Differences in Water Sorption and Proton Conductivity Between Nafion and SPEEK

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ABSTRACT: Water sorption, volumetric expansion, and proton conductivity of 1100 EW Nafion and 555 EW sulfonated polyetheretherketone (SPEEK) were compared as functions of water activity at 60 and 80 °C. Water sorption in Nafion occurs with a small positive volume of mixing, ~ 0.005 cm^3/cm^3. In contrast, water sorption in SPEEK has a large negative volume of mixing ~ -0.05 cm^3/cm^3. The percolation thresholds for proton conduction occur at hydrophilic volume fractions of 0.10 in Nafion and 0.30 in SPEEK. Proton conductivity increases quadratically with hydrophilic volume fraction above the percolation threshold. The different percolation thresholds suggest the hydrophilic domains in Nafion grow from lamella, whereas the hydrophilic domains in SPEEK grow from spheres. © 2011 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 49: 1437–1445, 2011

KEYWORDS: conducting polymers; conductive network; ionomers; membranes; microstructure; poly(ether ketones); swelling

INTRODUCTION Sulfonated polyetheretherketone (SPEEK) is one of many different polymer electrolytes that have been suggested as an alternative for Nafion in polymer electrolyte membrane (PEM) fuel cells.[1–14] Both polymers show good proton conductivity at high water content. However, Nafion has higher proton conduction at lower volume fraction of sulfonic acid groups than SPEEK.[1,5,8,11,12,15] Increasing the sulfonic acid substitution to SPEEK to achieve comparable proton conductivity to 1100 EW Nafion results in the SPEEK losing mechanical strength and becoming soluble in liquid water.

Both Nafion and SPEEK microphase separate into hydrophilic and hydrophobic domains. The hydrophobic domains consist of the perfluorinated backbone and perfluoro alkyl ether in Nafion and the PEEK backbone in SPEEK. The hydrophilic domains originate from the sulfonic acid groups. Water sorbs into the polymers associating with the sulfonic acid groups swelling the hydrophilic domains. Proton conduction occurs through the hydrophilic domains. Useful PEMs must identify an optimal concentration of sulfonic acid groups which balance the increased conductivity with and decreased mechanical strength with increased acid concentration.

PEMs have hydrophilic domains dispersed in a continuous hydrophobic matrix. At low water content, the hydrophilic domains may not be sufficiently connected to carry a proton current. Water sorbs into the hydrophilic domains swelling them and creating percolation paths for proton conduction. A common model for PEMs, originally proposed by Gierke, is that the hydrophilic groups aggregate as spherical inclusions within the hydrophobic matrix.[16,17] As water is sorbed the hydrophilic domains swell and percolate permitting protons to be conducted. Water sorption and proton conductivity of Nafion has been extensively studied.[18–27] Several researchers have measured proton conduction in SPEEK and composites of SPEEK.[6,8,10–12] Those studies show that for comparable equivalent weights (EW= g-polymer/mole HSO_3) SPEEK had proton conductivity comparable to Nafion at high water activity, but at low water activity, SPEEK had lower proton conductivity than Nafion.

Kreuer modeled the proton conduction mechanism in both Nafion and SPEEK.[25] He attributed the reduced proton conductivity in SPEEK to differences in the microstructure and pKa of the acid functional groups in Nafion and SPEEK. On the basis of the differences in small-angle X-ray scattering patterns, Kreuer suggested that at high water contents, the tortuosity of the hydrophilic domains in SPEEK was greater than in Nafion, and, hence with equivalent acid group concentration for SPEEK and Nafion, SPEEK had low proton conductivity.

To better understand the differences in proton conductivities of SPEEK and Nafion at low water activities, we have compared the water uptake, volumetric expansion, and proton conductivity of 1100 EW Nafion and 555 EW SPEEK. We report here that the volume of mixing for water sorption and the proton conduction percolation thresholds are dramatically different between the two polymers. We suggest that these differences arise from different morphologies of the hydrophilic domains reflecting different coordination of the sulfonic acid groups.

EXPERIMENTAL

Materials

SPEEK was prepared by sulfonation of polyetheretherketone with sulfuric acid.[28] PEEK (VESTAKEE® 4000G: density = 1.30 g/cm^3, melting temperature ~340 °C) was purchased from Professional Plastics. PEEK (5g) was dissolved in 100 mL of 95% concentrated sulfuric acid at ambient temperature. The solution was placed in a 60 °C water bath and stirred for 50 min. The reaction was quenched with ice water, precipitating the SPEEK. The SPEEK was washed with deionized water until neutral and then dried in vacuum at 80 °C for 24 h. SPEEK films were cast from solution. SPEEK was dissolved in *N*-methyl-2-pyrrolidone (10 wt %), and the solution was cast on a glass plate to the desired mass loading for 70 μm films. After evaporation of the solvent at 50 °C, the film was carefully removed from the glass and dried in vacuum at 80 °C to evaporate the residual solvent. The degree of sulfonation (DS) and equivalent weight (EW) of the final SPEEK films were determined by titration. The SPEEK films in this study were circa 70 μm thick with DS = 1.58 and EW555 g/mol.

