

V.K.2 Alternate Fuel Cell Membranes for Energy Independence*

Robson F. Storey (Primary Contact),
Daniel A. Savin, Derek L. Patton
The University of Southern Mississippi
118 College Drive #5050
Hattiesburg, MS 30406
Phone: (601) 266-4879
Email: Robson.Storey@usm.edu

DOE Managers

HQ: Dimitrios Papageorgopoulos
Phone: (202) 586-5463
Email: Dimitrios.Papageorgopoulos@ee.doe.gov
GO: David Peterson
Phone: (720) 356-1747
Email: David.Peterson@go.doe.gov

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blocks composed of *N,N*-diisopropylethylammonium 2,2-bis(*p*-hydroxyphenyl)pentafluoropropanesulfonate (HPPS) and 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (sDCDPS).

- Introduce amphiprotic 1-H-1,2,3-triazole moieties onto side chains into poly(arylene ether sulfone) (PAES) to provide PEMs that can operate at high temperatures and low humidity.
- Prepare poly(perfluorinated propylene oxide) (PFPO)-sPAES block copolymers to serve as strongly segregated model systems to explore morphology-proton conductivity relationships.
- Prepare membranes from selected polymers above and measure water uptake, conductivity, mechanical properties, accelerated degradation, and fuel cell in situ properties. Compare properties to performance standards established by the DOE.

FY 2012 Accomplishments

- Two sPAES multi-block copolymers were prepared, with hydrophilic blocks consisting of HPPS and sDCDPS monomer units and hydrophobic blocks consisting of 4,4'-biphenol (BP) and 4,4'-dichlorodiphenylsulfone (DCDPS) monomer units, designated MB-1 and MB-2.
- 4-Fluorophenylsulfonyl-terminated PFPO was prepared and successfully chain coupled in a model reaction with hydrophobic PAES blocks.
- Comparison of fuel cell performance and mechanical properties, under fuel cell operating conditions, of PAES-based multiblock membranes showed improvement in variables affecting mechanical durability and performance, relative to baseline materials.



Fiscal Year (FY) 2012 Objectives

- Synthesize novel, low-cost hydrocarbon fuel cell membrane polymers with high-temperature performance and long-term chemical/mechanical durability.
- Investigate fundamental structure-property relationships of these polymers.
- Identify superior membrane materials and optimize membrane electrode assembly (MEA) processing.
- Investigate the nature and mechanisms of coupled chemical and mechanical degradation during accelerated ex situ chemical degradation and in situ proton exchange membrane (PEM) fuel cell testing.

Technical Barriers

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

- (B) Cost
- (C) Performance

Technical Targets

- Develop sulfonated poly(arylene ether sulfone) (sPAES)-based multi-block copolymers possessing hydrophilic

Introduction

Ours is a vertically-integrated project of synthesis, characterization, and evaluation of novel hydrocarbon fuel cell membranes for high temperature performance with excellent durability. The synthetic effort seeks to produce PEMs based on aromatic hydrocarbon polymers of the PAES type, containing ion exchange groups, which in some cases are tethered to the backbone via perfluorinated alkylene linkages. Both protic (sulfonic acid-based) and amphiprotic (nitrogen-containing heterocyclic-based) resin types are being explored. In addition, we are exploring block copolymers, created via coupling reactions between PFPO and a proton-conducting block, including any of the aromatic hydrocarbon polymers discussed above and optionally

other polymers that are ionic or polar. Some synthesized membranes have been inorganically modified using domain-targeted sol-gel polymerization schemes to impart greater hydration, increased mechanical durability and reduced fuel crossover.

The synthesized materials have been characterized within the context of proton conductivity and mechanical/chemical/thermal stability over a broad temperature and humidity range using a variety of spectroscopic, dielectric, microscopic, and viscoelastic methods, and evaluated for proton conductivity and performance in operating fuel cells.

Approach

In the past year, much of the synthetic effort was phased out in favor of polymer characterization, ex situ properties measurements, and MEA fabrication and testing. The exception was sPAES-based multi-block copolymers containing HPPS and sDCDPS.

