

# Toward Improved Conductivity of Sulfonated Aromatic Proton Exchange Membranes at Low Relative Humidity

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Three sulfonated aromatic polymers with different sequence lengths were studied in order to better understand the relationship between molecular structure, morphology, and properties of proton exchange membranes as a function of relative humidity. A random copolymer with a statistical distribution of sulfonic acid groups had very small domain sizes, whereas an alternating polymer with sulfonic acid groups spaced evenly along the polymer chain was found to have larger, but quite isolated, domains. The multiblock copolymer studied herein showed highly phase-separated hydrophilic and hydrophobic domains, with good long-range connectivity. Scanning force microscopy as a function of relative humidity was used to observe water absorption and swelling of the hydrophilic domains in each of the three membranes. The conductivity, water sorption kinetics, and fuel cell performance, especially at low relative humidity, were found to be highly dependent upon the morphology. The multiblock copolymer outperformed both the random and alternating systems at 100 °C and 40% RH fuel cell operating conditions and showed similar performance to Nafion.

## Introduction

The search for renewable, clean energy sources is one of the most pressing challenges facing global society. Proton exchange membrane fuel cells (PEMFCs) have the potential to alleviate major problems associated with the production and consumption of energy. One of the major technical challenges that faces current PEMFCs is operation under low relative humidity (RH) (i.e., <50%) and elevated temperatures (i.e., >100 °C). Under these conditions, the ohmic resistance of fuel cells increases significantly due to the high resistance of proton exchange membranes (PEMs), adversely impacting fuel cell performance. Therefore, improving proton conductivity of PEMs operating in a low RH and elevated temperature environment has been of great interest.<sup>1–3</sup>

Early studies using pulsed field gradient spin echo <sup>1</sup>H NMR indicated that the dominant mode of proton conduction in sulfonated PEMs at low humidity is via a vehicular mechanism, whereas in the sulfonated membranes at high humidity, protons are rapidly exchanged between hydrated

proton exchange sites via the Grøtthuss mechanism.<sup>4,5</sup> Proton conduction at low RH requires water to diffuse throughout the membrane thickness, which can only occur successfully through continuous hydrophilic pathways such as those found in perfluorosulfonic acid copolymers such as Nafion. Proton conduction at low RH for sulfonated aromatic polymers has been shown to be less effective than that for Nafion, even though excellent thermal, oxidative, and hydrolytic stability and low permeability to reactant gases of sulfonated aromatic PEMs make these PEMs attractive alternatives to Nafion.<sup>6,7</sup> The low conductivity of sulfonated aromatic PEMs at low RH has been attributed to the fact that sulfonated aromatic polymers have less connected water domains as well as more phase mixing of hydrophobic and hydrophilic domains.<sup>8</sup> Although the higher degree of phase mixing in sulfonated aromatic PEMs is mainly due to the similar chemical structure between the hydrophilic and hydrophobic parts and increased backbone stiffness, lack of phase continuity and more “dead end” water domains is largely due to the irregular distribution (randomness) of the sulfonic acid groups. To date, most sulfonated aromatic PEMs prepared by postsulfonation of commercial membranes or by direct copolymerization of disulfonated monomers have been random or

