DOE award #	DE-FG02-08ER46501
Title of Project	New fluoroionomer electrolytes with high conductivity and low SO ₂ crossover for use in electrolyzers being developed for hydrogen production from nuclear power plants.
Institution	Department of Chemistry, Clemson University Clemson, SC 29634
Principal-Investigator	Professor Dennis W. Smith, Jr. Department of Chemistry The University of Texas at Dallas Email: dwsmith@utdallas.edu Surrogate PI: Professor Stephen E. Creager Department of Chemistry Clemson University, Clemson, SC 29634 Email: screage@clemson.edu
Start Date	06/ 15/ 2008
End Date	06/14/ 2011
Period covered by report	2008- June 2011
Objectives	<ul style="list-style-type: none"> • Develop optimum fluoroionomer electrolytes, hydrophobic-hydrophilic PFCB block copolymers, for Hybrid Sulfur (HyS) process. • Characterize and analyze thermal properties of polymers and membranes. • Evaluation of the membrane properties (SO₂ cross-over and chemical stability against H₂SO₄) under electrolyzer condition. • Optimize the degree of sulfonation of PFCB polymers and thickness of membrane • Develop highly sulfonated membranes with improved thermal and mechanical properties using cross-linking approach
Accomplishments	<ul style="list-style-type: none"> • Prepared sulfonated hydrophobic-hydrophilic PFCB copolymers with controlled ionic content • Characterized good chemical / thermal stability and hydrophilic channel morphology of membranes • Evaluated MEA performance compared with Nafion family membranes for Hybrid Sulfur process and found less SO₂ crossover and less sulfur build up • Developed cross-linked membranes of highly sulfonated PFCB polymers using Friedel-Crafts acylation method

Introductions

Thermochemical water splitting cycles, using the heat of nuclear power plants, offer an alternate highly efficient route for the production of hydrogen. Among the many possible thermochemical cycles for the hydrogen production, the sulfur-based cycles lead the competition in overall energy efficiency. A variant on sulfur-based thermochemical cycles is the Hybrid Sulfur (HyS) Process, which uses a sulfur dioxide depolarized electrolyzer (SDE) to produce hydrogen. [1-4]

The Savannah River National Laboratory (SRNL), which is leading the electrolyzer component development effort for the Hybrid Sulfur Process, selected the fuel cell MEA design concept for the SDE in the HyS process since the MEA concept provides a much smaller cell footprint than conventional parallel plate technology. The electrolyzer oxidizes sulfur dioxide to form sulfuric acid at the anode and reduces protons to form hydrogen at the cathode. The overall electrochemical cell reaction consists of the production of H_2SO_4 and H_2 . This smaller footprint is a major benefit in scaling the electrolyzer to the size that will be required for commercial production. Key attributes of the SDE are high energy efficiency and long operating lifetime. To achieve high energy efficiency, the electrolyzer must exhibit rapid reaction kinetics at each electrode, little crossover of reagents and products across the membrane, and excellent chemical stability of each of the components to concentrated sulfuric acid solutions. Therefore, the ion conducting proton exchange membrane is a key component of the electrolyzer.

However, commercially available membranes, such as the Nafion[®] family of perfluorinated sulfonic acid membranes have shown excessive transport of sulfur dioxide across the membrane resulting in reduced electrical efficiency and the production of undesirable sulfur-containing byproducts while commercial hydrocarbon type membranes (e.g., sulfonated polyetherketones (SPEKs)), showed good conductivity in water, but quickly degraded when exposed to high sulfuric acid concentrations. Thus, there is a significant need to provide the

membrane materials that exhibit reduced sulfur dioxide transport characteristics without sacrificing other important properties such as high ionic conductivity and excellent chemical stability in highly concentrated sulfuric acid solutions saturated with sulfur dioxide.

