

V.M.19 Advanced Materials for Proton Exchange Membranes

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Objectives

- The goal of this research is to develop a superior material for polymer electrolyte membranes (PEMs), which will meet performance requirements associated with higher temperatures and lower relative humidities (RHs) by the year 2010.
- The new materials will outperform the present standard material, Nafion®.
- The work builds upon earlier results from Virginia Tech (VT) wherein thermally, oxidatively, hydrolytically stable, tough, high T_g ion-containing copolymers based on polyarylene ethers were successfully used as PEM systems under relatively high humidity conditions.
- The new objectives are to examine the behavior of block copolymers based upon hydrophilic-hydrophobic moieties as an approach to develop performance criteria at high temperatures and low RH.
- Use process modeling coupled with convection drying studies to establish drying conditions, which will lead to a PEM with optimum performance.
- Develop a fundamental understanding of the role played by the rate of solvent removal and the self-

assembly process for the block copolymer systems which will lead to optimum PEM performance.

- Translate the results from the fundamental studies to the design of a continuous film casting system.
- Determine the configuration of a continuous film casting system based on the rheological and thermodynamic properties of polymer solutions, which will produce PEMs with optimum performance.
- Design and construct a continuous film casting system, which will allow the production of PEMs from small quantities of polymer (5 g) and from larger quantities (100 g).

Technical Barriers

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

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

- The primary target is to develop block copolymer membranes that show enhanced performance at higher temperatures and lower humidities.
- To define a casting methodology to transform the novel copolymers into void-free uniform ductile films with optimum performance (control the self-assembly process).
- The third target is to characterize the films by both classical polymer science and electrochemical methodologies to meet the goals and objectives.

Some of the key results obtained during the first year of the project are listed in Table 1. Other significant results are presented in the sections which follow. The cost of these membranes is known to be low and meet the cost targets. It is the performance and durability which will be emphasized in this project.

Accomplishments

- New methodologies for the synthesis of hydrophobic-hydrophilic block copolymers based upon stable polyarylene ether systems were developed.

TABLE 1. Key Properties of the Membranes

Properties	Units	DOE Target	VT status (2007)
Membrane Conductivity at inlet water vapor partial pressure (50 kPa)			
Temp 80°C	S/cm	0.10	0.13
Temp 20°C	S/cm	0.07	0.08
Temp 80°C, RH 50	S/cm	-	0.03
Volume Swell	%	-	20-70
Water Uptake	%	-	20-50
Diffusion Coefficient of water	10 ⁻⁶ cm ² /s	-	7-12
Synthesis of hydrocarbon multiblock copolymers	-	As per project objectives	Synthesized, BisSF-BPSH & BPS-BPSH (refer results section)
Investigation of solvent casting conditions on PEM properties	-	As per project objectives	Investigated (refer results)

- Reactive hydrophilic oligomers were successfully coupled with reactive hydrophobic oligomers to make tough film forming compositions with good mechanical strength and conductivities either in liquid water or as function of relative humidity, which are as good as, and in cases somewhat better, than the Nafion[®] benchmark controls.
- Define methodologies for predicting protonic conductivity from diffusion characteristics of water through PEM systems.
- Designed and constructed a continuous casting system using a reverse roll coating technique, with which pinhole-free copolymer films with a satisfactory uniformity in their thickness (about 30 microns ± 5 %) were successfully cast from a few grams of polymer.
- Developed a mathematical model of drying which eventually will incorporate the development of structure which will lead to optimum PEM performance.
- An initial investigation of the effects of solvent casting conditions (drying rate, drying temperature, shearing, initial solution concentration) on PEM performance and its association with the morphology of random and block copolymer systems was undertaken.



Introduction and Approach

The Virginia Tech research effort on Advanced Materials for Fuel Cells began in May 2006. The approach was quite broad and included the development of important membrane materials for automotive fuel cell applications. It was recognized that the membrane variables included molecular weight, ion content, chemical composition, and sequence. It was proposed to conduct extensive mechanical and electrochemical characterization of the components, and to generate membrane electrode assemblies as a function of time, temperature, and electrochemical history. The overall objective was to relate molecular design in the membrane to transport at low or ambient relative humidities. The remainder of the project will provide highlights of the progress made throughout the latest period. Finally at the end of the report we show a significant list of publications and preprints that have evolved from the Department of Energy, The National Science Foundation, and NASA.