Results

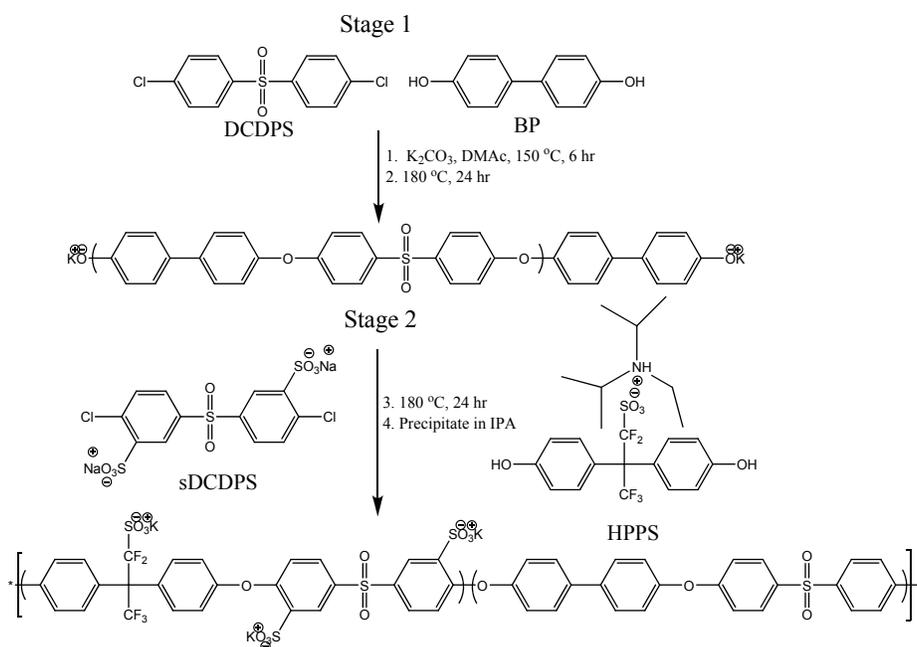
PAES polymers based on HPPS and sDCDPS. We synthesized PAES multi-block copolymers with hydrophilic block composed of HPPS and sDCDPS, using a two stage reaction sequence (one-prepolymer method). The monomers BP and DCDPS were used to synthesize phenoxide-terminated hydrophobic prepolymers in the range of 5,000 -15,000 g/mol. HPPS and sDCDPS were then added to the reaction to increase the molecular weight and incorporate hydrophilic sequences in the polymer (Scheme 1).

Two block copolymers of this type were prepared, designated MB-1 and MB-2. Table 1 lists ion exchange capacity (IEC), conductivity, molecular weight (gel permeation chromatography, GPC), and composition of these two materials. As reported below, we observed improved water uptake and conductivity performance in these PAES-based block copolymers compared to recently published block copolymers [1], which contained HPPS but not the combination of HPPS and sDCDPS.

TABLE 1. Characterization Data for Multi-Block sPAES Copolymers MB-1 and MB-2

Multi-block sPAES	IEC (meq/g)	Conductivity mS/cm	M _n (g/mol)	M _w (g/mol)	wt% hydrophilic block
MB-1	1.68	49.9	18,550	27,330	23
MB-2	1.08	2.2	25,120	35,170	49

We also explored an alternate, two-prepolymer synthetic method toward PAES-based block copolymers with hydrophilic blocks composed of HPPS and sDCDPS. Early efforts to couple the blocks by reaction of a terminal phenoxide with a terminal aromatic chloride were unsuccessful. We attributed this to the low reactivity of the aromatic chloride, since coupling reactions involving an aromatic fluoride have proven successful [1,2]. Therefore, we adopted a strategy that would allow coupling to take place using an aromatic fluoride. First, hydrophilic prepolymers carrying phenoxide end groups were synthesized from sDCDPS and HPPS. Then, hydrophobic prepolymers carrying aromatic fluoride functions were prepared in a



SCHEME 1. Synthesis of PAES based multi-block copolymers

two-step procedure. First, DCDPS and BP were reacted to produce prepolymers carrying phenoxide end groups. Then these prepolymers were reacted with hexafluorobenzene to create the desired aromatic fluoride-terminated hydrophobic prepolymers. The number average molecular weight of the product was measured using GPC and exhibited a slight increase from 17,530 to 19,310 g/mol. However, ^1H NMR analysis of the product indicated that phenoxide end groups were present and that full conversion of end groups to aromatic fluoride was not achieved. We believe this was due to the volatility of hexafluorobenzene, which led to its evaporation during the course of the reaction. We are currently attempting the analogous reaction with difluorodiphenyl sulfone (DFDPS), which is non-volatile under these reaction conditions.

