electrically-insulating barrier between the anode and cathode and serves as the electrolyte for conducting protons from the anode to the cathode. Key attributes of the ion exchange membrane are chemical stability to hot, concentrated H_2SO_4 solutions, electrically insulating, good ionic conductivity and low permeability to sulfur dioxide. From previous testing on the Hybrid Sulfur electrolyzer development as well as recent developments in fuel cell and industrial electrolyzers, the perfluorinated sulfonic acid (PFSA)

class of membranes such as the Nafion[®] family offered by the E.I. DuPont Co. appeared especially suited for use in the electrolyzer. Other candidate membranes included (1) sulfonated Diels-Alder polyphenylene (SDAPP), (2) perfluoro-sulfonimide (PFSI), (3) perfluorocyclobutane-biphenyl vinyl ether (PBVE) and perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene (PBVE-6F) polymer blends, (4) polyetheretherketone (PEEK) and (5) polybenzimidazole (PBI).

The chemical stability of the membranes in a corrosive environment was examined to provide insight into long-term performance. The PEEK family of membranes was found to be unstable in hot, concentrated H₂SO₄ solution and, therefore, is not a suitable material for this application. Testing indicated that all PFSA-type membranes exhibited no measurable degradation when exposed to 9.2 M H₂SO₄ solution for 24 hours at 80° C. Also, no degradation was observed for SDAPP, PBVE and PBVE-6F membranes. We did observe small changes in peak intensities in the 800 to 1200 cm⁻¹ region for the Celtec V PBI membrane sample. We attribute the changes to the substitution of H₂SO₄ for H₃PO₄ in the membrane. No other spectral shifts are observed for the PBI membrane indicating the polymer backbone remained intact during the test.

The membranes exhibiting excellent chemical stability were further evaluated to determine SO₂ transport characteristics, conductivity and performance in a bench-scale liquid –fed electrolyzer. Table 1 provides a summary listing of the membrane characteristics. The reported conductivity is the through-plane conductivity and current density is that measured in the 2.5 cm² single cell electrolyzer operated at a potential of 1.0 V at 80 °C and atmospheric pressure.

The Nafion[®] 115 membrane showed a high through-plane conductivity (0.0241 S cm⁻¹) and good electrolyzer performance (270 mA cm⁻²) at 80 °C, while having among the highest measured SO₂ transport (6.10 x 10⁻⁸ cm² s⁻¹). Nafion[®] 211, which is a much thinner membrane, exhibited a much lower conductivity (0.0159 S cm⁻¹), but lower (i.e., better) SO₂ transport (5.09 x 10⁻⁸ cm² s⁻¹) and excellent electrolyzer performance (393 mA cm⁻²) compared to the Nafion[®] 115 membrane. Introduction of a layer of fluorinated ethylene propylene (FEP) to a PFSA membrane produced a material (Case Western PFSA/FEP blend) with much lower SO₂ transport (1.99 x 10⁻⁸ cm² s⁻¹). Note, however, that this membrane exhibited a lower conductivity (0.0096 S cm⁻¹) and poorer electrolyzer performance (228 A cm⁻²) compared to the baseline Nafion[®] 115 membrane.

Table 1. SO₂ flux, SO₂ transport, conductivity, and current density (performance in HyS electrolyzer) is shown along with membrane thickness for a number of commercially available and experimental membranes.

Supplier	Membrane Classification	Thickness (μm)	SO ₂ Flux (mol SO ₂ s ⁻¹ cm ⁻²) x 10 ⁻⁹	SO ₂ Transport (cm ² s ⁻¹) x 10 ⁻⁸	Conductivity (S cm ⁻¹)	Current Density (mA cm ⁻²)
Dupont Nafion® 115	PFSA	127	5.23	6.10	0.0241	270
Dupont Nafion® 211	PFSA	25	21.8	5.09	0.0159	393
Case Western Reserve University	PFSA-FEP Blend	53	4.09	1.99	0.0096	228
Sandia National Laboratories	SDAPP	50-85	11.1	7.79	0.0328	286
Clemson University	BPVE	18	21.2	3.50	0.0048	320
Clemson University	BPVE/BPVE-6F 1:1 Blend	16	16.2	2.37	0.0063	337
Clemson University	BPVE/BPVE-6F 2:1 Blend	19	17.6	3.07	0.0109	335
BASF Celtec-V	PBI	100	2.14	1.99	nd	344

The SDAPP membrane exhibited excellent proton conductivity (0.0328 S cm⁻¹) and good electrolyzer performance (286 A cm⁻²). However, the SO₂ transport (7.79 x 10⁻⁸ cm² s⁻¹) was the highest of any tested membrane. The perfluorinated cyclobutyl-based membranes supplied by Clemson University also show promise for this application. The BPVE and BPVE/BPVE-6F blends all showed reduced SO₂ transport, lower conductivity and better electrolyzer performance compared

to the baseline Nafion[®] 115 membrane. The PBI membrane, Celtec-V, performed very well in the electrolyzer with low SO₂ transport ($1.99 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$).