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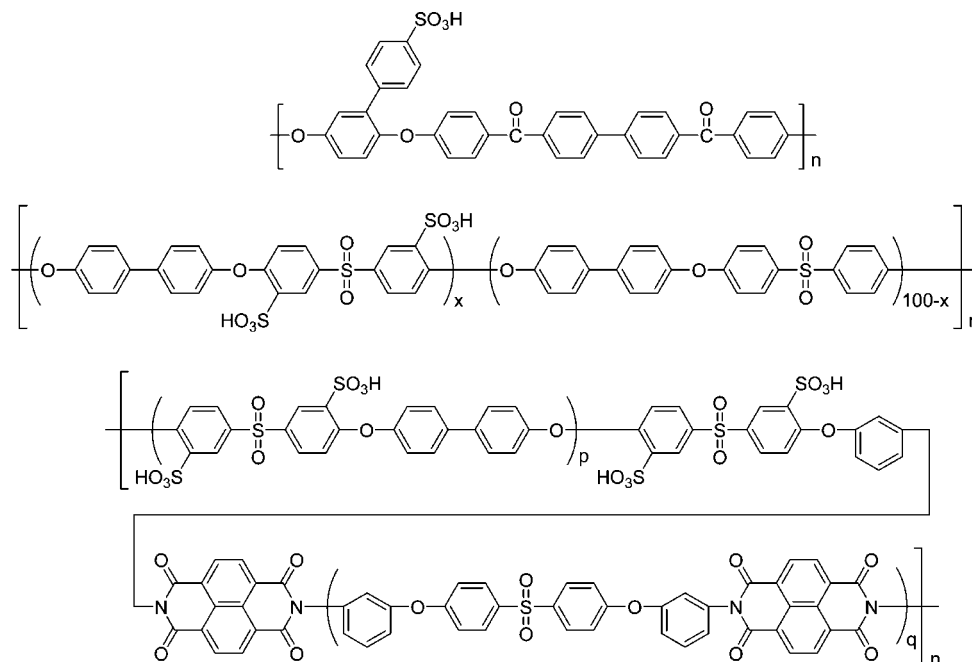
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**Figure 1.** Structure of sulfonated aromatic PEMs used for this study (top, Ph-PEEKDK alternating polymer; center, BPSH-35 random copolymer; bottom, BPSH-15-PI-15 multiblock copolymer); the mole percentage of sulfonated repeat units,  $x$ , for BPSH-35 is 35; the molecular weights of the segments  $p$  and  $q$  for BPSH-15-PI-15 are 15k; acronyms are found in the original papers.

statistical copolymers.<sup>7</sup> If sulfonated aromatic polymers are to be successful as PEMs, the morphology must be understood and controlled in such a way that will provide more distinct phase separation between hydrophilic and hydrophobic domains as well as connectivity between hydrophilic domains, even at low RH. Recently, several viable synthetic strategies have been attempted to improve the electrochemical properties of sulfonated aromatic PEMs, including multiblock or graft copolymers which have controlled segment length,<sup>9–17</sup> as well as alternating polymers which have controlled sulfonation sites with one substituted sulfonic acid per repeat unit via postsulfonation.<sup>18</sup>

In this contribution, three sulfonated aromatic PEMs (alternating, random, and multiblock polymers) having different microstructures were used to discern the influence of morphology on electrochemical properties, thus allowing for conclusions regarding the molecular design of sulfonated aromatic PEMs. Water transport, proton conductivity, and polarization behavior of an alternating sulfonated poly(arylene ether ketone),<sup>18</sup> a random sulfonated poly(arylene

ether sulfone),<sup>19</sup> and a multiblock copolymer composed of a hydrophobic polyimide block and a poly(arylene ether sulfone) hydrophilic block<sup>20</sup> were measured using water sorption isotherms, ac impedance, phase mode scanning force microscopy, and fuel cell testing under controlled RH conditions. Since the three membranes have similar water uptake, ion-exchange capacity (IEC), and acid groups, differences in properties can be in large part be attributed to the morphological organization of the PEMs.

## Experimental Section

**Materials.** An alternating sulfonated polymer with a phenyl pendant group (Ph-PEEKDK) was prepared by postsulfonation of the starting homopolymer of phenylhydroquinone and 4,4'-bis(4-fluorobenzoyl)biphenyl using concentrated sulfuric acid.<sup>18</sup> A random copolymer of 4,4'-biphenol, 4,4'-dichlorodiphenylsulfone, and 3,3'-disulfonated-4,4'-dichlorodiphenylsulfone (BPSH-35, where 35 refers to the mole percentage of disulfonated repeat units) was synthesized by step or polycondensation as described in the literature.<sup>19</sup> A multiblock copolymer containing a hydrophilic poly(arylene ether sulfone) block and a hydrophobic polyimide block (BPSH-15-PI-15, where 15 refers to the molecular weight of each segment in kg/mol) was synthesized as previously reported.<sup>20</sup> The molecular weights of the blocks were controlled using a modified Carothers equation. Chemical structures of the PEMs are shown in Figure 1.

