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The Effect of BPSH Post Treatment on DMFC Performance and Properties

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ABSTRACT

Direct methanol fuel cells (DMFCs) are being investigated for applications ranging from milliwatt (cell phones) to kilowatt (APUs) size scales. A common pitfall for DMFCs has been the inability of the electrolyte, typically Nafion, to act as an effective methanol barrier. Methanol crossover adversely affects the cell by lowering the cell voltage due to a mixed potential at the cathode and lower fuel utilization.

Improved DMFC performance was demonstrated with sulfonated poly(arylene ether sulfone) copolymer membranes (1). Another study has shown the dependence of polymer properties and morphology on the post treatment of such membranes (2). In agreement with measurements on free-standing films, the fuel cell characteristics of these membranes have been found to have a strong dependence on acidification treatment. Methanol permeability, proton conductivity, and electro-osmotic drag coefficient all were found to increase when the membranes were acidified under boiling conditions versus a low-temperature process.

INTRODUCTION

Direct methanol fuel cells (DMFC) have become an increasingly attractive alternative to other energy storage/conversion technologies for portable power applications. Current fuel cell membrane materials, particularly perfluoronated ionomers such as Nafion, have too much methanol permeation or "crossover" from anode to cathode for efficient cell operation. Unoxidized methanol at the anode travels through the membrane and reacts at the cathode causing lower cell voltages and decreased efficiency. Fuel cell engineering strategies exist for combating the effects of methanol crossover such as lowering the feed concentration, modifying the gas diffusion layers, increasing the thickness of the membrane, or increasing the cathode catalyst loading, but these solutions have their drawbacks and limitations. To make large gains in DMFC performance new membranes with lower intrinsic methanol crossover are needed. There has been and continues to be research on other types of membrane polymers with lower methanol permeability, but this lower methanol permeability often comes at the expense of conductivity. Both conductivity and methanol permeability must be taken into account when designing a new DMFC membrane.

The synthesis and characterization of a new class of sulfonated poly(arylene ether sulfone) proton conducting copolymers for use in DMFCs has been reported previously (2). Generally, these materials display low methanol permeability and high proton conductivity. Of note is that the selectivity of these copolymers is greater than that of Nafion. Selectivity is a measure of a membrane's proton transport (conductivity) relative to the membrane's methanol permeability, and has been used as a gauge of the potential for DMFC electrolytes (3). Sulfonated poly(arylene ether sulfone) copolymers with sulfonation levels between 30 and 50 % are attractive candidates for use in DMFCs because of their increased selectivity compared to Nafion. The nomenclature for these copolymers is BPSH (biphenol sulfone $\underline{H}^+$ form) to denote the backbone chemical structure followed by a number to indicate the molar ratio of sulfonated sulfone monomer. Therefore, BPSH-40 is a biphenol sulfone based poly(arylene ether) in the acid form with 40% of the sulfone monomer in the disulfonated form.

As fuel cell performance studies of these copolymers have progressed, the processing of the membrane has become a key variable in determining the membrane properties. Specifically, the temperature of acidification affects the methanol permeability and the conductivity, thereby affecting the selectivity of the membrane. In addition, the treatment of the membrane has an influence on its electro-osmotic drag coefficient. The electro-osmotic drag of a membrane has a large effect on the water management requirements of a DMFC. These property changes can be correlated to microstructural information obtained by atomic force microscopy (AFM).

While the properties of BPSH-40 and other sulfonation levels of the sulfonated poly(arylene ether sulfone) copolymers seems to be affected by the membrane processing temperature during acidification, Nafion is relatively insensitive to acidification temperature.

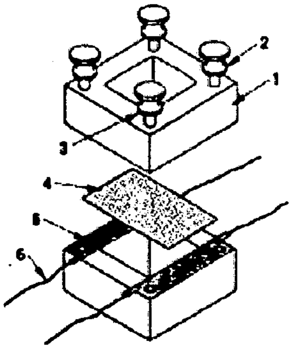
EXPERIMENTAL

Atomic Force Microscopy

Tapping mode atomic force microscopy (TM-AFM) was performed with a Digital Instruments Dimension 3000, using the micro-fabricated cantilevers with a force constant of approximately 40 N/m. The samples were imaged in relative humidity of about 35%.