Synthesis of Pendant *N*-heterocycle Aromatic Main-chain Polymers. We have continued to explore the introduction of 1-*H*-1,2,3-triazole moieties into PAES to provide PEMs that can operate at high temperatures and low humidity. Results reported last year suggested that proton conduction could be improved by spacing the triazole moieties away from the PAES backbone. This was done by polymerizing 1-*H*-1,2,3-triazole functionalized methacrylate from chloromethylated PAES using atom transfer radical polymerization.

Chloromethylated PAES with degrees of chloromethylation ranging from 0.25-1.9 chloromethyl groups per repeat unit was produced according to a literature procedure [3] by varying the time of the reaction. As a model reaction, we successfully grafted methyl methacrylate from PAES; however the degree of polymerization was less than desired. Once the conditions are optimized, substitution of the methyl methacrylate with a triazole functionalized methacrylate will allow for a high weight percent of the triazoles in the material to allow for better phase separation and wider channels for proton transport to occur. PAES with methacrylate-based triazole grafts were successfully prepared; however, preliminary proton conductivity measurements under low humidity environments showed poor performance.

Synthesis and Phase Behavior of PFPO-Based Block Copolymers. We synthesized block copolymers containing a proton-conducting block and PFPO blocks, to serve as strongly segregated model systems to explore morphology-proton conductivity relationships. PFPO-COOH was modified to afford terminal benzimidazole functionality through imidization with 3,4-diaminobromobenzene. Post reaction with 4-fluorobenzenesulfonyl chloride yielded 4-fluorophenylsulfonyl end groups, which are better suited for nucleophilic aromatic substitution. Reaction of the 4-fluorophenylsulfonyl-terminated PFPO with hydrophobic (non-acid containing) PAES blocks in hexafluoroisopropanol at 120°C for 24 h was successful. However, in the case of sPAES, we obtained only black, insoluble materials that we were unable to characterize.

Membrane Characterization and MEA Fabrication.

Free standing films of the PAES-based block copolymers shown earlier in Scheme 1 were obtained by solution casting in polytetrafluoroethylene dishes using a 10% (w/v) solution of polymer in dimethylacetamide. After acidification the films were titrated to determine their IEC, followed by water activity and conductivity measurements. The water activity of the new films (MB-1 and MB-2) was determined by isothermal desorption at 80°C and compared to PAES-based block copolymers (MB-3 and MB-4) in which HPPS is the only sulfonated monomer (Figure 1).

Samples MB -1 and MB-2 were synthesized via the method shown in Scheme 1, and had IEC values of 1.68 and 1.08 meq/g, respectively. Samples MB-3 and MB-4 were synthesized via a coupling reaction between hydrophobic and hydrophilic prepolymers in which the hydrophilic block was composed of HPPS and DCDPS, and had IEC values of 1.17 and 1.35 meq/g, respectively. The water activity data show that the acid groups of MB-1 and MB-2 absorbed fewer moles of water at a given humidity, than MB-3 or MB-4. Early results from conductivity measurements suggest block copolymers incorporating both HPPS and sDCDPS in the hydrophobic block will display improved conductivity without increased water uptake. More testing is being conducted to confirm our results; however MB-1 exhibited a conductivity of 49.9 mS/cm at 80°C and 100% relative humidity (RH). Conductivity values of MB-3 and MB-4 at 80°C and 100% RH were reported to be 34 and 14 mS/cm, respectively [1].

The data obtained from water activity and conductivity measurements, for samples with similar IEC values, suggest that improved performance of the new copolymers is due to a change in morphology, resulting from a difference in composition of the hydrophilic block. The sulfonic acid groups of MB-1 and MB-2 are spaced more closely together along the backbone of the chain than MB-3 and MB-4. The