Membranes of alternating polymer and random copolymer in the acid form and potassium salt form, respectively, were obtained by solution casting from 10 wt % solutions in dimethylacetamide (DMAc), whereas multiblock copolymers were cast similarly from *N*-methylpyrrolidone (NMP) solutions. The solutions were filtered

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through 0.45  $\mu\text{m}$  Teflon syringe filters and cast onto clean glass substrates. The solvent was evaporated under an infrared lamp for 24 h, followed by further drying in a vacuum oven at 100 °C for 24 h. The membranes were boiled in 0.5 M  $\text{H}_2\text{SO}_4$  for 2 h followed by boiling in deionized water for 2 h for acidification and morphological stabilization.<sup>21</sup> Commercial Nafion membranes were treated first by boiling in a 3% hydrogen peroxide solution for 2 h, washed with boiling deionized water for 2 h, and finally acidified and washed by the same method as the sulfonated aromatic PEMs. All acid-form membranes were stored in deionized water until use.

**Water Sorption.** Water sorption was measured on small pieces of membrane suspended inside a Mettler Toledo microbalance maintained at 30 °C. RH was controlled using lithium chloride solutions of various concentrations in the RH range of 20–90% and was monitored by a capacitive humidity sensor connected to a computer interface and software. The samples were dried in a 95 °C vacuum table for a preliminary weighting and then suspended in the balance. The mass change over time was recorded and used to calculate water diffusion coefficients. The water diffusion coefficients of the membranes at various humidity levels can be described using the following equation:

$$\ln(1 - m_t/m_\infty) = \ln(8/\pi^2) - D\pi^2 t/l^2 \quad (1)$$

where  $m_t$  and  $m_\infty$  are the masses of water vapor absorbed after time  $t$  and after equilibrium, respectively,  $D$  is the diffusion coefficient, and  $l$  is the membrane thickness. By plotting  $\ln(1 - m_t/m_\infty)$  as a function of  $t/l^2$ , the diffusion coefficient was obtained from the slope of the linear portion.<sup>22</sup> The water diffusion coefficients of the sulfonated aromatic PEMs, as well as Nafion, were determined in this manner.

**Conductivity.** In-plane ionic conductivity measurements were conducted at a variety of temperatures and relative humidities, which were controlled using an Espec SH-241 environmental chamber. A Solartron SI 1260 impedance/gain-phase analyzer was used to measure the membrane resistance over the frequency range of 10 Hz to 1 MHz. The conductivity was calculated from the membrane dimensions and the resistance at the frequency with the minimum imaginary response.

**Scanning Force Microscopy.** Scanning force microscopy (SFM) techniques were used to characterize membrane samples as a function of RH using a Veeco Metrology MultiMode microscope, Nanoscope IIIa controller, and commercial 125  $\mu\text{m}$  SFM cantilevers (NanoDevices) with typical resonance frequencies around 300 kHz. Intermittent contact (tapping) mode of operation, which is sensitive to variations in local mechanical stiffness, was used to obtain both surface topographic and local phase segregation information. The MultiMode wet cell cantilever holder was set up as part of a closed circulating pumping system that included a bubbler tube filled with a saturated salt solution, a flow meter, and a humidity sensor. Various saturated salt solutions were used to achieve the different RH environments. Samples were initially subjected to a flow of air passed through a drying tube for several hours before imaging. A single cantilever maintained at the same drive amplitude and set point throughout the measurements was used for the entire RH range. Actual RH was monitored using the in-line humidity sensor.

**Fuel Cell Tests.** Membrane electrode assemblies (MEAs) were prepared from standard Los Alamos National Laboratory inks using unsupported platinum catalyst for both the anode and cathode.<sup>23</sup> The active area was 5  $\text{cm}^2$ , and the catalyst loading was ap-

**Table 1. Intrinsic Viscosity and IEC Data for the PEMs**

PEM	$[\eta]$ (dL/g)	IEC <sub>W(dry)</sub> (meq/g)		water uptake (wt %)	IEC <sub>V(wet)</sub> (meq/cm <sup>3</sup> )
		theor	exptl <sup>a</sup>		
alternating (Ph-PEEKDK)	3.35 <sup>b</sup>	1.60	1.60	32	1.41
random (BPSH-35)	0.80 <sup>c</sup>	1.53	1.50	40	1.31
multiblock (BPSH-15-PI-15)	0.67 <sup>c</sup>	1.51	1.55	51	1.21
Nafion 212		0.95–1.01 <sup>d</sup>		19	1.45

<sup>a</sup> Measured by titration with standardized sodium hydroxide solution.

