



Evaluation of proton-conducting membranes for use in a sulfur dioxide depolarized electrolyzer

Mark C. Elvington^a, Héctor Colón-Mercado^a, Steve McCatty^b, Simon G. Stone^b, David T. Hobbs^{a,*}

^a Savannah River National Laboratory, Aiken, SC, United States

^b Giner Electrochemical Systems, LLC, Newton, MA, United States

ARTICLE INFO

Article history:

Received 24 September 2009

Received in revised form 5 November 2009

Accepted 6 November 2009

Available online 14 December 2009

Keywords:

Sulfur dioxide transport
Proton exchange membrane
Hybrid Sulfur Process

ABSTRACT

The chemical stability, sulfur dioxide transport, ionic conductivity, and electrolyzer performance have been measured for several commercially available and experimental proton exchange membranes (PEMs) for use in a sulfur dioxide depolarized electrolyzer (SDE). The SDEs function is to produce hydrogen by using the Hybrid Sulfur (HyS) Process, a sulfur-based electrochemical/thermochemical hybrid cycle. Membrane stability was evaluated using a screening process where each candidate PEM was heated at 80 °C in 60 wt% H₂SO₄ for 24 h. Following acid exposure, chemical stability for each membrane was evaluated by FTIR using the ATR sampling technique. Membrane SO₂ transport was evaluated using a two-chamber permeation cell. SO₂ was introduced into one chamber whereupon SO₂ transported across the membrane into the other chamber and oxidized to H₂SO₄ at an anode positioned immediately adjacent to the membrane. The resulting current was used to determine the SO₂ flux and SO₂ transport. Additionally, membrane electrode assemblies (MEAs) were prepared from candidate membranes to evaluate ionic conductivity and selectivity (ionic conductivity vs. SO₂ transport) which can serve as a tool for selecting membranes. MEAs were also performance tested in a HyS electrolyzer measuring current density vs. a constant cell voltage (1 V, 80 °C in SO₂ saturated 30 wt% H₂SO₄). Finally, candidate membranes were evaluated considering all measured parameters including SO₂ flux, SO₂ transport, ionic conductivity, HyS electrolyzer performance, and membrane stability. Candidate membranes included both PFSA and non-PFSA polymers and polymer blends of which the non-PFSA polymers, BPVE-6F and PBI, showed the best selectivity.

© 2009 David T. Hobbs. Published by Elsevier B.V. All rights reserved.

1. Introduction

Continually increasing energy demands coupled with reliance on a diminishing supply of nonrenewable fossil fuels provides the impetus for innovative research into alternative energy genera-

tion and storage systems. One possible solution is centered on the energy carrier hydrogen, which contains the highest energy per mass ratio of any conventional fuel. Global scale quantities of hydrogen will be required for the ensuing economic transformation and major efforts are underway worldwide to develop the technologies required for this transition. These demands can be met by water electrolysis or through thermochemical water splitting cycles. Water electrolysis offers several advantages over other production methods [1], 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 [2]. Among the many possible thermochemical cycles for the production of hydrogen, the sulfur-based cycles lead the competition in overall energy efficiency.

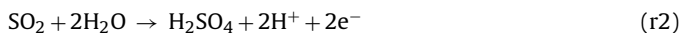
The Hybrid Sulfur (HyS) Process is a sulfur-based thermochemical cycle containing a low energy electrolysis step making it a thermo/electrochemical hybrid process. In this process sulfuric acid is thermally decomposed at high temperature (>800 °C) producing SO₂ (r1). H₂SO₄ saturated with SO₂ is then pumped into a sulfur dioxide depolarized electrolyzer (SDE). The SDE electrochemically

Abbreviations: ATR, attenuated total reflectance; BPVE, perfluorocyclobutane-biphenyl vinyl ether; BPVE-6F, perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene; EIS, Electrochemical Impedance Spectroscopy (EIS); EW, equivalent weight; FEP, fluorinated ethylene propylene; FTIR, Fourier transform infrared spectroscopy; GES, Giner Electrochemical Systems; HyS, Hybrid Sulfur; IR, infrared spectroscopy; MEA, membrane electrode assembly; OCP, open circuit potential; PA, phosphoric acid; PBI, polybenzimidazole; PEM, proton exchange membrane; PFSA, perfluorinated sulfonic acid; S-PFCB, sulfonated perfluorocyclobutyl aromatic ether polymer; SDAPP, sulfonated Diels-Alder polyphenylenes; SDE, sulfur dioxide depolarized electrolyzer; SEM, scanning electron microscope; SHE, standard hydrogen electrode; SNL, Sandia National Laboratory; SRNL, Savannah River National Laboratory.

* Corresponding author at: Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, Bldg. 773-A, B-117, Aiken, SC 29808, United States. Tel.: +1 803 725 2838; fax: +1 803 725 2756.

E-mail address: david.hobbs@srnl.doe.gov (D.T. Hobbs).

oxidizes sulfur dioxide to form sulfuric acid at the anode (r2) and reduces protons to form hydrogen at the cathode (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).



HyS electrolysis (SO_2 oxidation) (r2) has a reversible half cell potential of -0.158 V (SHE) [3], while low temperature water electrolysis has a reversible half cell potential of -1.23 V (SHE). Thus the HyS process requires much less electrical energy input than water electrolysis. Due to ohmic, kinetic, and mass transport overpotential losses, an operating potential of 0.6 V has been targeted for the HyS electrolyzer at a current density of 500 mA cm^{-2} .