Membrane testing has identified a number of candidate materials in addition to the current baseline material, Nafion[®] 115. Modifications to the Nafion[®]-class of membranes as well as new types of fluorinated polymers have been shown to reduce SO₂ transport while maintaining good performance in a bench-scale electrolyzer at 80 °C. Hydrocarbon membranes such as the SDAPP and PBI materials also are attractive candidates based on testing results described above as well as the potential for even better performance at higher temperatures. For example, preliminary results indicate excellent current densities at low cell voltages in tests with these experimental membranes in a SO₂-gas fed electrolyzer.

Sulfur Layer Formation

Cell voltage is influenced by a number of operating parameters and conditions including the current density, cell temperature, concentration of sulfur dioxide in the anolyte, anolyte flowrate, membrane type and thickness and concentration of sulfuric acid. Over the course of testing various MEAs in the single cell electrolyzer (see Fig 2), it was observed that the cell voltage generally increased

while maintaining constant current conditions.^[16] The small gradual increase in cell voltage suggested that there may be chemical and/or physical changes to the MEA over the course of a test. Thus, after a 100-hour test, we recovered the MEA from the cell and used scanning electron microscopy (SEM) to determine if there were any visible signs of change.

Figure 5 shows a SEM image of MEA-12 indicating a sulfur-rich layer between the cathode and membrane that is almost as thick as the membrane. The layer is conductive as evidenced by the small increase in cell voltage. However, as a result of the layer formation, the MEA is becoming thicker and is pushed into the flow field channels. The expansion of the MEA into the flow channel also increases the pressure drop by restricting flow in the flow field. Ultimately, the formation of the sulfur-rich layer would result in mechanical failure of the MEA. Additional tests established that the sulfur-rich layer began forming within about 10 hours of cell operation. Interestingly, the sulfur-rich layer is not observed when the electrolyzer is operated at atmospheric pressure or with a gas fed anolyte.

MEA-12
(Nafion® 115)

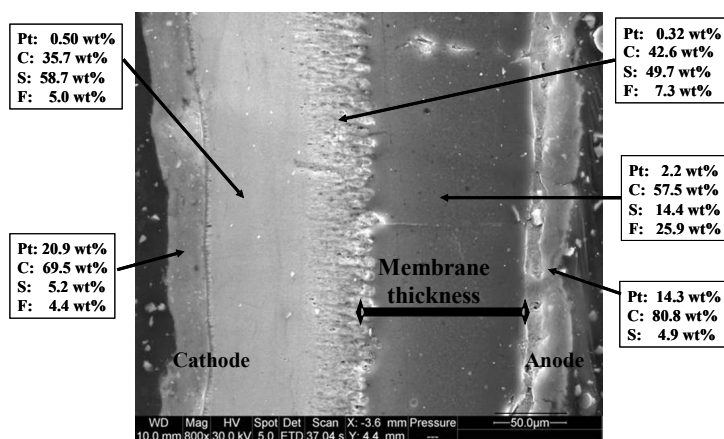
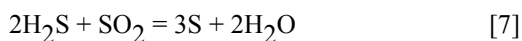
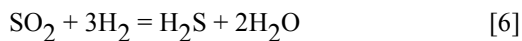


Figure 5. SEM image of MEA-12 showing a sulfur-rich layer between the cathode and membrane. Elemental content is that determined qualitatively by energy dispersive analysis of x-rays.

The formation of a sulfur-layer at the cathode and membrane interface is believed to be due to chemical reactions involving sulfur dioxide that has reached the cathode/membrane interface. These reactions include sulfur dioxide reacting with hydrogen to form hydrogen sulfide (reaction 6) and hydrogen sulfide reacting with sulfur dioxide to form elemental sulfur (reaction 7).^[16] Reaction 6 is more energetically favored than reaction 7 and is preferable in that hydrogen sulfide is a gas and would not likely form a physical layer to the degree that elemental sulfur would under the cell operating conditions.



We hypothesized that by minimizing the amount of sulfur dioxide that reaches the cathode, we could limit reactions to that of reaction 6 and not form a sulfur-rich layer in the MEA. Changes that would minimize sulfur dioxide reaching the cathode/membrane interface include (1) reducing the concentration of sulfur dioxide in the anolyte, (2) increase the current density to consume more sulfur dioxide at the anode, (3) increase the net water flux from the cathode to anode and (4) decrease the permeability of the membrane to sulfur dioxide. Thus, we conducted additional tests to determine if the sulfur-rich layer could be eliminated by modifying the electrolyzer operating conditions.

