

V.D.16 Alternate Fuel Cell Membranes for Energy Independence*

Kenneth A. Mauritz (Primary Contact),
Robson F. Storey

University of Southern Mississippi
118 College Drive #10076
Hattiesburg, MS 39406
Phone: (601) 266-6298; Fax: (601) 266-5635
E-mail: Kenneth.Mauritz@usm.edu

DOE Technology Development Manager:
Dimitrios Papageorgopoulos

Phone: (202) 586-5463; Fax: (202) 586-2373
E-mail: Dimitrios.Papageorgopoulos@ee.doe.gov

DOE Project Officer: Lea Yancey

Phone: (303) 275-4944; Fax: (303) 275-4753
E-mail: Lea.Yancey@go.doe.gov

Contract Number: DE-FG36-08GO88106

Project Start Date: August 1, 2009

Project End Date: January 31, 2011

*Congressionally directed project

Technical Barriers

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

- (B) Cost
- (C) Performance

Technical Targets

- Synthesize novel membrane polymers and fabricate membrane electrode assemblies (MEAs).
- Achieve DOE area specific resistance goals.
- Attain good MEA performance in fuel cells.
- Attain good MEA operation at higher temperature (>100°C).
- Investigate physical and chemical durability (ex situ and fuel cell - in situ accelerated and long term tests, including relative humidity [RH] and temperature cycling).
- Identify MEA degradation mechanisms.
- Low-cost membranes.

Objectives

- Combine desirable qualities of Nafion[®] and sulfonated poly(arylene ether sulfone) (sPAES) polymers in new comonomers for use in proton exchange membrane fuel cells (PEMFCs).
- Develop synthetic strategies for sPAES comonomers containing perfluoroalkyl sulfonic acid moieties using fairly inexpensive and readily available reagents.
- Reproduce existing sPAES polymer membrane forms and establish benchmark data regarding performance and durability against which the novel membranes will be prepared.
- Compare fuel cell performance of our new comonomer membranes with Nafion[®] benchmark performance data.
- Understand the coupling between hydration microstructure, proton migration and morphology at temperatures above 100°C for Nafion[®] benchmark membranes.
- Establish the same for novel synthesized membranes and correlate results with membrane performance at high temperatures.
- Perform accelerated fuel cell in situ studies of membrane degradation.
- Affect inorganic oxide in situ modification of Nafion[®] membranes to improve performance and durability and apply improvements to novel membranes.

Accomplishments

- Synthesis of 2,2-bis(*p*-hydroxyphenyl) pentafluoropropanesulfonic acid, a fluorinated bisphenolic comonomer devoid of aliphatic hydrogen atoms.
- Sulfonation of bis(4-chlorophenyl) sulfone.
- Generation of sPAES polymers using established synthetic sequences
- Changes in macromolecular relaxation and conduction processes in Nafion[®] membranes upon annealing at temperatures above 100°C were identified. Conclusions from this study are useful in explaining drop in performance of Nafion[®] in fuel cells at high temperatures.
- Discovered that membrane degradation severely reduces modulus, ductility and ability to withstand stress, as related to stresses generated from humidity and temperature changes in actual fuel cells.



Introduction

PEMFC research and development has been highly influenced by Nafion[®] membranes despite their shortcomings. Nafion[®]'s perfluorinated chemical

structure of renders it relatively resistant to chemical attack and beneficially increases the acidity of sulfonic acid groups. Although Nafion[®] remains the benchmark against which PEM performance is measured, it is expensive and exhibits undesirable mechanical durability. It suffers from a moderate glass transition temperature, which reduces mechanical durability during operation in a fuel cell; swelling - de-swelling upon RH cycling causes crack and pinhole formation leading to fuel crossover. Membrane performance suffers greatly around and above 100°C owing to dehydration. The objective is to engage in the fine molecular tailoring and evaluation of novel hydrocarbon membranes that overcome these problems in PEMFCs. This project aims to develop aromatic copolymers that should (1) exhibit enhanced chemical and mechanical durability over a broad temperature and humidity range, (2) have high proton conductivities at high temperatures and low humidity, and (3) be synthesized from readily available and inexpensive materials.

In this work we will characterize the synthesized novel membranes for structure, viscoelastic properties (and within the context of mechanical degradation), macromolecular chain dynamics, proton conductivity, accelerated ex and in situ degradation and fuel cell performance. To improve membrane durability, mechanical and barrier properties will be adjusted by polymer in situ sol gel processes for metal alkoxides.

Approach

To achieve these objectives, sPAES polymers will be synthesized using nucleophilic aromatic substitution to link successive aromatic moieties via oxidatively resistant groups *e.g.*, ether, carbonyl, sulfone, and hexafluoroisopropylidene. Copolymerization of sulfonic acid-containing monomers will be pursued in preference to post-polymerization sulfonation. To enhance the performance of known sPAES polymers used in PEMFCs, new bisphenolic comonomers containing ion-exchange moieties on a perfluorinated alkyl tether will also be synthesized.