Development of the SDE began in the late 1970s utilizing a parallel-plate electrolyzer with a separator/membrane to keep the anolyte and catholyte compartments separate [4]. Since this work in the early 1980s, significant advances have occurred in electrolyzer technology principally in the area of hydrogen fuel cells. Advanced hydrogen fuel cells employ proton conductive membranes with catalyst layers deposited on both sides of the membrane, forming the respective anode and cathode of the electrochemical cell. The layered structure containing membrane and electrode catalysts is referred to as the MEA. Upon resumption of HyS work in 2005, the fuel cell MEA design concept was applied to the SDE [5,6]. The MEA concept results in a much smaller cell footprint than conventional parallel-plate technology, which is a major benefit when implementing the SDE on a commercial scale.

There are several requirements of a PEM for the successful functioning of a HyS electrolyzer. The PEM must be stable in highly corrosive solution ($>30\text{ wt}\%$ H_2SO_4 saturated with SO_2) and at high operating temperature ($>80^\circ\text{C}$), allow minimal transport of SO_2 , and must maintain high ionic conductivity. Ideally, operating temperatures well above 80°C are desired with acid concentrations greater than $50\text{ wt}\%$ H_2SO_4 . These conditions allow the

electrolyzer to function at low cell potential and high current density thus minimizing the energy input and maximizing hydrogen output. Lastly, the PEM serves to separate the anolyte reagents from the hydrogen output to prevent the production of undesired sulfur-based side reaction products and poisoning of the cathode catalyst.

2. Experimental

2.1. Membrane procurement and preparation

The selection process of commercially available and experimental membranes took into account: thickness, equivalent weight (EW), conductivity, chemical stability, and permeability to uncharged molecules. Prior to testing, all membranes were hydrated by immersing in deionized water for several minutes. Commercial membranes included perfluorinated sulfonic acid (PFSA) membranes [7] from DuPont and polybenzimidazole (PBI) [8] membranes from BASF, Fig. 1. Experimental membranes were synthesized with the primary objective of reducing the transport of neutral charge species such as dissolved SO_2 . These membranes included hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP) [9] from Sandia National Laboratory (SNL); stretched recast Nafion® and PFSA/fluorinated ethylene propylene (FEP) blends from Case Western Reserve University; hydrated treated Nafion® 115 from Giner Electrochemical Systems (GES); and perfluorocyclobutane-biphenyl vinyl ether (BPVE) and perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene (BPVE-6F) polymer blends from Clemson University (Fig. 1) [10].

2.2. Membrane characterization

2.2.1. Chemical stability measurements

The chemical stability of the membranes in a corrosive environment was examined using a screening method to provide insight into the potential long-term performance. All membranes were exposed to 9.2 molar ($60\text{ wt}\%$) H_2SO_4 at 80°C for 24 h . Following acid exposure, the membranes were rinsed and stored in deionized water until analysis. Fourier transform infrared spectroscopy (FTIR) was used with the attenuated total reflectance (ATR) sampling technique. IR spectra taken before and after acid exposure were

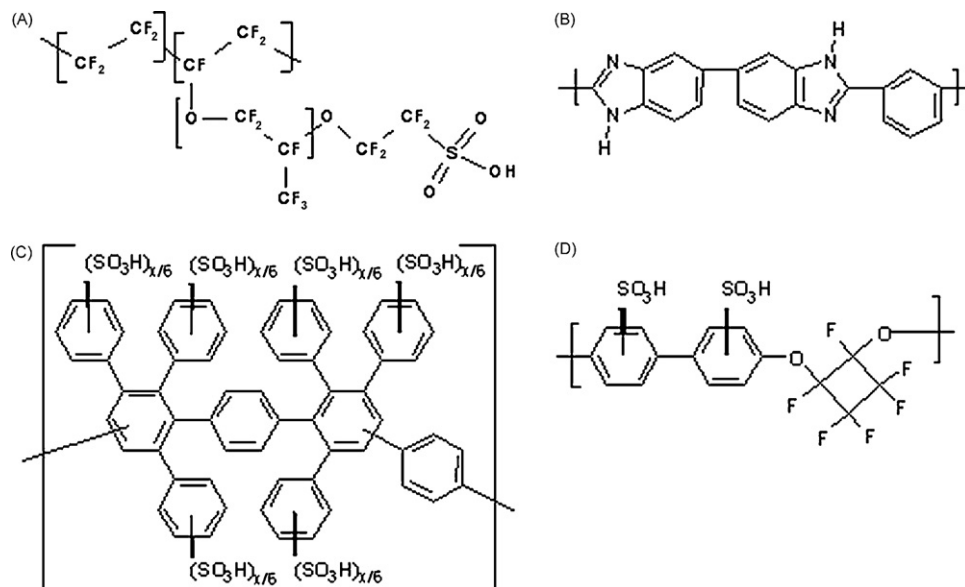


Fig. 1. Evaluated commercial and experimental membranes including (A) perfluorinated sulfonic acid, (B) polybenzimidazole, (C) sulfonated Diels-Alder polyphenylenes, and (D) perfluorocyclobutane-biphenyl vinyl ether hexafluoroisopropylidene.

compared to determine impact on membrane functional groups. FTIR spectra were measured with a Jasco FT/IR-6300 instrument before and after exposure to sulfuric acid solution.