Membrane Conductivity

Conductivity at room temperature under full hydration conditions was determined using a Solatron 1260 Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz - 1 MHz. The "window cell" or in-plane geometry was chosen to ensure that the membrane resistance dominated the response of the system (4). The geometry of the cell is shown in Figure 1.



1. Kel-F support block
2. thumbscrew
3. open area to allow equilibration
4. membrane sample
5. blackened Pt foil
6. Pt ribbon lead

Figure 1: Conductivity Cell Geometry

The resistance of the film was taken at the frequency that produced the minimum imaginary response. The conductivity of the membrane could then be calculated from the measured resistance and the geometry of the cell.

Membrane Permeability

Stand-alone methanol permeability was determined using a membrane-separated diffusion cell. The experimental apparatus is shown in Figure 2.

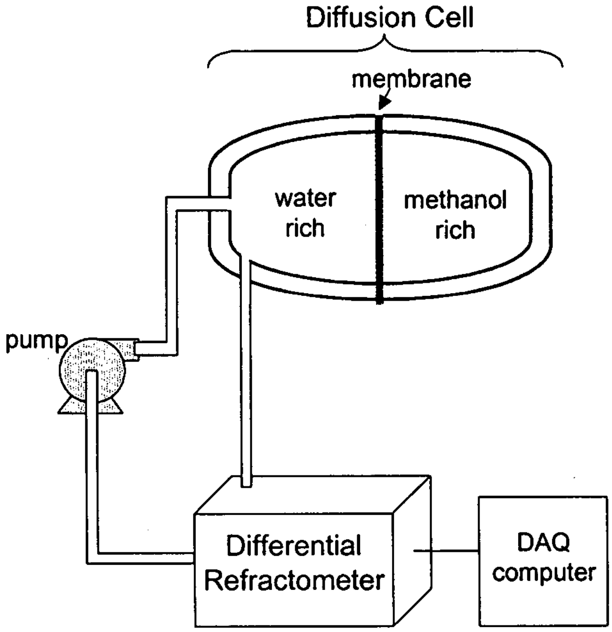


Figure 2: Membrane Separated Diffusion Cell Apparatus

At the outset of the experiment, the membrane of interest is placed between two compartments: one filled with DI water, and the other filled with a methanol/water solution. The rate of methanol diffusion through the membrane can be computed by measuring the change in methanol concentration in one side of the cell versus time using a differential refractometer and a recirculating pump. The permeability data were calculated using equation [1]

$$\frac{c_{1,R} - c_{1,L}}{c^o_{1,R} - c^o_{1,L}} = e^{-D_1 H_1 \chi t} \qquad [1]$$

A plot of $\ln[(c_{1,R}-c_{1,L})/(c^o_{1,R}-c^o_{1,L})]$ versus t should yield a straight line with slope $-D_1H_1\chi$. Once χ is determined by measuring the geometry of the cell, the permeability of methanol through the membrane (D_1H_1) can be calculated. The specifics of the data analysis have been outlined by Cussler (5).

Synthesis of Membrane Electrode Assemblies (MEAs)

MEAs were prepared from standard catalyst inks containing either unsupported platinum or platinum-ruthenium, water, and Nafion 1100 solution. These inks were mixed by sonication and then applied to the membranes by direct painting. All the membranes tested had identical electrodes. Nafion 117 films were pretreated by boiling for 1.5 hours in each step in 3% H_2O_2, deionized water, 0.5 M H2SO4, and again in deionozed water.

BPSH-40 polymer in the potassium neutralized form were solution cast from N,N,-dimethylacetamide under vacuum at 150°C. Two different treatment methods were applied to convert the sulfonated poly(arylene ether sulfone) random copolymer membranes to the acid form. Method 1 will refer to converting the membranes to acid form by soaking in 1.5 M H_2SO_4 for 24 hours, then soaking in DI water for 24 hours. Conversion method 2 involves boiling the cast membrane in 0.5 M H_2SO_4 for 2 hours, then boiling in DI water for 2 hours to remove the excess H_2SO_4.

Fuel Cell Experiments

The resulting MEAs were tested in fuel cell hardware to determine membrane properties and DMFC performance. Relevant DMFC membrane properties such as methanol permeability, proton conductivity and electro-osmotic drag were obtained from these experiments.

Fuel cell test results reported here are for tests run in 5 cm^2 cells at 60°C with 1M methanol at a flow rate of 2 mL/min, and an air flow rate (humidified to a dew point of 60°C) of 250 sccm at 0 psig backpressure. Polarization curves were obtained under these conditions, and proton conductivities were determined from high frequency resistance measurements.

