

V.O.4 Alternate Fuel Cell Membranes for Energy Independence*

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Contract Number: DE-FG36-08GO88106

Project Start Date: August 1, 2009

Project End Date: January 31, 2011

*Congressionally directed project

Objectives

- Molecular-morphological tailoring and evaluation of novel, low-cost hydrocarbon fuel cell membranes with high-temperature performance and long-term chemical/mechanical durability. This effort supports the Hydrogen Program stated in the Multi-Year Program Plan by developing high-temperature, low relative humidity (RH), high proton conductive membranes for use in polymer electrolyte membrane (PEM) fuel cells – focus is on alternative materials with performance up to 120°C at low RH.
- Synthesis of aromatic hydrocarbon polymers. Organic structure tailoring includes variation of linking moieties between aromatic groups, ion exchange density/distribution, molecular weight and block vs. random copolymers. Three synthetic directions by Storey, Patton, and Savin.
- Fundamental information regarding microstructure and physical properties and correlation using advanced characterization tools (Mauritz, Savin).
- Having identified superior materials and optimized membrane electrode assembly (MEA) processing, the nature/mechanisms of coupled chemical and mechanical degradation and morphological alteration investigated during accelerated ex situ degradation and PEM fuel cell testing (Mauritz).

- Mechanical/chemical/thermal stability of the membranes will be increased over a broad temperature-humidity range. MEAs fabricated from synthesized ionomers and tested for fuel cell performance and durability.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (C) Performance

Technical Targets

- Synthesize bisphenolic comonomers for poly(arylene-ether-sulfone) (PAES) that contain an ion-exchange moiety on a perfluoroalkyl chain tether. Polymerize new comonomers and study membrane conductivity, accelerated degradation, and fuel cell in situ properties. Reproduce known sulfonated poly(arylene-ether-sulfone) (sPAES) benchmark polymers and subject to identical testing. Compare our materials to performance standards established by the DOE.
- Investigate influence of annealing on macromolecular structure, chain dynamics and morphology.
- Knowledge of chemical and mechanical degradation mechanisms and their inter-relationship in membranes.

Accomplishments

- Synthesized/characterized new ion-containing bisphenolic monomer, *N,N*-diisopropylethylammonium 2,2-bis(*p*-hydroxyphenyl) pentafluoropropanesulfonate (HPPS).
- Synthesized PAES copolymers with various ion contents from HPPS, bisphenol (BP), and bis(4-fluorophenyl)sulfone (FPS). Molecular weight, polydispersity index, copolymer composition characterized with nuclear magnetic resonance (NMR) and gel permeation chromatography. Thermal properties characterized with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).
- Developed chemistry for synthesis of triazole tethers and postmodification of PAES backbones.

- Initial studies of poly(perfluoropropylene oxide)-b-poly(styrene sulfonate) (PFPO-PSS) model copolymers and extended to use novel proton conducting blocks.
- Determined equivalent weights, proton conductivities of sPAES membranes.
- Generated water vapor pressure isotherms for sPAES membranes.
- Established thermal degradative stabilities and T_g s of sPAES membranes using dynamic mechanical analysis (DMA).
- Uncovered molecular motions in, monitored kinetics of formation of sPAES membranes using broadband dielectric spectroscopy.



Introduction

The scope is a vertically-integrated project of synthesis-characterization-evaluation of novel hydrocarbon fuel cell membranes for high-temperature performance with excellent durability. While we continue research performed in Fiscal Year (FY) 2008 and FY 2009, the synthetic scope is broadened. The basic theme is continued which is synthesis of polymers of the PAES or poly(arylene ether ketone) type, containing ion exchange groups, e.g., sulfonic or phosphonic acid, tethered to the backbone via perfluorinated alkylene linkages. In the renewal grant, new structural variations are examined, e.g., nature of the attachment point of tether to backbone, tether length, tether branchiness, number of ion exchange sites at a comonomer. Use of N-based heterocyclics instead of acid groups for proton conduction broadens the synthetic scope. Polymer backbones will also be of the PAES and poly(arylene ether ketone) type. Use of nitrogen-based heterocyclics is proposed for high-temperature, low-RH membranes that combine high mechanical/thermal/chemical stability of aromatic hydrocarbon polymers with pendant moieties that exhibit high proton conductivities in the absence of water.

In a second new theme that broadens the synthetic scope, block copolymers will be synthesized via coupling reactions between a proton conducting block, including any of the aromatic hydrocarbon polymers discussed above and acidic polymers. Phase behavior will be mapped vs. block composition using

transmission electron microscopy (TEM), atomic force microscopy (AFM), small angle X-ray scattering (SAXS). Synthesized materials will be characterized for proton conductivity and mechanical/chemical/thermal stability over broad temperature and RH ranges using a variety of spectroscopic, dielectric, microscopic and viscoelastic methods and evaluated for performance in fuel cells.