The main direction over the last year, which continues, is to maintain proton conductivity under partially hydrated conditions. We have presented arguments, some of which have been published, that block copolymers displaying nanophase separation will permit transport and enhance conductivity by a co-continuous hydrophilic sequence. The microphase separation follows along classical ideas that the two-phase structure should develop at some critical degree of polymerization and as a function of the interaction parameter. Unfortunately, the interaction parameter was developed from Flory Huggins theory on hydrocarbon systems with no ionic groups. Thus, the χ parameter for ionomer systems is quantitatively unknown. However, we can model this empirically using the concept of hydrophobic-hydrophilic interactions. We succeeded in making for the first time well developed block copolymers based on a hydrophobic partially fluorinated arylene ether linked together with a very hydrophilic reactive water soluble oligomer. The resulting block copolymer materials make very good films. The strength properties are quite satisfactory. Proton conductivity in liquid water is better than Nafion[®], and is a function of the block lengths. It was demonstrated that proton conductivity under partly hydrated conditions improved with block length and this was related to the morphological development that one can achieve in these systems.

Quite recently we have developed a simplified methodology for synthesizing the block copolymers using endcapping of either decafluorobiphenyl or hexafluorobenzene on the hydrophobic block, which allows the polymerization temperature to be much lower, around 100°C. This produces a very clean reaction which has definite characteristics and long-range order, not only by atomic force microscopy (AFM) but also by

transmission electron microscopy (TEM). Interestingly, all of the block copolymers show anisotropic swelling with relatively low, in many cases, x-y swelling which is considered to be very important for the fuel cell membranes.

Results

A series of multiblock copolymers (BisSF-BPSH) were synthesized using the detailed procedures [13]. The multiblock copolymers were varied in ion exchange capacity and block length. The multiblock copolymers were prepared using the BPS hydrophilic macromonomer and perfluoro hydrophobic macromonomer, as shown in Figure 1.

Proton conductivity as a function of RH is studied and the results are displayed in Figure 2. This demonstrates the effect of morphology on proton

conductivity under partially hydrated conditions. For the random copolymer, BPSH-35*, proton conductivity drops significantly at lower RH values. Random copolymers show decent performance under fully hydrated conditions since there are sufficient water molecules to provide proton transport. However, due to the scattered hydrophilic domains in the membranes they lack the connectivity among sulfonic acid groups for proton transport under partially hydrated conditions. With the multiblock copolymers, on the other hand, as the block length increases the performance under partially hydrated conditions also increases. This suggests the presence of long, co-continuous channels at higher block lengths through which protons can be transported along the sulfonic acid groups and water molecules. Hence the connectivity between the hydrophilic domains governs the proton transport under partially hydrated conditions. On account of enhanced nanophase separation, the BisSF-BPSH(15:15)K

multiblock copolymer exhibited higher proton conductivity than Nafion® at all RH values.

We have recently demonstrated a novel way to make nearly all hydrocarbon hydrophobic-hydrophilic block copolymers. The chemical structure and chemical composition is very similar to BPSH copolymers. However, the microstructure and the morphology are very different. The procedure that has been shown to work (Figure 3) is to first synthesize the hydrophobic oligomer (e.g., with 5,000, 10,000 and 15,000



- Nanophase separated morphology may be precisely controlled through synthesis.
- Enhanced proton conductivity, water diffusion coefficient and mechanical strength are expected.

Our work:



Hydrophilic segments, provides Proton conductance

Hydrophobic segments, imparts mechanical integrity

A. Noshay and J. E. McGrath, "Block Copolymers: Overview and Critical Survey," Academic Press, New York, January 1977, p.91.an S-B diblock copolymer

Yu, Xiang; Roy, Abhishek; Dunn, Stuart; Yang, Juan; McGrath, James E. Synthesis and characterization of sulfonated-fluorinated, hydrophilic-hydrophobic multiblock copolymers for proton exchange membranes. Macromolecular Symposia (2006), 245/246(World Polymer Congress--MACRO 2006), 439-449.

FIGURE 1. Highly Hydrophobic-Hydrophilic Multiblock Copolymers

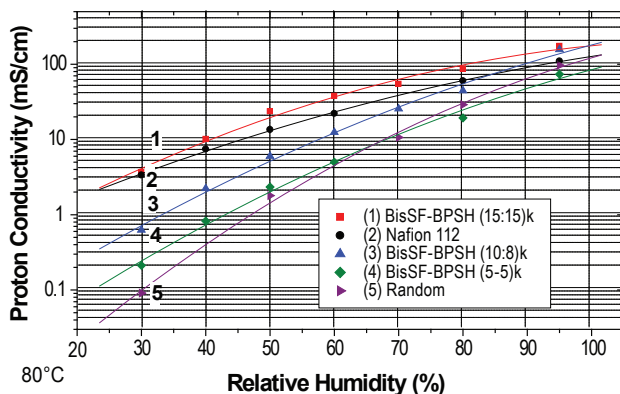


FIGURE 2. Proton conductivity under partially hydrated conditions increases with block length. (X and y are black lengths in kg/mole of hydrophobic and hydrophilic unit, respectively.)