By operating the cell at a constant current, the water flux through the membrane and the methanol crossover as a function of current density could be obtained from an analysis of the cathode effluent. In this experiment, the water in the cathode exhaust was collected in a Drierite filled U-tube, and the CO_2 content of the dry effluent was determined using a nondispersive linearized CO_2 sensor. The details of this experiment are described in greater detail elsewhere (6). The electro-osmotic drag coefficient of the membrane was also extracted from the constant current data.

RESULTS AND DISCUSSION

Three types of membrane were included in this study. Nafion 117 processed in the usual fashion, BPSH-40 acidified by soaking (Method 1), and BPSH-40 acidified by boiling (Method 2). Both stand-alone membrane properties and DMFC performance is reported in this work.

Effect of Processing Method on Morphology and Membrane Properties

The morphological change induced by the method of acidification can be observed using atomic force microscopy. Figure 3 shows the morphology of BPSH-40 processed using the two different acidification methods.

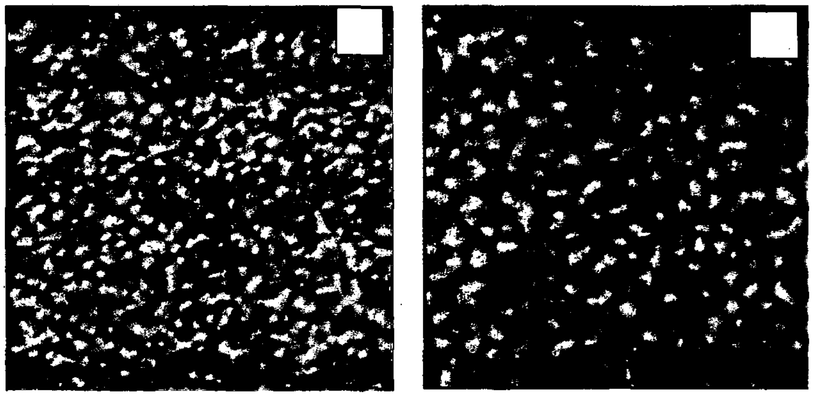


Figure 3: Influence of treatment Method upon Tapping Mode AFM Phase Image (a) BPSH-40 Method 1 (b) BPSH-40 Method 2

The dark areas represent hydrophilic sulfonic acid rich domains whereas the lighter areas are primarily unsulfonated polymer. The micrograph on the left where the membrane was acidified by soaking shows a finer domain structure than that on the right where the membrane was acidified by boiling. The higher temperature treatment may cause swelling of the existing domains, reorganization of the morphological structure into larger features, or a combination of the two, both reorganization and swelling.

The morphological change due to acidification treatment is accompanied by a corresponding change in membrane properties. Generally, an increase in water uptake, conductivity, and methanol permeability are observed for the higher temperature treatment of BPSH-40. Nafion 117 has proven to be relatively insensitive to acidification treatment. Table I provides a comparison membrane properties between Nafion 117 and the BPSH-40 membranes after Method 1 and Method 2 processing.

Table I: Effect of Treatment Process on Membrane Properties

	Water Uptake (weight %)	Conductivity (S/cm)	Methanol Permeability (cm^2/s)	Electro-osmotic Drag Coefficient ($N\ H_2O/H^+$)
Nafion 117	19	0.113	$16.7 * 10^{-7}$	3.6
BPSH-40 (M1)	39	0.077	$3.6 * 10^{-7}$	1.5
BPSH-40 (M2)	58	0.104	$8.1 * 10^{-7}$	1.9

Conductivity at 30°C, Methanol Permeability at 25°C and Electro-osmotic Drag at 60°C
M1 – acidification by Method 1: low temperature soaking
M2 – acidification by Method 2: high temperature boiling

The methanol permeability and electro-osmotic drag coefficient of BPSH-40 greatly reduced as compared to Nafion no matter which processing method is used. Additionally, the conductivity of the BPSH-40 membranes is close to that of Nafion indicating that the BPSH-40 membranes have a greater selectivity and could potentially show superior performance in direct methanol fuel cells.