2.2.2. SO₂ flux, SO₂ transport measurements

Membrane transport of SO₂ was evaluated under non-polarized conditions using a permeation cell designed and fabricated at Savannah River National Laboratory (SRNL); a schematic of the cell is shown in Fig. 2. The cell consists 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 SO₂ is forced by pump A into the anolyte–membrane interface. Additionally, the diffusion layer 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 by pump B to the counter electrode without short circuiting the cell.

During measurements both chambers were filled with 30 wt% sulfuric acid and purged of oxygen by flowing nitrogen. A two-electrode system consisting of a platinum mesh working electrode and a porous carbon counter electrode was used during measurements. SO₂ transport was determined by measuring the current as a function of time while a constant potential of 1.2 V was applied using a PARSTAT 2273 electrochemical analyzer. Once the background current stabilized close to zero, SO₂ was introduced into the cell within the left chamber by bubbling. SO₂ permeating through the membrane was oxidized to sulfuric acid by the working electrode. The permeation current increased with time until steady-state conditions are reached and no change in flux is observed. SO₂ transport was measured for a period of 1 h and then analyzed. If the current did not reach a steady state within the first hour, the experiment was continued for an additional hour and then reassessed. The time required to reach steady state is mostly dependent on the equilibration time between the membrane and the liquid electrolyte. Assuming all the SO₂ transported was electrochemically oxidized (r2), the SO₂ flux, J_{SO_2} , can be calculated from the current response using Faraday's Law,

$$J_{SO_2} = \frac{i}{nF} \quad (1)$$

where i is the current density in $A\text{cm}^{-2}$, F is Faraday's constant ($96,487\text{ C equiv.}^{-1}$), and n is the number of electrons transferred. Nafion® 115 and Nafion® 211 were used as baselines for all SO₂

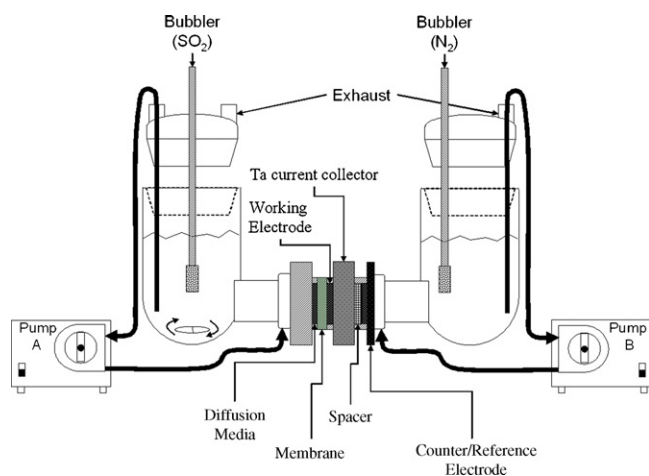


Fig. 2. Simplified schematic of the SO₂ transport characterization cell consisting of two glass chambers joined by a Teflon bridge which houses the membrane, working electrode, and counter/reference electrode.

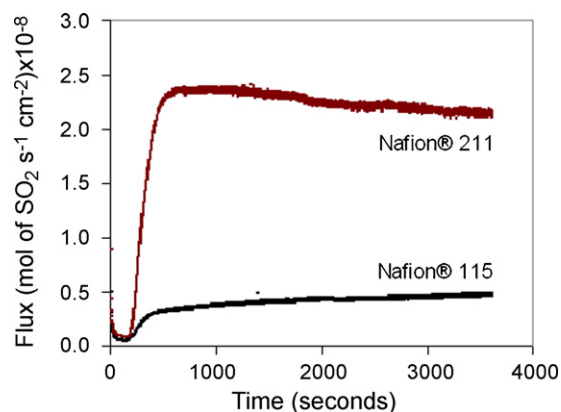


Fig. 3. Measured SO₂ flux for Nafion® 115 and Nafion® 211.

flux and SO₂ transport measurements. A plot of SO₂ flux over time for the two baseline materials is shown as an example, Fig. 3.

The solubility of SO₂ within the membranes is unknown so D , the SO₂ diffusion coefficient, cannot be determined. SO₂ transport can, however, be estimated from Fick's first law of diffusion by substituting the solubility of dissolved SO₂ in the membrane for the bulk SO₂ concentration,

$$SO_2 \text{ transport} = \frac{J_{SO_2} L}{C_0} \quad (2)$$

where J_{SO_2} is the SO₂ flux, L is the thickness of the membrane, and C_0 is the bulk concentration of SO₂ (estimated to be 1.09 M in 30 wt% H₂SO₄ and 0.952 M in 50 wt% H₂SO₄) [3].

2.2.3. Ionic conductivity measurements

The ionic conductivity of each membrane was measured as was the performance in a HyS electrolyzer cell. Membrane Electrode Assemblies (MEAs) were prepared in order to measure these properties. A Paasche Millennium double action airbrush was used for MEA preparation to apply the catalyst "ink" via the spray-deposition technique. Typical catalyst layers consist of 25 wt% Nafion® ionomer as a binder, and 75 wt% platinumized carbon (TKK; 45.9 wt% Pt). Anode and cathode catalyst layers were targeted at 1.8 mg Pt cm⁻² and 0.9 mg Pt cm⁻² respectively. A PARSTAT 2273 potentiostat (Princeton Applied Research) was used for all electrochemical measurements.