Approach

There are three synthetic directions in the project (Storey, Patton and Savin). Storey will synthesize bisphenolic comonomers that contain one or two ion-exchange moieties connected through perfluoroalkyl tethers and copolymerize them with bisphenol and FPS to create PAES. Patton will synthesize N-heterocycle (i.e. 1H-1,2,3-triazoles) containing tethers that will be installed on PAES backbones via a post-polymerization functionalization approach. Savin will synthesize block copolymers containing proton conducting blocks (PSS) with perfluoroether blocks (PFPO) using a modular coupling approach.

Fundamental information is gathered regarding microstructure, physical properties and how they are related using advanced characterization tools by Mauritz and Savin. Having identified superior membranes and optimized MEA processing, the nature/mechanisms of coupled chemical-mechanical degradation and morphological alteration will be investigated during accelerated ex situ chemical degradation and PEM fuel cell testing by Mauritz.

Results

We synthesized the ion-containing bisphenolic monomer, HPPS, in three steps from hexafluoroacetone. A monomer structure was confirmed using NMR and X-ray. HPPS was copolymerized with BP and FPS to form a series of PAES with the general structure shown in Figure 1 and specific compositions as shown in Table 1.

We successfully synthesized a series of model tethers with terminal triazole moieties. Intermediate alkynyl bromides (**1**) were prepared by phase transfer catalyzed alkylation of propargyl alcohol with excess of appropriate dibromoalkanes (3 equivalent) to minimize bis-alkylation products. Copper-catalyzed 1,3-dipolar cycloaddition of **1** with (2-azidomethoxyethyl) trimethylsilane gave terminal N-protected triazole

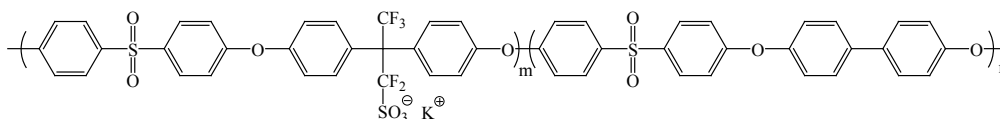


FIGURE 1. Copolymers derived from HPPS, BP, and FPS Monomers

TABLE 1. Comonomer Charge Amounts and Copolymer Yield for Copolymerizations

Copolymer	FPS		HPPS		BP		Copolymer Yield (g)
	(g)	(mmol)	(g)	(mmol)	(g)	(mmol)	
PEAS-20	0.7943	3.1240	0.3205 ^a	0.6008	0.4563 ^b	2.4675	1.23
PEAS-31	0.7873	3.0965	0.4818 ^a	0.9031	0.3976 ^b	2.1501	1.32
PEAS-40	0.7777	3.0588	0.6401 ^c	1.2060	0.3380 ^d	1.8006	1.47
PEAS-49	0.7775	3.0580	0.8003 ^c	1.5078	0.2817 ^d	1.5007	1.53
PEAS-61	0.7797	3.0666	0.9647 ^c	1.8176	0.2257 ^d	1.2023	1.59

Purity of monomers back-calculated from polymerization degree: ^a 98.9%; ^b 100.7%; ^c 99.4%; ^d 99.2%

alkylbromides (**2**). De-protection of **2** under acidic conditions gave the terminal 1*H*-1,2,3-triazole alkylbromide in near-quantitative yields. These model tethers will be used for modification of PAES polymer backbones to achieve N-heterocycle containing polymers for membrane fabrication.

Optimal reaction conditions were determined for modular coupling of PFPO and polystyrene with five varying molecular weight and block ratios. Successful coupling was verified using light scattering. A sulfonation protocol was determined using acetyl sulfate under dilute conditions and successful sulfonation to afford PFPO-PSS was demonstrated using light scattering. Initial studies were performed using DSC and AFM to determine thermal transitions and thin film morphology.

EW, water vapor pressure isotherms and proton conductivities were determined for sulfonated (s) PAES and HPPS membranes and conductivities are low. Thermal degradation was studied using TGA. Glass transitions related to upper fuel cell operating temperature were identified for HPPS variants using DMA. Thermal degradation occurs immediately after the glass transition temperature (T_g). Sub- T_g relaxations can be related to physical durability in RH cycling. Evolving macromolecular motions in sPAES and HPPS were monitored in real time as kinetics of film formation was tracked using BDS. Figure 2 shows ion viscosity (IV) vs. film formation time for HPPS and sPAES samples and 2-step processes and gelation asymptotes are seen. BDS was used to study drying of these materials.