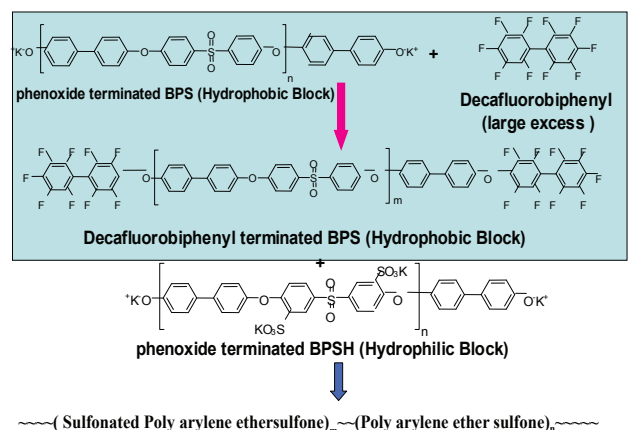


FIGURE 3. Synthesis of BPSH – BPS Multiblock Copolymers at 100°C

g/mole molecular weights) and then endcap these systems with a molar excess of decafluorobiphenyl. It can be noted that the weight of the fluorinated capping reagent is small since the BPS oligomer can be 15,000 g/mole or even higher. The resulting endcapped oligomer is subsequently reacted with the hydrophilic phenoxide terminated hydrocarbon system. A detailed synthetic procedure will be reported separately.

An increase in block length for a given series of block copolymer under the same ionic concentration was associated with the formation of co-continuous hydrophilic and hydrophobic domains. This is supported by TEM micrographs (Figure 4) obtained for a BPSH-10-BPS-10 copolymer.

The multiblock BisSF-BPSH copolymers also showed significant and anisotropic swelling compared to the random copolymer (Figure 5). This is true for all higher block length materials. They possess very low in-plane swelling, which is regarded as an important factor in durability during low RH cycling.

Continuous Casting Results

As shown in Table 2, the proton conductivity of block copolymer films strongly depended on the solvent-casting conditions such as coating method, initial polymer concentration, and drying temperature, whereas no obvious differences in the proton conductivity of the random copolymer films was observed in Table 3.

The variation in properties of the block copolymer is believed to be due to the hindrance of the self-assembly process which occurs as the solvent is removed. If the solvent removal is too rapid, then there is insufficient time for the assembly process to be completed.

As shown in Figure 6, the continuous casting process is used to form the uniform thickness membrane films.

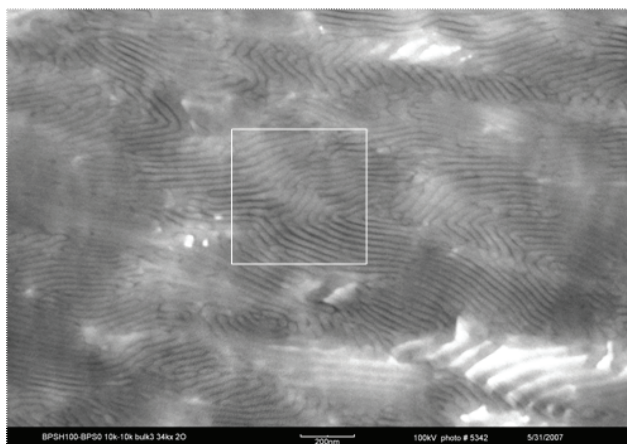


FIGURE 4. BPSH100-BPS0 10k-10k TEM

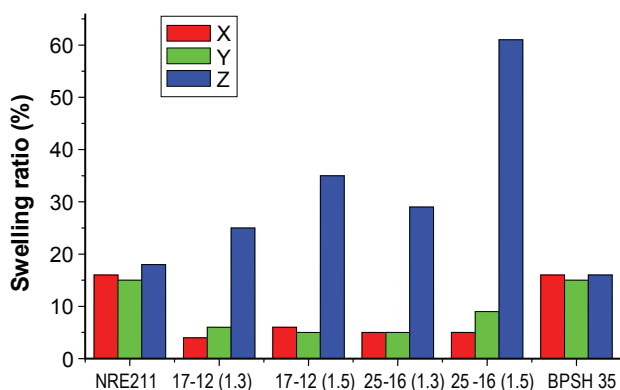


FIGURE 5. Very Low In-Plane Swelling is Observed for the Multiblock

TABLE 2. Solvent-Casting Conditions and Proton Conductivity of BisSF Block Copolymer Films