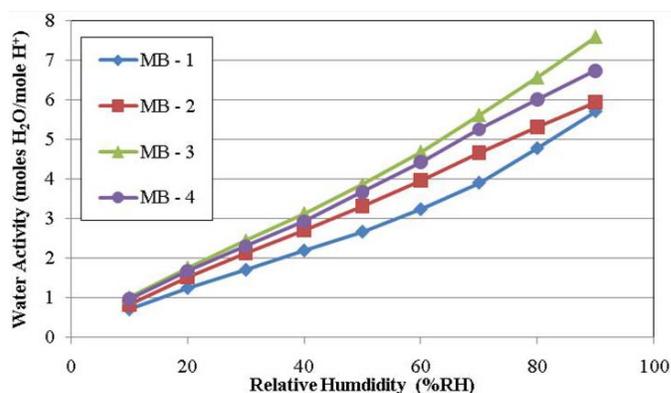


FIGURE 1. Water activity (moles H₂O/ mole H⁺) versus %RH at 80°C. Samples MB-3 and MB-4 above are the same as samples MB-2 and MB-3, respectively, in Ref. 1.

increase in hydrophilicity of these chain segments results in an increase in phase separation leading to fewer isolated sulfonic acid groups and the formation of less tortuous channels for proton conduction. The improvement in morphology allows better conductivity at lesser hydration levels, which is beneficial from a swelling/durability standpoint.

Membrane Ex Situ Durability Characterization - Mechanical Durability: We performed several tests to compare the mechanical durability of sPAES multiblock copolymer MB-1 vs. Nafion[®] 112 membrane at operating fuel cells conditions. Tensile properties were measured using an MTS Alliance RT/10 tensile setup equipped with a 100 N load cell. A custom-design environmental chamber and a sparger were built to control chamber temperature and humidity. Samples, 13 mm wide, were punched from the membrane for all of the mechanical experiments. The membranes, after being clamped in the chamber, were conditioned for 2 h with a 100% RH nitrogen stream at a flow rate of 300 cc/min and a temperature of 80°C. Samples were then strained at a rate of 10 mm/min, as shown in Figure 2. An expansion of the initial strain region of Figure 2 (not shown) showed that the curve for Nafion[®] is displaced rightward along the strain axis because of dimensional increase due to water uptake; this is not the case for sPAES. This indicates low water uptake and higher dimensional stability for sPAES compared to Nafion[®]. After this stress lag, however, the curves for both samples are “typical” and a modulus can be computed from the initial, displaced linear regions. The failure of sPAES at low strain shows reduced ductility compared to Nafion[®]. sPAES shows much higher stress-at-break compared to Nafion[®], 47 MPa vs. 22.4 MPa, respectively. sPAES also showed a very high modulus (897 MPa) compared to that for Nafion[®] (41.5 MPa). The lower modulus for the Nafion[®] membrane suggests that it can

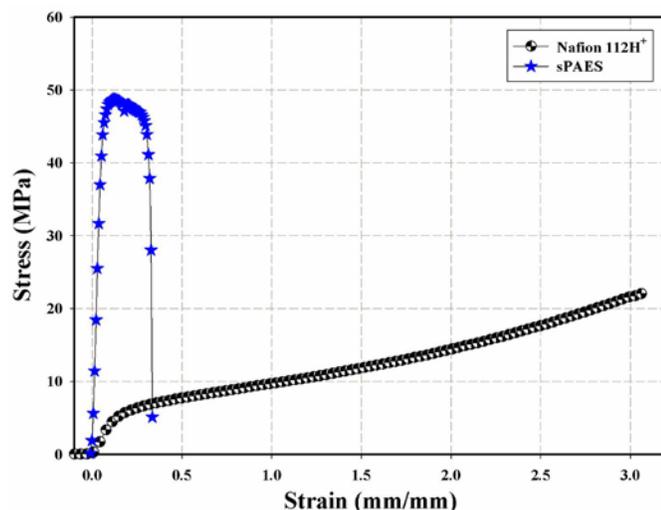


FIGURE 2. Stress-strain curves for sPAES vs. Nafion[®] at 100% RH and 80°C

easily deform when subjected to stresses and rupture due to reduced stress-at-break, thereby promoting pathways for fuel crossover and membrane failure.

Membrane Ex Situ Durability Characterization - Contractile Stress Test: Contractile stresses generated by the membranes as they attempted to shrink when subjected to a drop in RH were monitored under the same conditions used in the tensile studies. Samples were held at their extended swollen length by zeroing the load cell and slowly adjusting the crosshead position until a tension of 0.4 N was reached. The crosshead position was then locked, and the 100% RH nitrogen stream was switched to dry nitrogen at the same flow rate while maintaining the temperature of the dry stream and chamber at 80°C. The ensuing contractile force was monitored as a function of time. The stress levels developed are diagnostic of the ability of the membrane to resist dimensional changes associated with drying and related to mechanical durability. The stress–time profiles for the membranes showed peaks at different times with the sPAES exhibiting higher stress than Nafion[®] (Figure 3).