<sup>b</sup> Measured at 30 °C in DMAc (no salt). <sup>c</sup> Measured at 25 °C in NMP with 0.05 M LiBr. <sup>d</sup> From the Dupont material data sheet (<http://www.fuelcell.com/techsheets/Nafion%20NRE-211%20212.pdf>).

proximately 6  $\text{mg}/\text{cm}^2$ . High catalyst loadings were used in order to isolate membrane effects by maximizing the performance of the electrodes. Humidified hydrogen and air were supplied to the anode and cathode, respectively. A Fuel Cell Technologies fuel cell test station was used to measure MEA performance.

## Results and Discussion

**Membrane Properties.** High molecular weight sulfonated aromatic PEMs were synthesized by polycondensation. The degree of sulfonation was carefully controlled by selection of the molecular weight of the two monomers (alternating polymer), the feeding ratio of sulfonated to nonsulfonated monomers (random copolymer), and the length of the block segments (multiblock copolymer). Film casting produced tough, ductile, transparent membranes which were acidified using sulfuric acid. In all cases, high molecular weight polymers were synthesized and confirmed by high intrinsic viscosity values (Table 1). Table 1 also shows the IEC for each polymer. Experimental IEC on a dry weight basis, IEC<sub>W(dry)</sub> of each PEM agreed with the theoretical values (<3% error), indicating that the degree of sulfonation in each PEM was precisely controlled. The IEC<sub>W(dry)</sub> values of the sulfonated aromatic PEMs were similar (1.51–1.60 meq/g). Ion-exchange capacity on a wet volume basis, IEC<sub>V(wet)</sub> has been proposed as a better relative gauge of sulfonic acid concentration per unit volume under hydrated conditions.<sup>24</sup> The calculated IEC<sub>V(wet)</sub> of each PEM under fully humidified conditions using known polymer density and water uptake was in the range of 1.21–1.41 meq/cm<sup>3</sup>. The multiblock copolymer had the lowest IEC<sub>V(wet)</sub> followed by the random copolymer and alternating polymers due to slightly higher water uptake of the multiblock copolymer under fully hydrated conditions. The IEC<sub>V(wet)</sub> of the multiblock copolymer approached those of other polymers under partially hydrated conditions (<100% RH) since vapor water sorption of the multiblock copolymer is decreased relative to that of the other polymers presented, as shown in Figure 2.

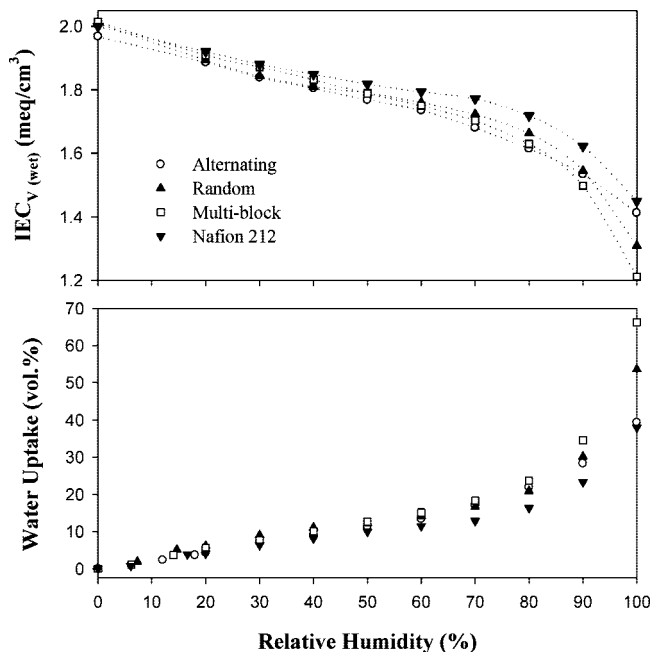
**Water Sorption.** Water sorption of the sulfonated aromatic PEMs and Nafion was measured at 30 °C as a function of RH (Figure 2). For more reasonable comparison, weight-based water uptake was converted to volume-based water uptake. All four membranes showed a slow increase in water sorption as a function of humidity below 80% RH, with a