Comparison of Fuel Cell Performance

The change in membrane properties according to treatment method can be observed in the direct methanol fuel cell behavior of the membrane. Membrane conductivity and methanol permeability have a direct effect on two distinct regions of the polarization curves. In the low current region (0 to 100 mA/cm^2), methanol crossover plays a large role in determining the voltage achieved at a given current. Higher voltages for a given current are an indication of lower methanol crossover. Above 100 mA/cm^2 as the methanol becomes depleted at the anode, membrane conductivity has a large influence on the voltage generated for a given current density. The slope of the nearly linear, ohmic region of the polarization curve is determined primarily by the bulk resistance of the membrane. Large ohmic losses result in increased slopes, which in turn suggest decreased membrane conductivity.

Fuel cell polarization curves for Nafion 117, BPSH-40 processed by method 1, and BPSH-40 processed by method 2 are shown in Figure 4.

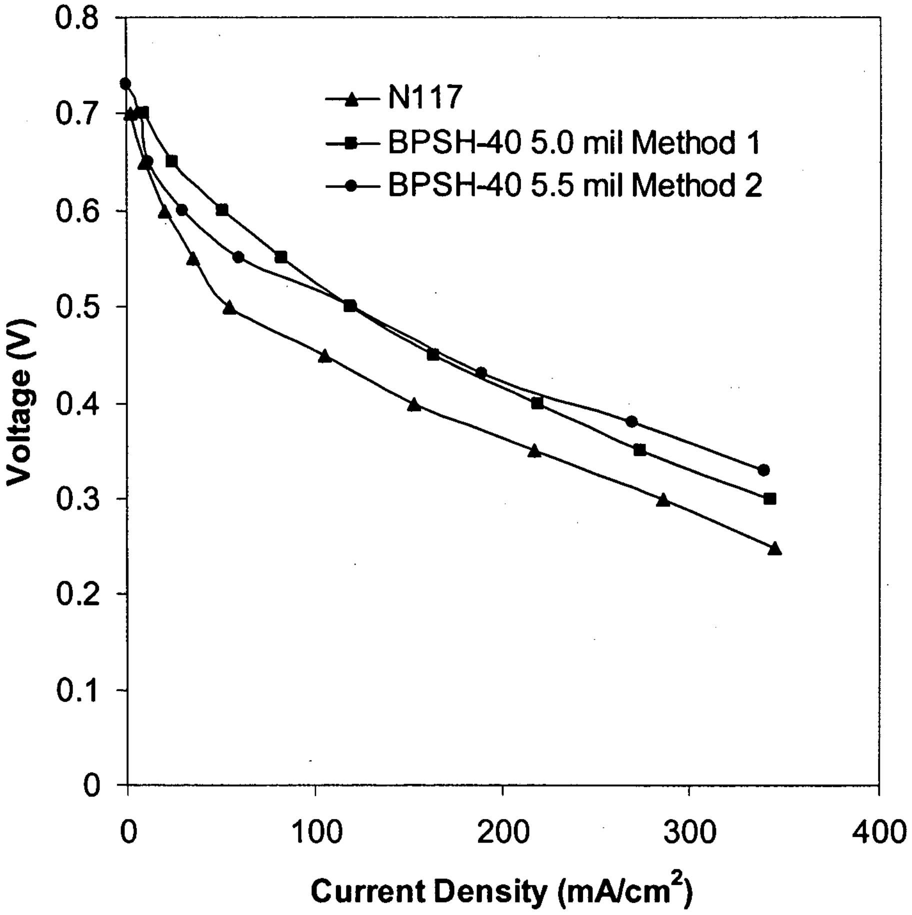


Figure 4: Comparison of Polarization Curves at 60°C with 1M Methanol

The general shift of both the BPSH-40 polarization curves to increased voltages over Nafion is a result of the dramatically reduced methanol permeation of BPSH-40 no matter what processing method is used to acidify the membrane. The open circuit voltages (OCVs) shown in Figure 4 are sensitive to test conditions, particularly the amount of time left at open circuit conditions. While care was not taken in these polarization curves to obtain true OCVs, the qualitative trend to higher OCVs with BPSH-40 (method 1), followed by BPSH-40 (method 2) and finally Nafion 117 agrees with expected changes in methanol permeability of the three membranes.