As an alternative membrane, sulfonated Perfluorocyclobutyl aromatic ether polymer (sPFCB) were expected to possess low SO₂ permeability due to their stiff backbones as well as high proton conductivity, improved mechanical properties. These sPFCB electrolytes have been developed for automotive PEMFCs by Smith and co-workers at Clemson and Tetramer Technologies, L.L.C. which has provided starting materials for this project. [5-9] The major accomplishments of this project were the synthesis, characterizations, and optimizations of suitable electrolyzers for good SDE performance and higher chemical stability against sulfuric acid. SDE performance results of developed sPFCB polyelectrolytes have shown that these membranes exhibit good chemical stability against H₂SO₄.

Results

Preparation of hydrophilic-hydrophobic block copolymer membranes Sulfonated hydrophilic and hydrophobic copolymers have been developed to study the influence of morphology on PEM applications. Using thermal step-growth [2+2] cyclopolymerization, block copolymers of bis(trifluoro-vinyl ether)biphenyl (BPVE) and bis(trifluorovinyl ether phenyl)hexafluoro-*i*-propylidene (6F) were synthesized (**Scheme 1**) and confirmed by ¹H NMR and ¹⁹F NMR as shown in **Figure 1**.

Scheme 1. Synthesis of PFCB Aryl Ether Block Copolymers

Figure 1. ^1H NMR (in CDCl_3^* , Left) and ^{19}F NMR (in CDCl_3 , Right) spectra of PFCB copolymer.

These PFCB aryl ether copolymers were easily sulfonated via post-sulfonation method (**Scheme 2**). PFCB aryl ether polymers showed outstanding selectivity of sulfonation with chlorosulfonic acid in a mild condition. The ^1H NMR confirmed that sulfonic acid groups were selectively introduced on the BPVE segments as shown in **Figure 2**. This selective post-sulfonation results in hydrophilic-hydrophobic polyelectrolytes with controllable ion content. The degree of sulfonation was optimized by controlling the equivalent of chlorosulfonic acid and confirmed by ^1H NMR and titration (Ion Exchange Capacity (IEC) = 0.8-2.05 meq/g).

Scheme 2. Selective Sulfonation of PFCB Aryl Ether Block Copolymers (Left)

Figure 2. ^1H NMR of Sulfonated PFCB Aryl Ether Block Copolymers (in DMSO, Right)

The membranes of these sulfonated block copolymers were obtained by solution casting. All sulfonated PFCB (sPFCB) polymers gave flexible and tough membranes. The determined molecular weight of unsulfonated polymers and properties of developed membrane (sPFCB1, sPFCB2, and sPFCB3) are summarized in **Table 1**. Homopolymer sample (M1) and copolymer samples (M2 and M3) were provided from Tetramer Technologies, L.L.C.

Table 1. Properties of homo and block copolymers and their membranes

Polymers	Mn ^a (g mol ⁻¹)	Sample Code	IEC ^b (meq/g)	Membrane Thickness (μm)
BPVE Homopolymer	80,000	M1	1.7	18
BPVE-6F (1:1) Copolymer	30,000	M2	0.8	16
BPVE-6F (2:1) Copolymer	70,000	M3	2.0	19
	38,000	sPFCB1	1.54	19
BPVE-6F Copolymer	38,000	sPFCB2	1.85	27
	38,000	sPFCB3	2.05	27

^a GPC data in CHCl₃ using polystyrene standard in Waters 2690 Alliance. ^b Ion Exchange Capacity (IEC) by titration method. All IEC values reported in this work are the average of three titrations

Thermal Properties of PFCB Aryl Ether Polymers and Membranes All of the unsulfonated block copolymers showed high thermal stability and only one transition temperature, 139.16 °C, which indicates their amorphous nature (**Figure 3**). After sulfonation, sulfonated polymers showed three-step weight loss pattern in TGA curve, dehydration, desulfonation, and degradation of polymer backbone as shown in Figure 3. With increase IEC values, the weight loss which is attributed to desulfonation increased accordingly (e.g., from 15 to 18%). Dynamic mechanical analyses (DMA) were performed on sulfonated PFCB membrane samples in air at heating rate of 10 °C/min. The DMA analyses presented glass transition temperatures (T_g) of the sulfonated membranes in the range of 130-220 °C. The sPFCB block copolymer samples exhibited two glass transitions (T_{g1} and T_{g2} , respectively). One transition was observed at T_{g1} of 136-139 °C and the other transition at T_{g2} of 192-196 °C, which are attributable to nonpolar domain and ionic cluster domain respectively. The

appearance of the second glass transition at T_{g2} of ~ 200 °C suggests that hydrophilic and hydrophobic domains have been well separated in the membranes.