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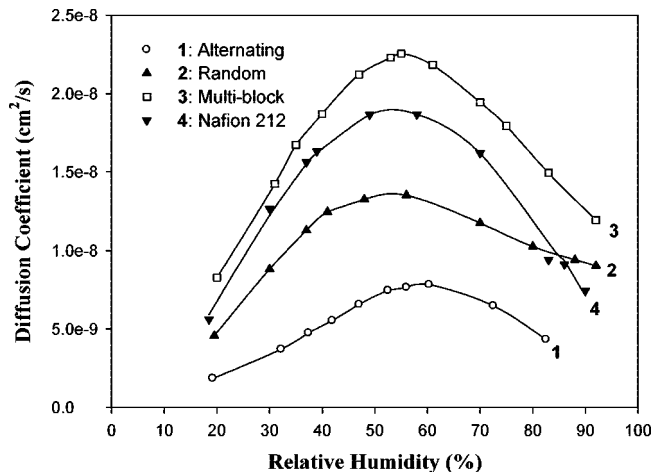




**Figure 2.** Water sorption and  $IEC_{V(wet)}$  of sulfonated aromatic PEMs as a function of RH at 30 °C; water uptake at 100% RH measured under liquid water equilibrium conditions (Nafion is shown for comparison).

much greater increase in absorbed water above 80% RH. All three sulfonated aromatic PEMs had higher water uptake than Nafion above 20% RH. The sulfonated aromatic PEMs had similar water uptake at low to moderate RH values (e.g., water uptake = 11.3–12.6% at 50% RH), but the multiblock copolymer was able to absorb larger amounts of water at high RH. Figure 2 also shows the  $IEC_{V(wet)}$  of each polymer as a function of humidity.  $IEC_{V(wet)}$  decreases with RH because membrane volume increases with RH, while the number of acid sites remains constant. All three aromatic PEMs exhibit comparable  $IEC_{V(wet)}$  values (<2% deviation) at 20–60% RH (e.g., 1.77–1.79 meq/cm<sup>3</sup> at 50% RH), with the small differences due to differences in  $IEC_{W(dry)}$ , water sorption, and density of the PEMs. The  $IEC_{V(wet)}$  of Nafion is higher than those of sulfonated aromatic PEMs (e.g., 1.82 meq/cm<sup>3</sup> at 50% RH) in spite of its low  $IEC_{W(dry)}$  due to its high polymer density and low water uptake. This indicates that the number of acid sites per given volume of Nafion is higher than that of the sulfonated aromatic PEMs. Because of the high degree of phase separation in Nafion, it also suggests that the average distance between sulfonic acid ion-exchange sites for Nafion is likely shorter than that of these sulfonated aromatic PEMs. From this data, it is concluded that the amount of water involved in proton conduction and sulfonic acid concentration per unit volume are similar in all three sulfonated aromatic PEMs, removing the effect of sulfonic acid concentration on conductivity from our comparative studies.

Although water uptake of the three aromatic PEMs showed similar water uptake at low to moderate RH values, sorption kinetics of the PEMs are significantly different. Figure 3 shows the diffusion coefficient values from water sorption experiments. The diffusion coefficient of Nafion obtained in this research is in the range of  $0.6\text{--}1.9 \times 10^{-8}$  cm<sup>2</sup>/s at 20–90% RH which was in close agreement with other data



**Figure 3.** Diffusion coefficients of sulfonated aromatic PEMs and Nafion as a function of RH at 30 °C (Nafion is shown for comparison).

in the literature.<sup>25,26</sup> The diffusion coefficients for all of the membranes increased as the humidity was increased up to 60%, then started to decrease as the membrane became saturated with water. Decreasing water diffusion at high RH has been reported to be due to interfacial transport that limits the water diffusion rate,<sup>27</sup> and the trend has appeared in other diffusion experiments for PEMs.<sup>28,29</sup> The alternating polymer had the lowest water diffusion coefficient, followed by the random copolymer, followed by Nafion. The multiblock copolymer had the highest water diffusion coefficient. For example, the diffusion coefficient of the multiblock copolymer at 50% RH at 30 °C was  $2.2 \times 10^{-8}$  cm<sup>2</sup>/s, which was much higher than those of the random copolymer ( $1.3 \times 10^{-8}$  cm<sup>2</sup>/s) and the alternating polymer ( $0.7 \times 10^{-8}$  cm<sup>2</sup>/s) under the same conditions.