In the high current region of the performance curves, the ohmic slopes of Nafion 117 and BPSH-40 processed by Method 2 are very similar. This is not surprising given that the stand-alone membrane conductivities of the two are also similar. An increased ohmic slope is observed for BPSH-40 processed by Method 1, which is a reflection of its lower membrane conductivity. The high frequency resistances (HFR) of the MEAs also agreed with the trend in membrane conductivity shown in Table I for the three materials. Nafion 117 had an HFR of 0.21 Ω–cm^2, which is indicative of the highest membrane conductivity. BPSH-40 had HFRs of 0.33 Ω–cm^2 and 0.27 Ω–cm^2 for method 1 and method 2 processing, respectively which follows the conductivity trend established in Table I.

If the Nafion curve is omitted for clarity and just the BPSH-40 polarization curves are plotted, the same effects as discussed above can be observed when comparing the acidification methods. Figure 5 shows only the two BPSH-40 polarization curves processed by Method 1 and Method 2.

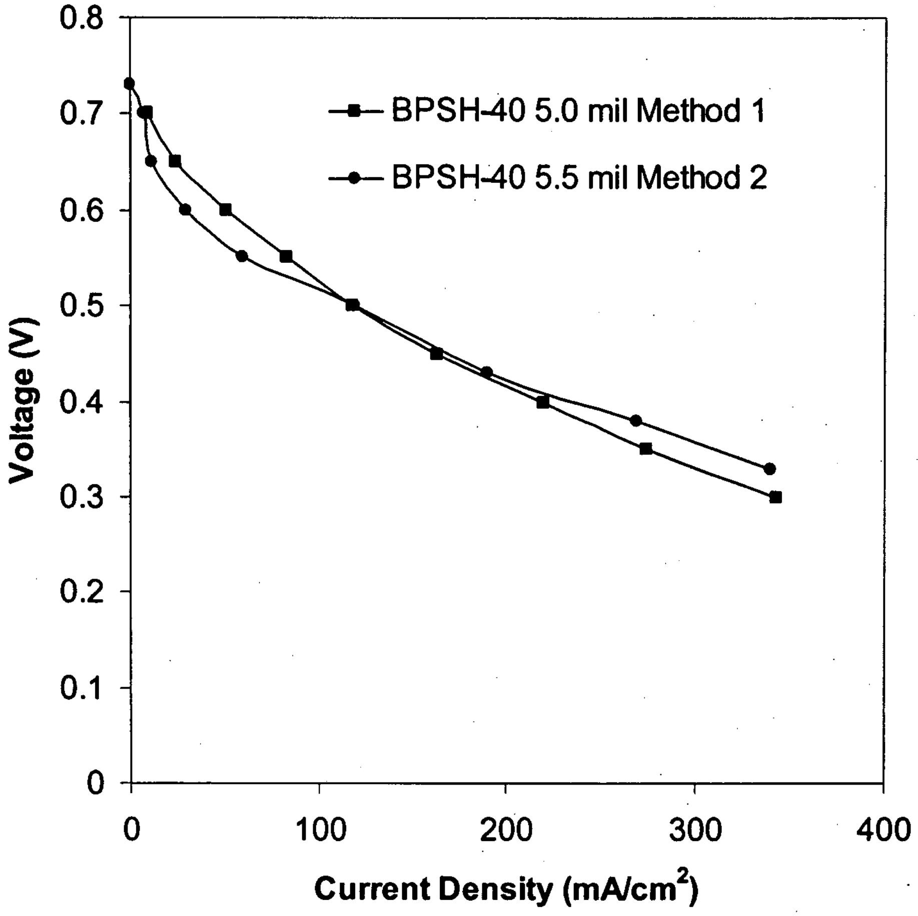


Figure 5: BPSH-40 Polarization Curves – Effect of Acidification Method on DMFC performance

The membrane processed by Method 1 has a lower methanol permeability and therefore, generated higher voltages for a given current density due to decreased methanol crossover in the low current region of the polarization curve. However, because Method 1 processing yields a BPSH-40 membrane with lower conductivity, the ohmic slope of the curve is larger than that of the curve generated using a membrane with Method 2 processing. The point where the two curves cross is the current density for these systems where the tradeoffs between methanol crossover and ohmic losses become equivalent. At higher current densities the membrane with higher conductivity processed by Method 2 shows better performance than the Method 1 processed membrane.

The methanol crossover of the MEAs in a DMFC was evaluated by measuring the amount of CO_2 generated at the cathode. The results can be expressed as an equivalent current density for the methanol molecules lost to crossover. Figure 6 shows the cell current versus the equivalent crossover current for the three membranes.