Electrochemical Impedance Spectroscopy (EIS) was used to evaluate the ionic resistivity (ρ) for each membrane. For this measurement MEAs were used in a HyS electrolyzer cell to minimize the contact resistance. After allowing the membrane to equilibrate for several minutes, a 10 mV vs. OCP (open circuit potential) sinusoidal voltage was applied across the membrane at frequencies ranging from 500 kHz to 200 Hz. The resulting response was displayed in the form of a Nyquist plot. The resistance was calculated from the value of the real impedance when the imaginary response was zero. The ionic conductivity, λ , was calculated using the following equation:

$$\lambda = \frac{L}{Z_{real} A} \quad (3)$$

where L is the thickness of the membrane, A is the area available for proton conduction, and Z_{real} is the real part of the impedance response when the imaginary impedance is zero.

2.2.4. Electrolyzer performance experimental design

Electrolyzer performance was evaluated in a HyS cell by applying a potential of 1 V across the MEA and measuring the current density over time. The anodic chamber contained 30 wt% H₂SO₄ saturated with SO₂ while the cathodic chamber contained deionized water. Prior to electrolysis both chambers were purged of

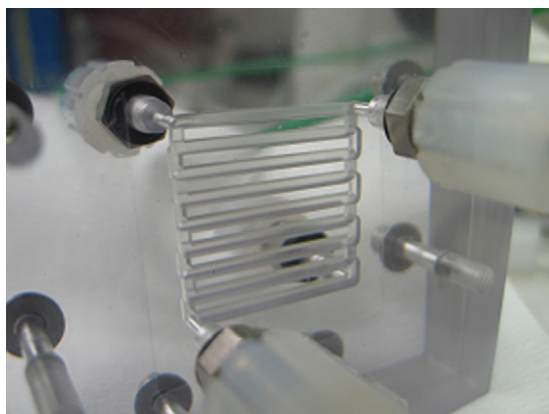


Fig. 4. Polycarbonate test fixture for sulfur formation experiment.

oxygen by flowing argon. A potential of 1 V was then applied. Once the background current stabilized close to zero, SO_2 was introduced into the anolyte by bubbling and the resulting current due to SO_2 oxidation was measured.

2.2.5. Sulfur formation experiment

A piece of Nafion[®] 1135 membrane was placed in a transparent polycarbonate test fixture, Fig. 4, designed to provide flow in strips on both sides of the sample, with reagent paths aligned for cross-membrane reaction testing. For the first experiment, deionized water saturated with SO_2 (Matheson Tri-Gas) was pumped at 2.0 g min^{-1} on one side of the membrane while dry H_2 was passed at 30 mL min^{-1} on the other side for a period of 3 h.

For the second test, water saturated with SO_2 was again pumped at 2.0 g min^{-1} on one side of the membrane using a fresh piece of Nafion[®] 1135. A mixture of N_2 and H_2S was prepared by bubbling N_2 through a solution of deionized water saturated with H_2S (Ricca Chemical, Arlington, TX). This gaseous mixture was passed at 30 mL min^{-1} on the other side of the membrane for a total of one hour. Following testing the membranes were removed from the cell and inspected for any visual change.

3. Results and discussion

3.1. Durability testing

The chemical stability of the membranes in a corrosive environment was examined to provide insight into the potential long-term performance. FTIR spectra taken before and after acid exposure were compared to determine impact on membrane functional groups. It was found that all PFSA type membranes suffered no measurable degradation when exposed to 63.5 wt% H_2SO_4 for 24 h at 80°C . Also, no degradation was observed for SDAPP and S-PFCB samples. A small change in peak intensities was observed in the $800\text{--}1200 \text{ cm}^{-1}$ region for the PBI membrane, Celtec-V, which corresponds to vibrations attributed to the doped acid anions, Fig. 5 [11]. The decrease in intensity of the peak centered at approximately 950 cm^{-1} and the increase in intensity of the peak located at 1100 cm^{-1} may indicate loss of H_3PO_4 from the membrane along with uptake of H_2SO_4 . It has been previously shown that a H_2SO_4 doped PBI membrane has comparable conductivity, depending on doping level, to a H_3PO_4 doped membrane [11,12]. The high electrolyzer performance, both initially and after multiple hours of electrolysis, also suggests that if $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ exchange is occurring, no detrimental impact is apparent. No other spectral shifts are observed for the PBI membrane indicating the polymer backbone is intact.

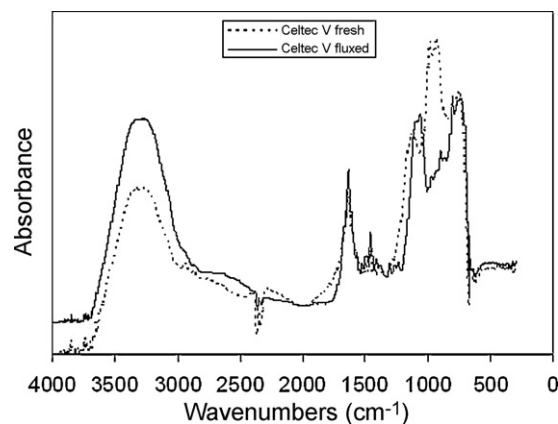


Fig. 5. FTIR spectrum for PBI membrane Celtec-V before (dotted line) and after (solid line) heating at reflux in 60 wt% H_2SO_4 at 80°C for 24 h.