Figure 3. (a) TGA curves and (b) DSC thermogram of unsulfonated BPVE-6F copolymer (solid line) and sulfonated PFCB copolymers (dash, dot, and dash dot)

Chemical Stability As sulfuric acid is produced in overall electrochemical cell reaction of Hybrid-Sulfur process, the chemical stability of these membranes were examined in 60 wt (%) of H_2SO_4 at 80 °C for 0-24 h. ATR-IR analysis indicated no degradation of perfluorocyclobutyl aryl ether polymer backbones for both block copolymer and homopolymer, while BPVE homopolymer membranes gave increased intensity at 1030 cm^{-1} corresponding to sulfonic acid group that indicates sulfonation occurred during the chemical stability test. Copolymer membranes were found to be more stable than homopolymer during chemical stability test.

Properties of Membranes in HyS Process Morphology and distribution of different elements was studied and compared for fresh and tested membranes by scanning electron microscope (SEM) analysis and energy dispersive X-ray spectroscopy (EDXS). (**Figure 4**) In cross-section SEM micrograph, morphology of Nafion117 membranes revealed sulfur deposition at the membrane-cathode interface after electrolysis. EDXS mapping data also supports the deposition

of sulfur after testing while uniform distribution of fluorine (F) and sulfur (S) was observed in fresh membranes.

Figure 4. Cross-section SEM micrograph and EDXS of (left) a fresh membrane electrode assembly (MEA) and (right) SO₂ cross-over tested MEA

The conductivity and performance (current density) measurements in HyS process were performed at 1 V, with 30 wt% H₂SO₄ saturated with SO₂ on the anode side, and H₂O on the cathode side using SO₂ transport characterization cell (Figure5). For both test, membrane electrode assemblies (MEAs) were prepared with Pt loading on the anode: 1.8 mg, Pt loading on the cathode: 0.9 mg, Nafion loading: ~25 wt%, and Catalyst for both sides: 45 wt% Pt/C in SRNL. In this process, the hybrid-sulfur electrolyzer consumes sulfur dioxide and water to produce sulfuric acid at the anode and hydrogen at the cathode. All the membranes of homopolymer (M1, $3.50 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) and block copolymers (M3, $3.07 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) showed less SO₂ transport than Nafion 115 ($6.10 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) and Nafion 211 ($5.09 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$). However, all membranes showed lower conductivities than Nafion but gave better current densities than Nafion 115. (Table 2) For high performance SDE material, higher current density

is required. Current density of our membranes ranged from 320 to 337 mA cm⁻², which is better than Nafion 115 as shown in Table 2. [Ref]

Figure 5. Simplified schematic and image of the SO₂ transport characterization cell (SRNL)

Table 2. SO₂ transport (cm² s⁻¹), Conductivity (Scm⁻¹), and Current Density (mA cm⁻²) along with membrane thickness for PFCB membranes and Nafion

Sample Code	Thickness (μm)	SO ₂ transport (cm ² s ⁻¹)	Conductivity (Scm ⁻¹)	Current Density (mA cm ⁻²)
M1	18	3.50 × 10 ⁻⁸	0.0048	320
M2	16	2.37 × 10 ⁻⁸	0.0063	337
M3	19	3.07 × 10 ⁻⁸	0.0109	335
Nafion 115	127	6.10 × 10 ⁻⁸	0.0241	270
Nafion 211	25.4	5.09 × 10 ⁻⁸	0.0159	393

Morphology of BPVE Homopolymer and BPVE-6F Block Copolymer Membranes

Morphology, connectivity and phase separation between hydrophilic and hydrophobic domains was studied by Atomic Force Microscopes (AFM), Figure 6. Domain size and connectivity are both different between the sulfonated BPVE homopolymer and BPVE-6F block copolymer. The block copolymer shows more uniform distribution of channels and co-continuous morphology than homopolymer. This morphology can be responsible for higher proton conductivity and current density as shown in Table 2.