**Conductivity.** Membrane conductivity was measured in a range of 20–90% RH as shown in Figure 4. Proton conductivity of the tested samples increased as RH increased, indicating that the presence of additional water enhances conduction by either vehicular or Grøtthuss conduction mechanisms. The dilution effect of sulfonic acid concentration is not pronounced. The conductivity of the multiblock copolymer was significantly higher than that of the random and alternating systems at low RH (e.g., 1.9, 0.7, and 0.2 mS/cm at 50% RH for multiblock, random, and alternating PEMs, respectively). The conductivity of Nafion is higher than that of the sulfonated aromatic PEMs (4.2 mS/cm at 50% RH). The relative slopes of the log (conductivity) versus RH plots for each polymer are of interest and can illustrate the effect of humidity on each membrane's conductivity. Nafion and the multiblock copolymer both had similar slope ( $\sim 0.026$ ), which was the lowest of all the membranes studied. The random copolymer had a higher slope (0.038), meaning

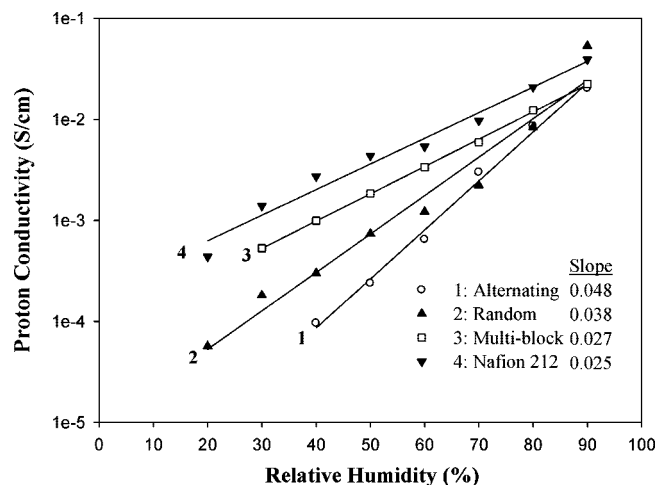
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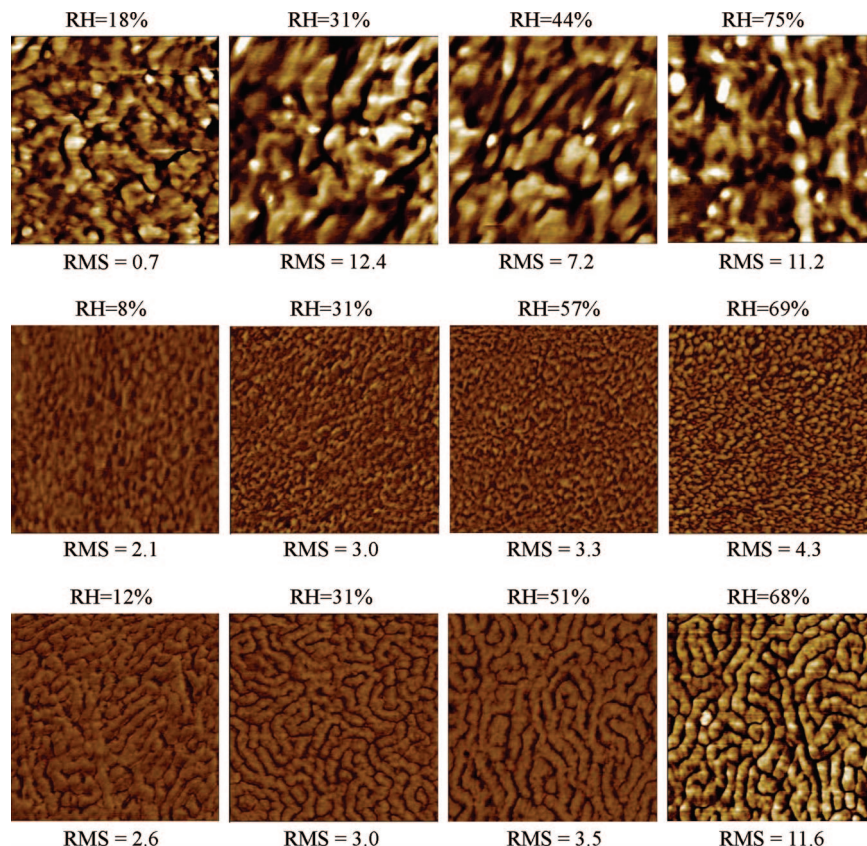
**Figure 4.** Conductivity as a function of RH at 80 °C (Nafion is shown for comparison).

that its conductivity was more dependent on RH than that of Nafion and the multiblock copolymer. The alternating polymer had the highest slope (0.048), because its conductivity was the most dependent on RH out of all the membranes studied herein. At high RH, the membrane conductivities were close to one another. This conductivity data (although showing some qualitatively similar trends at low RH) cannot be directly correlated with the diffusion data presented in Figure 3 because polymer reorganization effects during hydration/dehydration significantly affect the reported diffusion coefficients. Diffusion coefficients obtained from NMR or transport measurements under equilibrated conditions might lead insight into the proton conduction mechanism.