3.2. Membrane transport of SO_2 and electrolyzer performance

SO_2 flux, and SO_2 transport were determined for several commercially available and experimental membranes and tabulated along with membrane thickness in Table 1. Nafion[®] 115, equivalent weight (EW) 1100, is utilized in current HyS electrolyzer testing and, therefore, serves as a baseline for this work. PFSA membranes, developed for low temperature (80°C) PEM fuel cells, are known to have good chemical stability and conductivity, and have shown good performance in a HyS electrolyzer, Fig. 6. However, SO_2 transport is unacceptably high, leading to the formation of sulfur-containing impurities at the cathode and ultimately reduced operational lifetime.

A number of PFSA type membranes were prepared to reduce the transport of small neutral molecules such as SO_2 including: a bilayer of polyfluorinated carboxyl and sulfonic acid, Nafion[®] 1500 EW, and two treated Nafion[®] membranes from Dupont; two treated PFSA membranes from GES; and stretched recast PFSA membranes, and PFSA-FEP blends from Case Western Reserve University. Of the PFSA family of membranes, untreated Nafion[®] had the highest through-plane conductivity (0.0241 S cm^{-1}) and showed the best performance (270 mA cm^{-2}), while having mediocre SO_2 transport ($6.10 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$). Standard deviations for SO_2 flux and SO_2 transport measurements were typically less than 10% while standard deviations for electrolyzer performance was typically less than 2%. The 1500 EW Nafion[®] and the Nafion[®] bilayer had by far the lowest conductivity and performance but also had by far the lowest SO_2 flux and SO_2 transport of any membrane tested. Case 45-55-2, a PFSA-FEP blend, showed promise, having significantly lower SO_2 transport ($1.99 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) than the baseline Nafion[®] 115 ($6.10 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) while having only a small decrease in performance (228 mA cm^{-2} vs. 270 mA cm^{-2}). In general it was noted that most PFSA type samples that had higher conductivities and electrolyzer performance also had higher SO_2 transport, while most samples that had low SO_2 transport also had low conductivity and exhibited poorer electrolyzer performance.

Non-PFSA type membranes were also tested including SDAPP, S-PFCBs, and PBI. SDAPP membranes were originally developed as a low cost alternative to PFSA with improved thermal stability while maintaining good chemical stability, ionic conductivity, and barrier properties to small neutral molecules. Sulfonation of Diels-Alder polyphenylenes results in a membrane that has excellent proton conductivity (0.0328 S cm^{-1}). SDAPP membranes employ the same proton conduction mechanism as PFSA, where sulfonic acid groups generate water channels inside the membrane which solvate and transport protons [7]. The SDAPP membrane performed well in the

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.

Manufacturer and ID	Membrane classification	Thickness (μm)	SO ₂ flux ($\times 10^{-9}$ mol SO ₂ s ⁻¹ cm ⁻²)	SO ₂ transport ($\times 10^{-8}$ cm ² s ⁻¹)	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
Dupont bilayer	Perfluorinated carboxyl/sulfonic acid	140	0.11	0.14	^a	0.010
Dupont 1500 EW	1500 EW PFSA	100	0.14	0.13	^a	0.005
Dupont 112/pvp46	Treated PFSA	50	6.61	3.08	0.0036	128
Dupont 1135/pvp48	Treated PFSA	90	6.01	4.90	0.0064	123
GES 672-90-1	Treated PFSA	127	12.6	14.7		
GES 672-90-2	Treated PFSA	127	10.2	11.9		
Case 1	Stretched PFSA	55	10.5	5.28		
Case 4	Stretched PFSA	63	19.8	11.7		
Case 60-40-2	PFSA-FEP blend	62	5.88	3.35		
Case 50-50-2	PFSA-FEP blend	55	5.96	3.01	0.0034	155
Case 45-55-2	PFSA-FEP blend	53	4.09	1.99	0.0096	228
Sandia SDAPP5192C	SDAPP	50–85	11.1	7.79	0.0328	286
Clemson B(2)	BPVE	18	21.2	3.50	0.0048	320
Clemson B1F1(1)	BPVE-6F (1:1)	16	16.2	2.37	0.0063	337
Clemson B2F1(3)	BPVE-6F (2:1)	19	17.6	3.07	0.0109	335
BASF Celtec-V	PBI	100	2.14	1.99		344

^a Conductivity was too low to measure accurately.

HyS electrolyzer (286 mA cm⁻²), slightly higher than Nafion® 115 (270 mA cm⁻²), however the SO₂ transport was similarly increased (7.79×10^{-8} cm² s⁻¹ vs. 6.10×10^{-8} cm² s⁻¹). Thermal gravimetric analysis indicates SDAPP stability of up to 285 °C where SO₃ cleavage initiates, while DSC indicates a *T_g* well above the decomposition temperature [9]. Future testing will take advantage of this increased thermal stability which is expected to increase HyS electrolyzer performance by decreasing the kinetic overpotential.