Figure 6. AFM phase images of (a) BPVE Homopolymer (M1) and (b) BPVE-2F (2:1) Block Copolymer Membranes (M3)

Water Uptake, Swelling Ratio, and Proton Conductivity of Membranes The water uptake and swelling ratio of sulfonated PFCB membranes were measured at 25 °C and 80 °C. Sulfonated PFCB membranes presented generally similar characteristics in water uptake and swelling; that is, higher IEC membranes absorbed more water and exhibited greater swelling as shown in Table3.

Table 3. Water Uptake, Swelling Ratio, and Proton Conductivity of sPFCB Membranes along with IEC values

Membrane	Thickness (μm)	IEC (meq/g)	Water Uptake ^a (%)		Swelling Ratio ^b (%)		Conductivity (S/cm)	
			25 (°C)	80 (°C)	25 (°C)	80 (°C)	25 (°C)	80 (°C)
sPFCB1	19	1.54	20	40	7	15	0.0875	0.1684
sPFCB2	27	1.85	25	80	15	30	0.1159	0.2025
sPFCB3	27	2.05	100	320	50	100	0.1160	0.2205
Nafion212	56	0.92	5	50	10	15	0.1490	0.2890

^{a,b} Average values, ^a Calculated by $\text{Water Uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100$, ^b $\text{Swelling Ratio (\%)} = [(L_{\text{wet}} - L_{\text{dry}}) / L_{\text{dry}}] \times 100$ where W_{wet} , W_{dry} , L_{wet} and L_{dry} are the weight and length of hydrated and dry membrane, respectively

The proton conductivities of membranes were estimated from electrochemical impedance spectroscopy (EIS) using Solartron 1280B potentiostat/frequency analyzer (Figure 7). Each end of the hydrated membrane (26×10 mm) was sandwiched between two platinum electrodes and

tightened by clamping in a flame. The EIS was conducted by imposing a 10 mV sinusoidal voltage across the membrane at frequencies between 20 kHz and 200 Hz and the resulting impedance response data was computed by Z-view program. The resistance of the membranes was obtained from the real impedance response plot where the imaginary impedance is zero and the proton conductivity (σ) was calculated with the following equation: $\sigma = L / RdW$, where L is the distance between the electrodes and R is the membrane resistance, d and W are the thickness and width of the samples, respectively.

Figure 7. Simplified schematic of the ionic conductivity characterization cell

Preparation and Properties of Cross-linked Block Copolymer Membranes Highly sulfonated membranes to achieve sufficient proton conductivity showed high water uptake and volume swelling in an aqueous solution. Therefore, cross-linked hydrophilic-hydrophobic block copolymers were prepared to overcome the trade-off between proton conductivity and mechanical strength of hydrated membranes.

The cross-linked S-PFCB membranes were successfully prepared via Friedel-Crafts acylation using bisbenzoic acid type cross-linkers such as 4,4'-oxybis(benzoic acid) (O-BBA) as shown in **Scheme 3**. The cross-linking of S-PFCB polymers were confirmed by solubility test and NMR. The insolubility of the membrane in organic polar solvent, dimethylacetamide (DMAc), indicated that the S-PFCB block copolymer was successfully cross-linked. The ATR-

IR, conductivity and water uptake study was used to characterize these membranes. These membranes exhibited reduced water uptake and volume swelling, compared with those of the uncross-linked counterparts, while maintaining high proton conductivity. (Figure 7 and Table 4) Furthermore, all cross-linked membranes showed less SO₂ transport than uncross-linked membranes.

Scheme 3. Friedel-Craft acylation of sPFCB polymers with bis(benzoic acid)-based cross-linkers.