In the sPAES sample, stress initially drops below zero due to drying of the chamber. During the experiment it was observed that the load increased as the chamber was humidified, even though the sample was not yet extended. The excess load was attributed to condensation on the clamps and the load cell was zeroed before extending the swollen sample. Evaporation of water from the clamps occurred before the sample began to dry and contract, resulting in a decrease in the load below the point at which it was zeroed. Neither of the membranes could withstand the induced contractile stress and eventually yielded, most likely due to macromolecular chain slippage through entanglements. Previously it was determined that the second stress

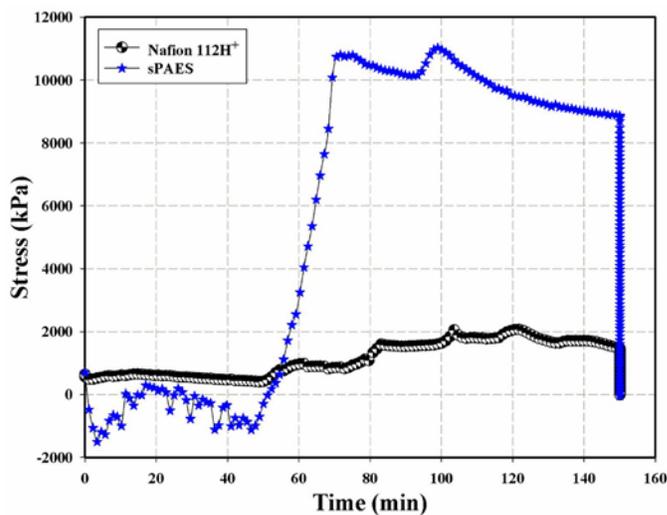


FIGURE 3. Contractile stress response to humidity decrease from 100 to 0% RH at 80°C for Nafion[®] 112 and sPAES

increase in Nafion[®] must be due to a longer range structural reorganization and that the series of peaks on the curve are not due to measurement error, but to a sequence of non-catastrophic crazes spanned by fibrils that prevent further damage growth in the region [4]. The absence of numerous peaks and relaxations in the sPAES curve indicates that the sample did not experience non-catastrophic deformations which would result in decreased fuel cell performance. These results agree with the stress-strain test and indicate that sPAES has a greater resistance to mechanical deformation at high temperature and humidity.

Conclusions and Future Directions

Conclusions

- The synthetic routes used in this work allow for a broad range of polymer compositions.
- The synthesized PAES-based multiblocks exhibit an increase in phase separation leading to fewer isolated sulfonic acid groups and the formation of less tortuous channels for proton conduction, improving water management and conductivity.
- sPAES membranes in this work have greater resistance to mechanical deformation at fuel cell operating conditions, providing improved mechanical durability compared to Nafion[®].

Future Directions

- Produce additional quantities of sPAES material to fabricate MEAs.
- Demonstrate that critical membrane properties, fuel cell performance, and accelerated degradation (both mechanical and chemical durability) are improved for MEAs fabricated from PAES-based multiblocks, relative to baseline materials.

FY 2012 Publications/Presentations

Publications

1. Mauritz, K.A.; Nalawade, A.; Hassan, M.K. "Proton Exchange Membranes for H₂ Fuel Cells Applications," In *Sol-Gel Processing for Conventional and Alternative Energy*; Aparicio, M., Jitianu, A., Klein, L.C., Eds.; Springer: New York, 2012; Chap. 5, pp 73-98.
2. Hassan, M.K.; Abukmail, A.; Mauritz, K.A. "Broadband Dielectric Spectroscopy Studies of Molecular Motions in a Nafion Membrane vs. Annealing Time and Temperature" *Eur. Polym. J.* **2012**, *48*(4), 789-802.
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Presentations

1. Baranek, A.; Suggs, S.; Patton, D. "Synthesis of Tethered Triazole Poly(arylether sulfones) toward High Temperature, Low Humidity Proton Exchange Membranes" Poster, American Chemical Society, Fuel Division, Denver, CO August 2012.

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