Sulfonated perfluorocyclobutyl aromatic ether polymer (SPFCBs) electrolytes were initially developed by Smith and co-workers at Clemson and Tetramer Technologies, LLC, for automotive PEM fuel cells [13,14]. Currently a variety of PFCB polymers and copolymers are under development, including BPVE and BPVE-6F, which are designed specifically for use in a HyS electrolyzer cell with the primary goal of suppressing SO₂ transport. The BPVE membrane, B(2), and BPVE-6F membranes, B1F1(1), and B2F1(3), all displayed high SO₂ flux (21.2, 16.2, and 17.6 mol SO₂ s⁻¹ cm⁻² respectively), however this is mostly a function of their relative thickness, all of which are less than 25 μm (1 mil). The SO₂ transport, which takes the membrane thickness into account, was found to be significantly lower than the baseline material (6.10×10^{-8} cm² s⁻¹) in all 3 membranes (B(2)=3.50, B1F1(1)=2.37, and B2F1(3)= 3.07×10^{-8} cm² s⁻¹) while displaying

increased electrolyzer performance (320, 337, and 335 mA cm⁻² respectively). A comparison to a PFSA membrane of similar thickness like Nafion® 211, however, may be more appropriate. All three BPVE membranes now show reduced SO₂ flux despite being thinner still, and lower SO₂ transport, while their conductivity and electrolyzer performance are somewhat lower than the excellent performance from Nafion® 211 (393 mA cm⁻²). BPVE-6F (1:1) showed the best combination of SO₂ transport, conductivity, and performance and will undergo further testing and development.

The PBI family of membranes were originally developed for phosphoric acid (PA) fuel cells and are known for their ability to operate at elevated temperatures and without humidification [15,16]. Unlike sulfonated membranes (PFSA, SDAPP, BPVE), that employ sulfonic acid groups to transport hydrated protons, PBI membranes employ a hopping mechanism in which immobilized anions, such as PA, can solvate protons whereby providing a path for rapid proton exchange. As a result, protons are conducted without the need of water channels. This can greatly reduce the transport of small neutral molecules, which is reflected in both the measured SO₂ flux (2.14×10^{-9} mol SO₂ s⁻¹ cm⁻²) and SO₂ transport (1.99×10^{-8} cm² s⁻¹), both of which are significantly lower than the baseline membrane. Amazingly, the HyS electrolyzer performance was also increased relative to the baseline (344 mA cm⁻² vs. 270 mA cm⁻²) indicating an effective proton exchange mechanism despite the decreased SO₂ transport. This combination of significantly improved performance and reduction of SO₂ transport make the PBI family of membranes a promising alternative demanding further study.

3.3. Sulfur formation analysis

Sulfur dioxide transport in a HyS cell is an undesirable process which can lead to the formation sulfur-containing contaminants at the cathode. Ideally, all of the reactant is consumed at the anode, but in practice some of the SO₂ is not oxidized, and can be driven across the membrane by diffusion due to the concentration gradient. Once SO₂ has diffused to the cathode it can be reduced to form other sulfur species, including elemental sulfur. Scanning electron microscope (SEM) analysis of MEAs after HyS electrolyzer testing has shown the formation of a sulfur-rich layer at the membrane–cathode interface, Fig. 7 [15].

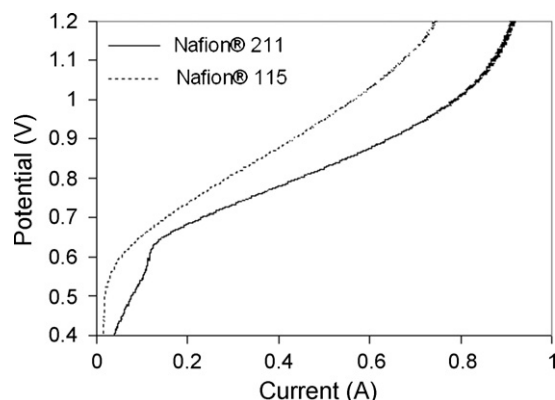


Fig. 6. Polarization curve for Nafion® 115 and Nafion® 211.

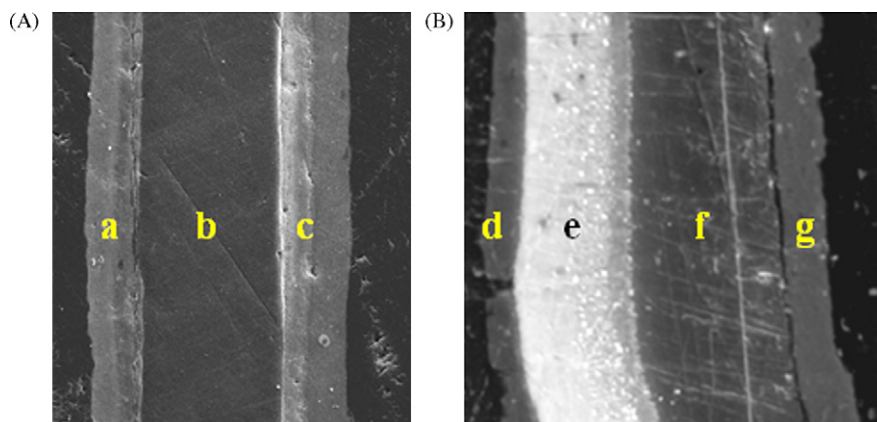


Fig. 7. Cross-section SEM micrograph including EDX of (A) a fresh MEA showing (a) cathode catalyst layer (Pt: 90.5 wt%, C: 7.87 wt%, S: 0.95 wt%, F: 0.68 wt%), (b) membrane (Pt: 8.54 wt%, C: 44.1 wt%, S: 25.14 wt%, F: 22.21 wt%), (c) anode catalyst layer (Pt: 88.34 wt%, C: 9.43 wt%, S: 1.57 wt%, F: 0.66 wt%) and (B) an MEA after 105 h of HyS electrolyzer operation at 80 °C and 4 atm showing (d) cathode catalyst layer (Pt: 54.03 wt%, C: 41.21 wt%, S: 1.66 wt%, F: 3.1 wt%), (e) sulfur layer (Pt: 0.77 wt%, C: 19.63 wt%, S: 75.48 wt%, F: 4.12 wt%), (f) membrane (Pt: 5.23 wt%, C: 53.75 wt%, S: 19.69 wt%, F: 21.32 wt%), (g) anode catalyst layer (Pt: 30.43 wt%, C: 56.32 wt%, S: 6.79 wt%, F: 6.47 wt%).