**Morphology.** Tapping-mode SFM was used to compare the morphological arrangements of the sulfonated aromatic PEMs as a function of RH. Each PEM is shown at a range of RH values (8–75% RH) in Figure 5. The hydrophilic domains seemed to swell or enlarge as the RH was increased from low to high; at a RH < 20%, hydrophilic domains for all three PEMs were substantially contracted. Morphological changes from 20 to 60% RH are insignificant except for moderately increased domain size, probably due to slightly increased water uptake in this humidity range (see Figure 2). Above 60% RH, the phase angle difference between the hydrophilic and hydrophobic domains increased, as evidenced by greater contrast, in addition to an increase in domain size. The increased phase contrast is accompanied by an increase in the root-mean-square surface (abbreviated rms) roughness measurement. The increase in rms roughness is probably due to increased absorption of water by the hydrophilic domains inducing swelling. Domain size and connectivity are both distinctly different among the three sulfonated PEMs studied herein. The alternating polymer shows large hydrophobic and hydrophilic domains, although the continuity between hydrophilic domains is poor. This lack of connectivity may explain this polymer's relatively low water diffusion and conductivity. The random copolymer exhibited a disordered morphology with some connectivity between the hydrophilic regions but no well-defined ionic pathways for proton or water transport. There was a small increase in the rms roughness of the random and alternating

polymers as the humidity increased. It is evident that there is some change in the phase contrast as the hydrophilic and hydrophobic domains undergo a small amount of further phase separation upon increasing RH. The multiblock copolymer, on the other hand, showed a well-defined "fingerprint-type" structure with continuous hydrophilic and hydrophobic pathways. This microstructure may be responsible for fast proton transport even at low humidity, as well as the faster water transport than that of the alternating and random polymers. The average domain sizes were estimated from the highest-RH image (~69% RH) of each of the three membranes. A line scan was used to measure the widths of hydrophobic and hydrophilic domains based on the points of crossing the zero line. The alternating polymer had hydrophobic domains with an average dimension of  $79 \pm 19$  nm and hydrophilic domains with an average dimension of  $65 \pm 18$  nm. The average sizes of the hydrophobic and hydrophilic domains in the random copolymer were  $25 \pm 8$  and  $18 \pm 6$  nm, respectively. Lastly, the hydrophobic and hydrophilic domain sizes in the multiblock copolymer were  $57 \pm 17$  and  $23 \pm 10$  nm, respectively. It is interesting that the alternating polymer had the largest hydrophilic domains even though it had the lowest conductivity, which illustrates that the connectivity of the diffusion path is crucial for high water diffusion and is even more influential than the domain size. These morphological features qualitatively explain why high water diffusion and thus improved proton conductivity can be obtained with multiblock copolymers at low RH. Further improvement of water diffusion and conductivity may be realized as domain size and tortuosity of hydrophilic domains decrease and phase contrast between hydrophobic and hydrophilic domains increases, which are areas of future investigation.

**Fuel Cell Performance.** To estimate the impact of morphology on fuel cell performance, polarization characteristics of single cells using each of the PEMs, Figure 6, were compared at two different gas inlet humidities (70% and 40% RH). Although experimental uncertainty and other properties such as differences in water diffusion, electro-osmotic drag, and membrane thickness limit the conclusions that can be drawn, the polarization curves clearly show the impact of conductivity of these PEMs under different RH conditions. When the inlet gases were both maintained at 70% RH, the random and multiblock copolymers performed similarly. However, much lower cell performance for the cell using the alternative membrane was found, probably due to the slow proton transfer rate of the alternating polymer even at moderate humidity. We have observed that the fuel cell performance of the cell using the alternating membrane was much improved under water-saturated conditions (polarization curve not shown here for brevity). At a much lower humidity of 40%, the performance of the random copolymer suffered significantly, whereas the multiblock copolymer maintained much of its performance, comparable to Nafion. This high performance at low RH is likely due to the multiblock copolymer's excellent transport properties at low RH that arise from its unique morphology. The alternating polymer had no measurable current at 40% RH. The low reactant permeability, low water swelling, and good con-