The MEA-31 test featured the same MEA construction as that of MEA-12, but under operating conditions that reduced the sulfur dioxide concentration in the anolyte, operated at relatively high current density and at a catholyte pressure of about 15 psig higher than that of the anolyte. This test operated continuously for 50 hours at 80 °C. Figure 6 shows a plot of the normalized cell voltage versus elapsed hours of cell operation. In the MEA-12 test, the normalized cell voltage increased from about 1.5 V to 1.9 V over the 100-hour test duration. In the MEA-31 test, there was no measured change in the cell voltage over the 50-hour test duration (see Figure 6). Furthermore, as shown in Figure 7, SEM analysis of MEA-31 after the test revealed no evidence of a sulfur-rich layer. Thus,

reducing the concentration of sulfur dioxide that reaches the cathode/membrane interface appears to be successful in preventing a sulfur-rich layer forming over a 50-hour test duration. Additional experiments are planned to confirm that this mode of operation will prevent the sulfur-rich layer over longer test durations.

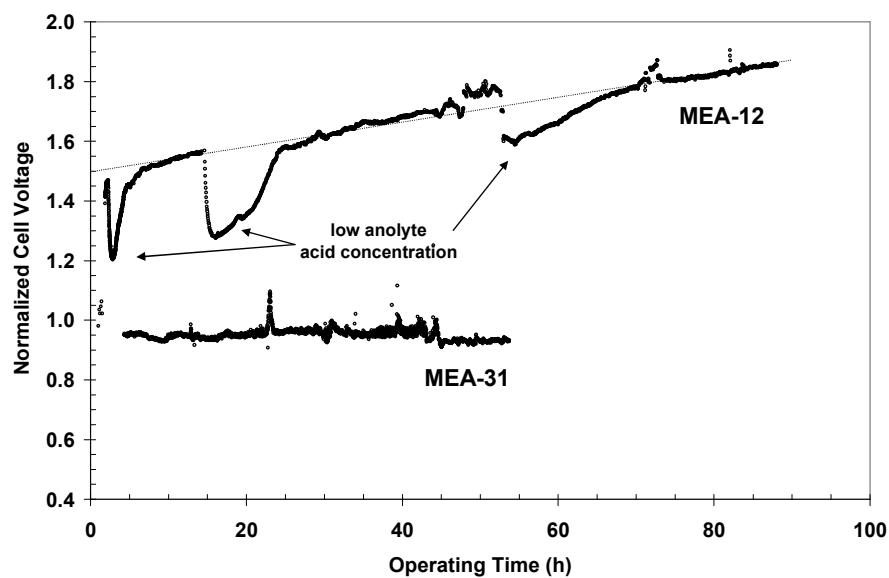


Figure 6. Normalized cell voltage of single cell electrolyzer experiments in which sulfur-rich layer formed (MEA-12) and did not form (MEA-31).

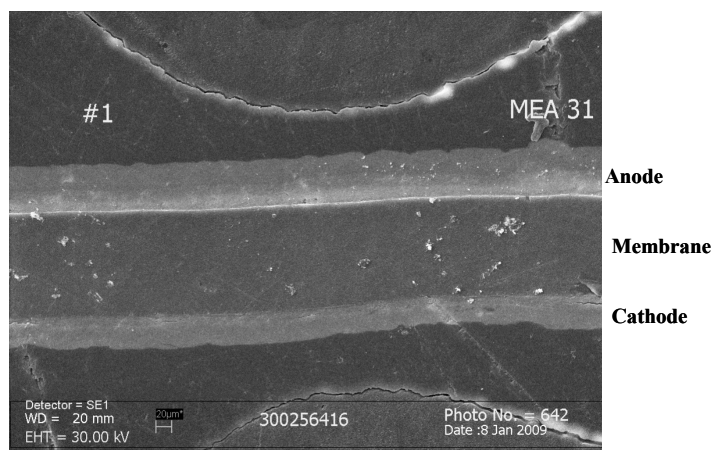


Figure 7. SEM image of MEA-31 showing the absence of a sulfur-rich layer between the cathode and membrane after 50-hours of continuous electrolyzer operation.

Conclusions

Catalyst testing indicates that Pt/C exhibits superior performance and stability compared to Pd/C for the oxidation of SO_2 in concentrated sulfuric acid solutions. Binary and ternary alloys containing platinum and other metals such as Co, Cr and Ni show promise as alternate anode materials. Based on the properties and performance characteristics of a variety of ion-exchange membranes, we have identified a number of candidate membranes for the sulfur dioxide-depolarized electrolyzer. At high operating pressures, we have observed the rapid formation of a sulfur-rich layer between the cathode and the Nafion[®] membrane in the liquid-fed electrolyzer. This layer can be eliminated in the short term by modifying the electrolyzer operating conditions to reduce the quantity of

SO₂ that passes beyond the anode layer in the MEA. Continued membrane development is needed to produce materials with lower SO₂ transport characteristics and high conductivity. We are currently modifying the bench-scale testing equipment to allow membrane and catalyst testing at higher temperatures (> 100 °C).

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