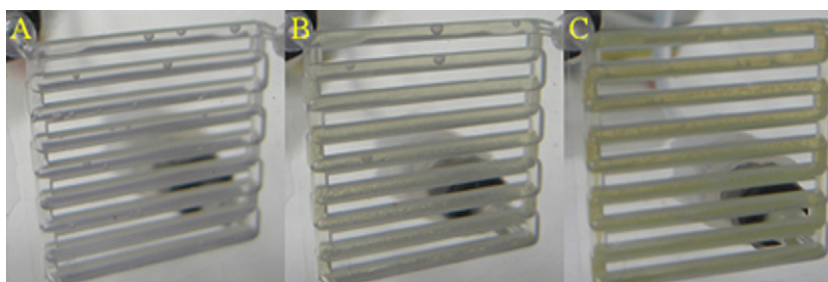


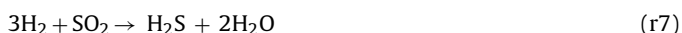
Fig. 8. Polycarbonate flow through cell for cross-membrane reaction testing showing (A) membrane before H₂S was passed through the cell, (B) initial sulfur formation after 5 min of flowing H₂S, and (C) sulfur deposits after 1 h of testing.

An experiment was designed to help elucidate the reaction conditions needed for sulfur formation in the HyS Cell. The first test, where deionized water saturated with SO₂ was pumped on one side of the membrane while H₂ was passed on the other side, resulted in no visible change. No apparent reaction occurred within 3 h of H₂/SO₂ exposure. In the second test, where deionized water saturated with SO₂ was pumped on one side while a mixture of N₂ and H₂S was passed on the other side, resulted in yellow discoloration within 5 min, Fig. 8B, and bulk deposits formed throughout the gas channels and gas exit port within 1 h, Fig. 8C.

Following testing the membrane was removed from the cell and rinsed with deionized water. The gas channel path was evident by yellow stains that were not non-destructively removable, Fig. 9. It is concluded that, for sulfur formation to occur in uncatalyzed regions of the Nafion[®] membrane, the presence of both SO₂ and H₂S is required according to the Claus Reaction (r6) [16] the H₂S presumably produced in appreciable quantities at the HyS cathode by the reduction of sulfur dioxide.

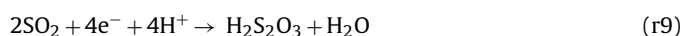
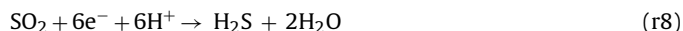


Further studies using this test configuration with platinum catalyst at the hydrogen/PEM interface will be helpful in further elucidating the requirements for sulfur layer formation in the HyS SDE environment. If sulfur layer formation is observed to be rapid when the first experiment (H₂ only, no H₂S) is repeated with catalyst at the hydrogen/PEM interface, then it may suggest that the H₂S implicated in the sulfur formation reaction (r6) is formed by the catalyzed reaction between H₂ and SO₂ (r7).



On the other hand, if the sulfur formation is not fast under these conditions, it would suggest that H₂S or an alternative sul-

fur progenitor (e.g., thiosulfate) may be formed preferentially by an electrochemical step (r8), (r9) exclusive of molecular hydrogen in the operating SDE.



Although the overpotential increase during the initial stage of sulfur layer formation is minimal, the continued expansion of this layer can lead to delamination of the cathode and compression damage to the carbon diffusion media, thus compromising the long-term functioning of the HyS cell. Identification of a membrane

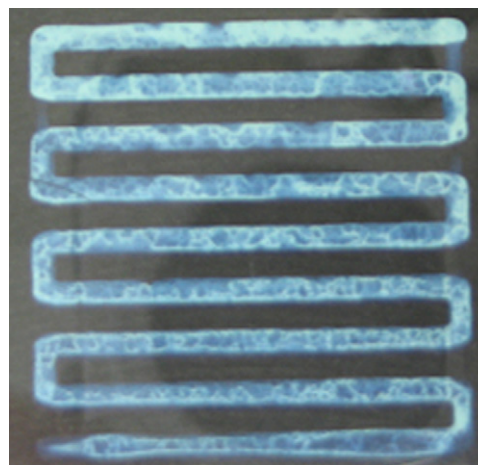


Fig. 9. Photograph of Nafion[®] 1135 membrane after removal from test hardware showing distinct areas of sulfur formation along H₂S flow path.

that limits SO₂ transport while improving or having comparable performance to the current baseline membrane, Nafion® 115, is a primary goal. In addition, the PEM must also be stable in a highly corrosive environment (>30 wt% H₂SO₄ saturated with SO₂) and at high operating temperature (>80 °C) while maintaining high ionic conductivity; thus, the chemical stability, SO₂ transport, ionic conductivity, and electrolyzer performance were all evaluated here.