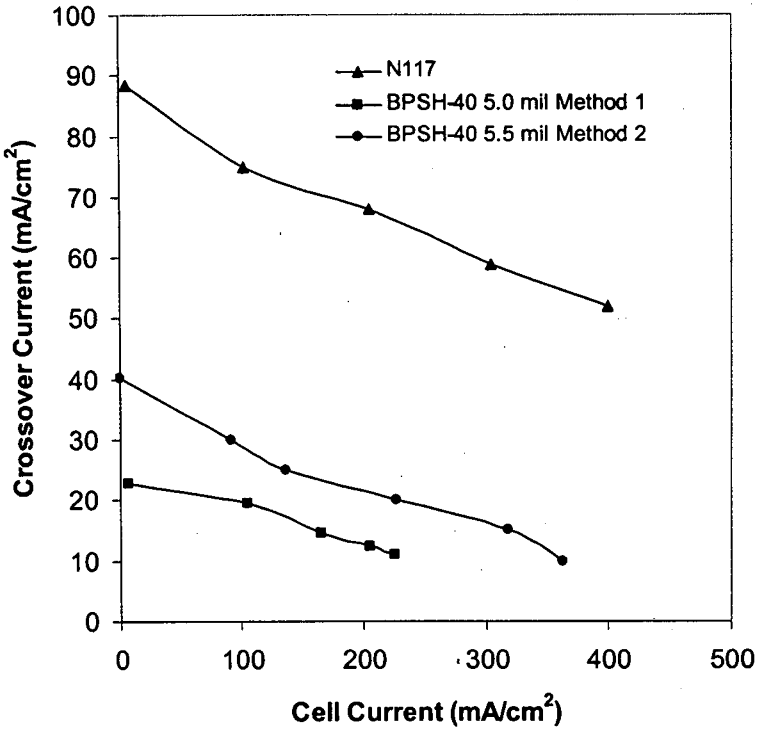


Figure 6: Methanol Crossover expressed as Crossover Current Density versus Cell Current

As can be seen from the figure, the methanol crossover of Nafion is much greater than BPSH-40 accounting for the shift to higher voltages in the polarization curves. Between the BPSH-40 membranes, Method 1 yields a membrane with lower methanol crossover over all current densities. The relative differences between these curves are mirrored in the stand-alone membrane methanol permeability experiments, the trend in open circuit voltages, and the increased performance shown in the polarization curves due to lower overpotentials at the cathode.

CONCLUSIONS

Sulfonated poly(arylene ether sulfone) copolymers have proven to consistently outperform Nafion in DMFCs principally because of their decreased methanol crossover without sacrificing protonic conductivity. However, the properties of the BPSH-40 membranes are highly influenced by the acidification process whereas Nafion is relatively insensitive to acidification temperature.

A relationship between the domain structure of the polymer and the resulting membrane properties has been established. Increased sulfonic acid domain size brought about by high temperature acidification causes an increase in electro-osmotic drag, conductivity, and methanol permeability. These properties were measured in both stand-alone membrane and in fuel cells.

The differences in methanol permeability and conductivity between the three types of membranes have a notable effect on the membranes' DMFC performance. At a given current density, shifts to higher voltages are observed for both BPSH-40 MEAs versus Nafion 117 because of the large difference in methanol crossover. When comparing the two BPSH-40 membranes processed by different acidification routes, behavior in the low current region is dominated by decreased methanol permeability, whereas the conductivity controls the performance at higher currents. The result is that the two BPSH-40 curves intersect with Method 1 processing showing advantages at low current, and Method 2 displaying higher performance at higher currents.

A likely cause for Nafion's insensitivity to processing may arise from the small amount of crystallinity that exists in the non-sulfonated part of the polymer. This crystallinity prevents swelling or reorganization of the sulfonated domains. No crystallinity exists in BPSH polymers resulting in the potential for morphological reorganization depending on how the membrane is processed. Additionally, the ion exchange capacity of Nafion is much lower than that of BPSH-40 (0.91 meq/g vs 1.72 meq/g, respectively). Less ions in the polymer leaves more unsulfonated matrix to stabilize the ionic domains. Nafion's unsulfonated tetrefluoroethylene regions – with or without crystallinity - may contribute to its behavior during processing.

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