Membrane chain dynamics, thermal transitions and conductivity aspects are explored using a broadband dielectric spectrometer with samples being tested between parallel plate electrodes. The real and imaginary components of the complex dielectric permittivity were determined over a range of frequencies and temperatures. Relaxation times and their distributions are extracted from the data. Viscoelastic/mechanical testing (stress-strain, creep, dynamic mechanical modes) is performed using a material test system device. Nafion[®] membranes are degraded under open circuit voltage conditions at 90°C, 30% RH for 45 and 72 h. A control Nafion[®] MEA was fabricated using Vulcan XC-72 carbon black and was subjected

to identical ink making and decal transfer process but was not assembled in a fuel cell. Some samples were degraded ex situ in Fenton's reagent.

Results

A bisphenolic comonomer, 2,2-bis(*p*-hydroxyphenyl)pentafluoropropanesulfonic acid, has been synthesized using hexafluoroacetone, sulfur trioxide, and phenol as building blocks. Hexafluoroacetone rapidly reacts with triethyl phosphite at -60°C to form the vinyl ether reagent, EtO(CF₃)C=CF₂ in good yields [1]. Fluoro-olefins are electron deficient and poor nucleophiles necessitating the use of liquid sulfur trioxide as a sulfonating agent. Addition of SO₃ to the vinyl ether reagent at -15°C creates a mixture of ethyl 2-ketopentafluoropropane sulfonate and the desired 2-ketopentafluoropropanesulfonic acid [2]. Conversion of the ester to the desired acid can be achieved via transesterification with excess trifluoroacetic acid. 2-ketopentafluoropropanesulfonic acid readily reacts with two equivalents of phenol to generate, 2,2-bis(*p*-hydroxyphenyl)pentafluoropropanesulfonic acid, which is isolated as a pyridinium or alkali metal salt [3]. This condensation reaction is self-catalyzed by the strong sulfonic acid reagent.

Synthesis of sPAES has continued for use in collecting benchmark data and to gain knowledge that will be applied to the synthesis of our novel copolymer. Recently a batch of sPAES was prepared and characterized by nuclear magnetic resonance to determine the percent sulfonation and the number average molecular weight. The percent sulfonation was determined to be 23.3% and the molecular weight was found to be 30,300 g mol⁻¹. The spectra also showed that a portion of the endgroups were composed of unreacted bisphenolic comonomer. This was attributed to addition of an insufficient amount of 3,3'-disulfonated 4,4'-dichlorodiphenyl sulfone monomer leading to unreacted phenolic endgroups in the copolymer.

Although reaction to form the sulfonated monomer has been successful, its isolation as a pure compound free of inorganic salts has been difficult, which in turn has caused difficulty in accurately charging the prescribed molar quantity into the polymerization reactor. Although the polymerization was slightly off-stoichiometric, the resulting polymer could be cast into tough films from a dimethyl acetamide solution.

Dielectric spectroscopy. Broadband dielectric spectroscopy (BDS) was used to investigate real time coupling between macromolecular motions and the proton conduction process in Nafion[®] membranes during annealing at temperatures above 100°C in the instrument. These studies will set the stage and provide benchmark data for similar investigations of our novel hydrocarbon membranes.

In Figure 1 are α and β relaxation time (τ) shifts with annealing time (t) at 140°C. This high temperature was chosen so that the α transition is on-scale. The β relaxation is attributed to long range backbone motions within an electrostatic network and the α relaxation involves the same but as influenced by disruption of polar aggregates that become dynamic [4]. The increase in each τ with increasing t indicates slower motions attributed to progressive water loss that decreases free volume. Polar domains dehydrate faster as seen in the more rapid increase in τ_α and the lesser increase in τ_β is rationalized in terms of the Yeager-Steck view of mixed interphases in which water is incorporated to a degree [5]. It would be important to determine relaxation times for both relaxations for annealing at other temperatures >100°C to compare the activation energies of each.

A parameter N , a coarse degree of connectivity of proton pathway networks, was derived and its behavior with regard to annealing time and relationship to conductivity was determined.

BDS was used to study chemical degradation (in Fenton reagent) on chain motions and meaningful correlations were established; degraded membranes showed a split in the β relaxation which might reflect chains with different lengths.