4. Conclusions

Chemical durability tests showed that all of the membranes exhibited excellent chemical stability in hot, concentrated sulfuric acid solutions. The PBI membrane Celtec-V did show some phosphoric acid-sulfuric acid exchange, which did not appear to negatively impact short term performance in a HyS electrolyzer.

Progress has been made in identifying PEMs that exhibit reduced transport of SO₂. Of the PFSA type membranes, the Dupont bilayer, the 1500 EW membrane, the two treated PFSA membranes from Dupont, and the PFSA-FEP blends from Case Western Reserve University all showed reduced SO₂ transport relative to the baseline membrane Nafion® 115. Of the non-PFSA membranes, BPVE and BPVE-6F from Clemson University, and the Celtec-V PBI membrane from BASF also showed reduced SO₂ transport. Only the BPVE, BPVE-6F, and PBI membranes exhibited increased electrolyzer performance coupled with lower SO₂ transport. The PBI membrane, Celtec-V, exhibited the best combination of performance and SO₂ transport, with a 27% increase in current density and a 67% decrease in SO₂ transport, compared to the baseline membrane Nafion® 115.

It should be noted that all of the non-PFSA type membranes tested were either designed for or should be capable of operating at higher temperatures (PBI < 200 °C, SDAPP < 285 °C, BPVE-6F > 100 °C) than that allowed in the current testing system (80 °C). Future work will involve testing at elevated temperatures (120 °C) and pressures. The increase in operating temperature is expected to decrease the kinetic overpotential loss thereby increasing the electrolyzer performance, for the high temperature membranes, SDAPP, BPVE-6F, and PBI.

Cross-membrane sulfur formation has been investigated. It is concluded that, for sulfur formation to occur in the uncatalyzed regions of the Nafion® membrane, the presence of both SO₂ and H₂S is required. Appreciable quantities of H₂S are presumably produced

at the HyS cathode by electrochemically reducing SO₂, which can then react with excess SO₂ via the Claus Reaction.

Acknowledgements

The authors would like to thank Dennis Curtin (Dupont), BASF, Bob McDonald (Giner), Michael Hibbs (Sandia National Laboratory), Peter Pintauro (Case Western Reserve University), John Wiedner and Brian Benicewicz (University of South Carolina), and Dennis Smith (Clemson University) for their supply of membrane samples, and Scott C. McWhorter (SRNL) for use of the Jasco FT/IR-6300.

This work was funded by the U.S. Department of Energy, Office of Nuclear Energy, Nuclear Hydrogen Initiative. SRNL is operated by Savannah River Nuclear Solutions for the U.S. Department of Energy under Contract DE-AC09-08SR22470.

References

- [1] J. Udagawa, P. Aguiar, N.P. Brandon, *Journal of Power Sources* 166 (2007) 127.
- [2] J.E. Funk, *International Journal of Hydrogen Energy* 26 (2001) 185.
- [3] M.B. Gorenssek, J.A. Staser, T.G. Stanford, J.W. Weidner, *International Journal of Hydrogen Energy* 15 (2009) 6089–6095.
- [4] Westinghouse Electric Corporation, A Study on the Electrolysis of Sulfur Dioxide and Water for the Sulfur Cycle Hydrogen Production Process, AESD-TME-3043, July 1980.
- [5] J.L. Steimke, T.J. Steeper, Characterization Testing of H₂O–SO₂ Electrolyzer at Ambient Pressure, Westinghouse Savannah River Company, Technical Report WSRC-TR-2005-00310, August 1, 2005.
- [6] J.L. Steimke, T.J. Steeper, Characterization Testing and Analysis of Single Cell SO₂ Depolarized Electrolyzer, Washington Savannah River Company, Technical Report WSRC-STI-2006-00120, September 15, 2006.
- [7] K.A. Mauritz, R.B. Moore, *Chemical Reviews* 104 (2004) 4535–4585.
- [8] L. Xiao, H. Zhang, E. Scanlon, L.S. Ramanathan, E. Choe, D. Rogers, T. Apple, B.C. Benicewicz, *Chemistry of Materials* 17 (2005) 5328–5333.
- [9] C.H. Fujimoto, M.A. Hickner, C.J. Cornelius, D.A. Loy, *Macromolecules* 38 (2005) 5010–5016.
- [10] J. Jin, J. Stanbro, D. Van Derveer, D.W. Smith, *PMSE Preprints* 91 (2004) 504–505.
- [11] R. Bouchet, E. Siebert, *Solid State Ionics* 118 (1999) 287–299.
- [12] X. Glipe, B. Bonnet, B. Mula, D.J. Jones, J. RozieAre, *Journal of Materials Chemistry* 9 (1999) 3045–3049.
- [13] K.A. Perry, G.A. Eisman, B.C. Benicewicz, *Journal of Power Sources* 177 (2008) 478–484.
- [14] C.B. Shogbon, J. Brousseau, H. Zhang, B.C. Benicewicz, Y.A. Akpalu, *Macromolecules* 39 (2006) 9409–9418.
- [15] J.L. Steimke, T.J. Steeper, D.T. Herman, H.R. Colon-Mercado, M.C. Elvington Savannah River Nuclear Solutions, Technical Report SRNS-STI-2009-00134, September 15, 2006.
- [16] A. Shaver, H. Boily, A. Lebus, *Inorganic Chemistry* 35 (1996) 6356–6357.