Figure 7. Before (green) and after (pink) water uptake at room temperature of uncross-linked sPFCB-3 (Left) and cross-linked sPFCB-3 (X-sPFCB) membrane (Right)

Table 4. Thickness (T), degree of cross-linking (DC), water uptake, swelling ratio, proton conductivity and SO₂ transport of sPFCB Membranes

Membranes	T (μm)	DC ^a (%)	Water Uptake (%)		Swelling Ratio (%)		Conductivity (S/cm)		SO ₂ transport ($\text{cm}^2 \text{s}^{-1}$)
			25	80	25	80	25	80	
			(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	
sPFCB1	20	0	23	43	60	82	0.12	0.22	1.90×10^{-8}
X-sPFCB1	24	20	24	34	15	35	0.06	0.13	1.26×10^{-8}
sPFCB3	28	0	100	320	50	100	0.09	0.17	3.99×10^{-8}
X-sPFCB3	24	16	55	155	5	20	0.11	0.18	1.54×10^{-8}
Nafion212	25.4	0	5	50	10	15	0.15	0.28	(Nafion211) 5.14×10^{-8}

^a Degree of cross-linking determined by ¹H NMR

Conclusions A series of PFCB copolymers were successfully synthesized and selective sulfonation of these polymers was carried out under mild condition. With help of base materials from collaborator, Tetramer Technologies, LLC., block copolymer membranes were characterized as comparison with homopolymer membrane. Hydrophilic and hydrophobic phase separation of membranes was confirmed by DMA and AFM. The sPFCB block copolymers exhibited relatively well-controlled phase separation, compared with homopolymer. The IEC, conductivity and acid stability of these block copolymers were better than homopolymer. The less SO₂ cross-over and higher current density were observed in our membranes as compared to Nafion 115 and Nafion 211 which are essential requirements of HyS process. In general, all of results indicate that the sPFCB block copolymers are suitable in use as a proton-exchange membrane. These membranes may find potential usage in the hybrid sulfur process for high-temperature hydrogen production in the next-generation of nuclear power plants.

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Publications/Presentations

1. Jiyoung Park, Neetu Tomar, Rahula Jayasinghe, Hector Colon-Mercado, David Hobbs and Dennis W. Smith, Jr. "Sulfonated Perfluorocyclobutyl (S-PFCB) Aryl Ether Polymers for Proton Exchange Membranes" *Symposium Proceeding of Excellence in Graduate Polymer Research, 241th National Meeting of the American Chemical Society, Anaheim, CA* **2011**.
2. Jiyoung Park, Neetu Tomar, Rahula Jayasinghe, Hector Colon-Mercado, David Hobbs and Dennis W. Smith, Jr. "Preparation and Characterization of Sulfonated Perfluorocyclobutyl (S-PFCB) Membranes for Hydrogen Production" *Polym Prepr (Am. Chem. Soc., Div. Polym. Chem.)* **2010**, *51*, 495.
3. Jiyoung Park, Neetu Tomar, Hector Colon-Mercado, David Hobbs and Dennis W. Smith, Jr. "PFCB Aryl Ether Ionomer Membrane For use in Electrolyzers for H₂ Production" *Proceeding of 19th Annual Meeting of the North American Membrane Society, Charleston, SC, August 22, 2009*.
4. Jiyoung Park, Neetu Tomar, Hector Colon-Mercado, David Hobbs and Dennis W. Smith, Jr. "PFCB Polymer Electrolytes: A Promising Material for Hydrogen Production", *Polym Prepr (Am. Chem. Soc., Div. Polym. Chem.)* **2009**, *50(2)*, 509- 560.
5. Dennis W. Smith, Jr., Jiyoung Park and Neetu Tomar, "New Fluoroionomer Electrolytes With High Conductivity And Low SO₂ Crossover", *Center for Hydrogen Research, SRNL, Aiken, SC, April 20, 2009*.

6. Dennis W. Smith, Jr., Jiyoung Park and Neetu Tomar, “PFCB polyelectrolytes for hydrogen production: new fluoroionomer electrolytes with high conductivity and low SO₂ crossover for use in electrolyzers being developed for hydrogen production from nuclear power plants” *DOE Semi-Annual Meeting, Center for Hydrogen Research, SRNL, Aiken, SC, October 7, 2008*.