Conclusions and Future Directions

- Synthesized PAES block copolymers from HPPS, BP, and bis(4-fluorophenyl)sulfone.
- Synthesized ion containing bisphenol monomers with two tethered sulfonate moieties per bisphenol monomer unit and longer perfluorinated tethers for enhanced H^+ conduction.
- Synthesized N-heterocycle aromatic polymer.

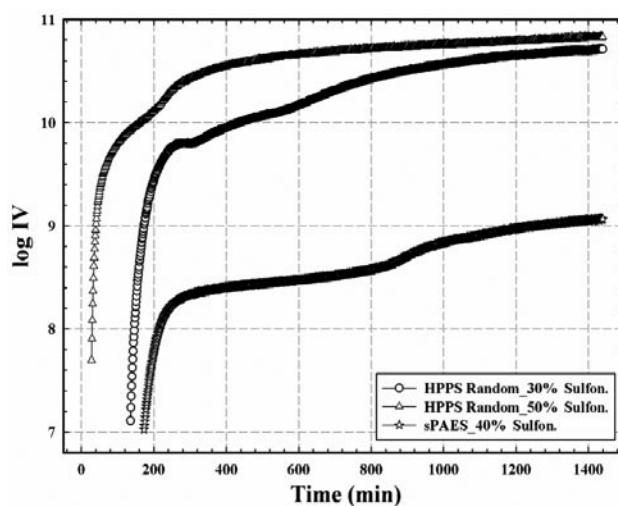


FIGURE 2. Kinetics of Membrane Film Formation from DMAc Solution via Sensor-Based, Real-Time Broadband Dielectric Spectroscopy

- Evaluated thermal properties/conductivity of 1,2,3-triazole tethered polysulfone vs. composition.
- Synthesize other compositions for model PFPO-PSS block copolymers and characterize morphology using TEM, AFM and SAXS
- Incorporate of other proton conducting blocks with PFPO using our modular approach: PBI, poly(arylene ester sulfones).
- Test membranes synthesized by Storey, Patton and Savin with BDS from -80 to 300°C; determine T_g and sub- T_g molecular motions relating to proton conductivity, high temperature stability and chemical and mechanical degradation (durability).
- Samples will be tested with 100% of either hydrophobic or hydrophilic blocks to assign broadband dielectric spectroscopy transition peaks in block copolymers.
- In situ annealing experiments will be conducted at temperatures from 80 to 140°C to obtain information on shifts in macromolecular dynamics and nature of water desorption during high temperature fuel cell operation.

- Generate water vapor pressure isotherms to correlate broadband dielectric spectroscopy results with water content.
- Perform complementary DMA-RH studies.

FY 2010 Publications/Presentations

Publications

1. Patil, Y.P.; Sambandam, S.; Ramani, V.; Mauritz, K.A. *J. Electrochem. Soc.*, Vol. 156, Issue 9, B1092. 2009.
2. Hassan, M.K.; Mauritz, K.A. *Electrochem. Soc. Transactions* Volume 25: Proton Exchange Membrane Fuel Cells. September 2009.
3. Patil, Y.P.; Mauritz, K.A. *J. Appl. Polym. Sci.* 113: 3269, 2009.
4. Patil, Y.P.; Kulkarni S.; Mauritz, K.A. *J. Appl. Polym. Sci.*, accepted (Sep-2009).
5. Patil, Y.P.; Jarrett, W.L.; Mauritz, K.A. "Deterioration of mechanical properties: A cause for fuel cell membrane failure," *J. Membrane Sci.* In Press.
6. Hassan, M.K.; Mauritz, K.A. "Broadband Dielectric Spectroscopic Studies of Nafion®/Silicate Membranes;" ACS Book series, A Herring and S. Hamrock, Eds. 2010.

Presentations

1. A.D. Baranek, S.A. Suggs and D.L. Patton "Synthesis of Tethered Triazole Poly(aryl ether sulfones) Toward High Temperature, Low Humidity Proton Exchange Membranes" ACS San Francisco POLY Division 2010.
2. Y.P. Patil and K.A. Mauritz, PMSE-121, Am. Chem. Soc. 238th Natl. Meet, PMSE Prepr. 121, Aug. 16-20, 2009, Washington, DC (2009).
3. Y.P. Patil, S. Kulkarni and K.A. Mauritz, FUEL-046, Am. Chem. Soc. 238th Natl. Meet. Fuel Prepr. 046, Aug. 16-20, 2009, Washington, DC.
4. K.A. Mauritz,; Hassan, M.K.; Rhoades, D.W. 216th Electrochem. Soc. Meet. Vienna, Austria 4-9 Oct. 2009.