Polymer	Casting Method	Concentration w/v %	Drying Temperature ¹ (°C)	Proton Conductivity ² (S/cm)
BisSF 17K/12K	Continuous	12.5	50	0.065
BisSF 17K/12K	Batch	5	~30	0.13
BisSF 17K/12K	Batch recast ³	5	~30	0.12
BisSF 18K/13K	Continuous	8	30, then 50	0.10
BisSF 18K/13K	Batch	5	~30	0.10
BisSF 22K/14K	Continuous	10	30, then 50	0.09
BisSF 22K/14K	Batch	5	~30	0.095

¹ Hot plate was used in continuous casting, infrared lamp was used in batch casting

² In liquid water at 30°C (±5%)

³ Batch cast films with the solution prepared by dissolving the continuous cast films in NMP

TABLE 3. Solvent-Casting Conditions and Proton Conductivity of Random Copolymer Films

Polymer	IEC [meq/g]	Casting Method	Proton Conductivity [S/cm]	Water uptake [%]
BPSH-32.5	1.40	Continuous	0.060	33
BPSH-32.5	1.40	Batch	0.055	37
6F35	1.15	Continuous	0.060	24
6F35	1.12	Batch	0.055	23



FIGURE 6. Continuous Casting Station

Conclusions

- Multiblock copolymers based on partially fluorinated hydrophobic block were synthesized.
- Proton conductivity increases with increasing block lengths.
- Unequal block length materials with higher hydrophobic block length can reduce swelling.
- Water uptake and volume swelling can be reduced by varying the hydrophobic and hydrophilic block lengths.
- Multiblock copolymers displayed very low in-plane swelling.
- Very high proton conductivity was observed at low uptake for the multiblocks.
- Transport properties scaled with the volume fraction of the copolymer.
- The final properties of the membranes produced from block copolymers strongly depend on the processing conditions, indicating that both the polymer system and preparation processes have to be considered in the development of new polymer electrolyte membranes.
- A model, which will allow one to determine drying conditions required to produce a desired morphology for optimum membrane performance, is needed because the self-assembly process is highly dependent on polymer concentration, block copolymer structure, and solvent removal rate.

Future Directions

- Continue ongoing efforts understanding structure-property relationships in PEM block copolymers and what controls conductivity at low RH.
- Further Investigate BPSH-0-100 multiblock copolymers utilizing hexafluorobenzene –linking.
- Investigate the influence of chemical structure on swelling-deswelling features in the block copolymers and its connection to fuel cell durability
- Scale up (20-50 gm) selected block copolymer PEMs, cast into films.
- Screen compatibility with PVF2 (Kynar); determine if lower modulus improves fatigue during RH transitions.
- Further develop film casting expertise to obtain membranes with improved properties.
- Refine the model for predicting conditions for the generation of membranes with optimum performance through a systematic investigation of the effects of solvent-casting conditions on a model block copolymer system using the newly designed batch convection drying apparatus.
- The methodology will be extended to novel block copolymer systems synthesized in our laboratories.

FY 2007 Publications/Presentations

1. Huang, J., Fan, G., Zhang, Z., Badami, A., Takamuku, S., McGrath, J. E., and Baird, D. G., Continuous Film Casting and Evaluation of Polymer Membranes for Fuel Cells, 2007 Society of Plastics Engineers Annual Conference, Cincinnati, OH (May 2007).
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3. Cho, Chang Gi; Kim, Yu Seung; Yu, Xiang; Hill, Melinda; McGrath, James E. Synthesis and characterization of poly(arylene ether sulfone) copolymers with sulfonimide side groups for a proton-exchange membrane. *Journal of Polymer Science, Part A: Polymer Chemistry* (2006), 44(20), 6007-6014.
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13. Yu, Xiang; Roy, Abhishek; Dunn, Stuart; Yang, Juan; McGrath, James E. Synthesis and characterization of sulfonated-fluorinated, hydrophilic-hydrophobic multiblock copolymers for proton exchange membranes. *Macromolecular Symposia* (2006), 245/246(World Polymer Congress--MACRO 2006), 439-449.