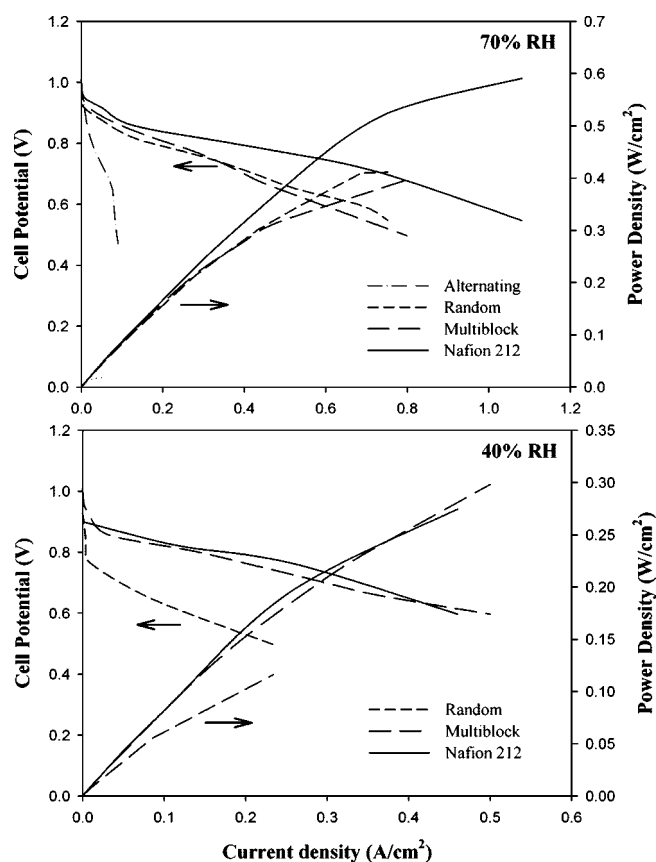


**Figure 5.** SFM images of alternating (top), random (center), and multiblock (bottom) PEMs as a function of RH. Image size is 1  $\mu\text{m}$ , and phase range is  $40^\circ$  for all images.

ductivity of fully hydrated alternating polymers are favorable properties in liquid feed fuel cells such as direct methanol fuel cells.<sup>30</sup> The power density curves from test membranes are also shown (Figure 6) and illustrate the same trends as the voltage–current curves. These data provide an idea of how multiblock copolymers bearing continuous hydrophilic domain structures could improve fuel cell performance at low RH.

### Conclusions

This research presents the effect of morphology on conductivity at low RH using an alternating, a random, and a multiblock PEM having similar water uptake and sulfonic acid concentration. The results confirm that membrane morphology plays a critical role in water sorption kinetics and proton conduction at low RH. In particular, phase connectivity of hydrophilic domains seems to be the critical parameter. Good phase connectivity of the multiblock copolymer provides relatively good conductivity and less dependency on RH compared to alternating and random polymers. The superior conductivity of a multiblock copolymer was confirmed by fuel cell performance under high temperature and reduced humidity. The fuel cell performance of a single cell using this multiblock copolymer at 40% RH was comparable to that of Nafion, which performed much better than the alternating and random polymers. Well-defined ionic channels, such as those shown herein for the



**Figure 6.** Hydrogen–air fuel cell performance of the alternating, random, and multiblock PEMs at 100 °C with gas inlet humidification at 70% (top) and 40% (bottom) (Nafion is shown for comparison).

(30) Liu, B.; Kim, Y. S.; Hu, W.; Robertson, G. P.; Pivovar, B. S.; Guiver, M. J. *Power Sources*, accepted in July 2008.

multiblock copolymer, are necessary for improved transport properties in PEMs and should be a major consideration in the design of novel PEMs. Recent efforts to form a distinct self-assembled morphology using segmented block and graft chains will provide further proof for the conclusions of the present study.<sup>31,32</sup>

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- (31) Lee, H. S.; Roy, A.; Lane, O.; Dunn, S.; McGrath, J. E. *Polymer* **2008**, *49*, 715.  
(32) Kim, D. S.; Robertson, G. P.; Guiver, M. D. *Macromolecules* **2008**, *41*, 2126.

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