Mechanical properties of degraded MEAs. Tensile properties at 80°C and 100% RH were measured by stretching control and degraded MEAs at 5 mm/min. Stress-at-break for 45 and 72 h degraded MEAs is 6 and 9 times lower while strain-at-break is 24 and 28 times lower, respectively, than that of the control. Modulus reduction due to decrease in molecular weight resulting from suggests that the membrane can easily deform under stress and rupture and pathways for fuel crossover – that leads to radical attack – can form. Figure 2 shows scanning electron microscope (SEM) images of control and degraded MEAs subjected to 10 MPa creep for 3 h

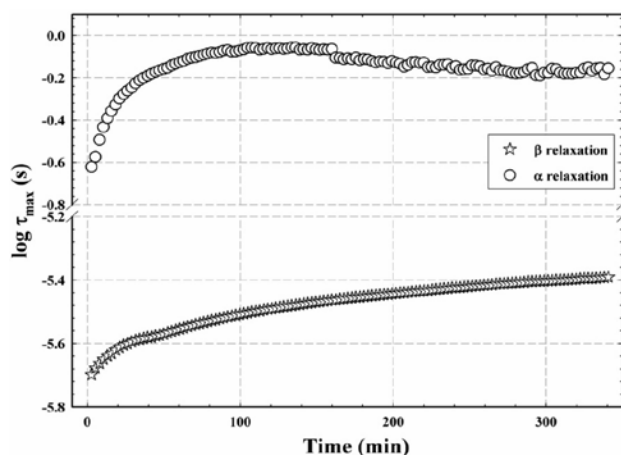


FIGURE 1. Nafion® β and α Relaxation Times vs. Time of Annealing at 140°C

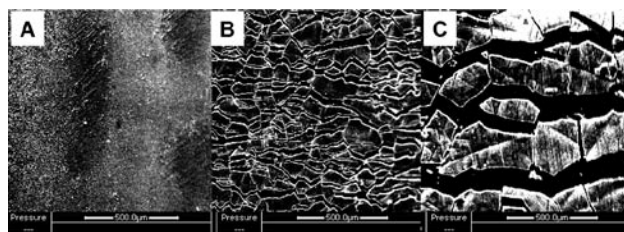


FIGURE 2. SEM Micrographs of Surfaces of (A) Control, (B) 48 h Degraded and (C) 72 h Degraded Nafion® MEAs After Creep Tests

at 80°C. Degraded MEAs developed cracks in response to applied stress. Cracks for 72 h degraded are wider than those for 45 h degraded MEAs due to reduced ductility of the former. No huge cracks were observed for the control although there was crazing associated with large scale deformation.

Conclusions and Future Directions

- Continue our synthetic strategies concerning development of new bisphenolic comonomers containing ion-exchange moieties attached to perfluoroalkyl tethers. Optimization of the synthesis of 2,2-bis(*p*-hydroxyphenyl) pentafluoropropanesulfonic acid will allow for use of this comonomer in polymerization reactions to create new SPAES polymers for fuel cell membranes. Additionally, we envision employing similar chemical methods described above to create a library of analogous compounds.
- BDS revealed macromolecular dynamics and nature of proton hopping pathways vs. time of annealing Nafion® at a high temperature above the α transition.
- BDS also revealed shifts in macromolecular dynamics in chemically degraded Nafion®.
- Preliminary mechanical deformation studies of Nafion® MEAs suggest significant deterioration in structure and properties over time in a fuel cell.
- Future directions include, for novel membrane materials: (1) BDS characterization of macromolecular motions and thermal transitions in the context of high T_g , high temperature fuel cells; and (2) BDS in situ real time investigations of membrane annealing and drying processes as related to equilibrium morphology attainment and high temperature stability and water retention. Viscoelastic investigations of the novel synthesized membranes will be conducted as related to mechanical durability in RH cycling in fuel cells.
- Membranes will be inorganically modified by the in situ sol-gel technique for metal alkoxides and the effect of these modifications on membrane performance and durability will be investigated.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review - Arlington, VA 18 May 2009. Presentation FC# 10.
2. K.A. Mauritz, Presentation: Polymer Membranes for Fuel Cells, C.A. Wilkie Ret. Symp, Marquette University, 6 Jun 2009.
3. M.K. Hassan and K.A. Mauritz, Broadband Dielectric Spectroscopic Studies of Nafion[®]/Silicate Membranes, ACS Symposium Series, 2009, submitted.
4. K.A. Mauritz and M.K. Hassan, Broadband Dielectric Spectroscopic Studies of Annealed Nafion[®] Membranes, ECS Transactions, 2009, accepted.

References

1. Wiley, D.W.; Simmons, H.E. *J. Org. Chem.* **1964**, *29*, 1876.
2. Krespan, C.G.; Smart, B.E.; Howard, E.G. *J. Am. Chem. Soc.* **1977**, *99*, 1214.
3. Krespan, C.G. *J. Org. Chem.* **1979**, *44*, 4924.
4. S.J. Osborn, M.K. Hassan, G.M. Divoux, D.W. Rhoades, K.A. Mauritz, R.B. Moore, *Macromolecules*, **40**, 3886 (2007).
5. H.L. Yeager and A. Steck, *J. Electrochem. Soc.*, **128**, 1880 (1981).