1100 EW Nafion films, 125 μm thick (Nafion 115) were obtained from Ion Power. These films were prepared by a standard procedure of vacuum annealing, placing in boiling H_2O_2/H_2SO_4 solution, and rinsing with deionized water; the protocol listed below has been demonstrated to make reproducible films that showed no memory of the history of the film.[29–35]

1. Anneal sample at $T \geq 80$ °C in vacuum for >2 h.
2. Boil in 3 wt % H_2O_2 solution for 1 h.
3. Rinse sample with deionized water.
4. Place membrane in boiling 1 M H_2SO_4 solution for 1 h.
5. Rinse with DI water.
6. Dry in vacuum oven or dry nitrogen at 80 °C for 2 h.

Polymer Characterization

The equilibrium water uptake and proton conductivity were measured as a function of water pressure at different temperatures using an isometric system.[36,37] A PEM is clamped between two electrodes in a fixed volume container as shown in Figure 1. The nominal membrane is ~2 cm (wide) × 6 cm (long) × 0.01 cm (thick).

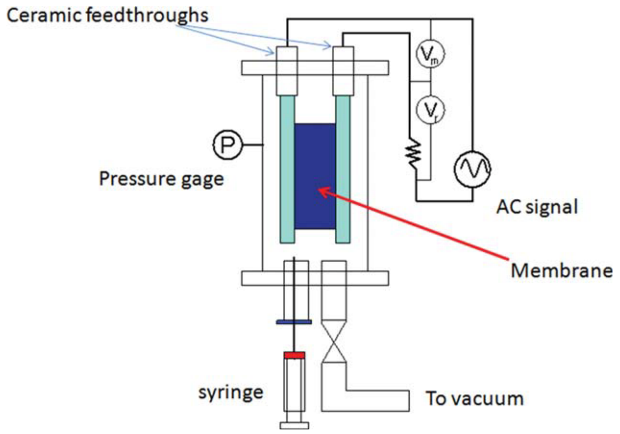

FIGURE 1 Water sorption and conductivity measurement cell. The polymer membrane is clamped inside a 510 cm^3 evacuated vessel. Liquid water aliquots are injected by syringe through a septum. The water sorbs establishing equilibrium between the vapor and the water in the membrane. The water partial pressure is measured, which also permits the number of moles of water sorbed to be determined. The membrane resistance is measured by from the AC voltage drop across the membrane.

The PEM sample was evacuated to below 1 Pa (<0.01 mbar) at 80 °C to remove all the water from the membrane. The container, with volume V_{vessel}, is sealed and equilibrated at the desired temperature. Aliquots of water, 5–50 μL, are introduced at intervals of 0.5–2 h and allowed to equilibrate with the Nafion. The pressure, *P*, inside the vessel is equal to the water pressure. The difference between the water in the vapor and the water injected is equal to the moles of water absorbed by the Nafion, *M*, as given by eq 1.

$$M = \left\{ \frac{V_{\text{water injected}}}{V_{\text{w}}} - \frac{V_{\text{vessel}} P}{RT} \right\} \tag{1}$$

Water sorption as a function of water activity was determined as a function of water activity, $a_{\text{w}} = P_{\text{w}}/P^0_{\text{w}}\ (T)$, where P_{w} = partial pressure of water and P^0_w = saturation water pressure at the temperature of interest.

The sample is clamped to measure the resistance laterally across a distance of ~1 cm. A 200-Hz AC voltage was applied across the PEM and a known resistance placed in series. The voltage drop across the PEM and the known resistance were measured. The membrane resistance was obtained by treating the circuit as a simple voltage divider. By measuring the resistance laterally through a large length and small cross-sectional area, the interfacial resistance and capacitance are insignificant to the overall impedance.[38] We have measured the membrane resistance in the frequency range of 1–10^5 Hz using this setup and have verified that the impedance is independent of frequency above 10 Hz.

The linear expansion coefficient of Nafion was also measured as a function of temperature and water activity in a dynamic creep apparatus.[39] Samples were clamped in an environmental chamber, dried in nitrogen at 80 °C for 2 h, brought to the desired temperature in dry nitrogen and then the dry nitrogen was replaced with a humidified nitrogen stream. The change in length was recorded as a function of time; the equilibrium swelling strain was assumed to be achieved when the rate of swelling was less than 0.001/h.

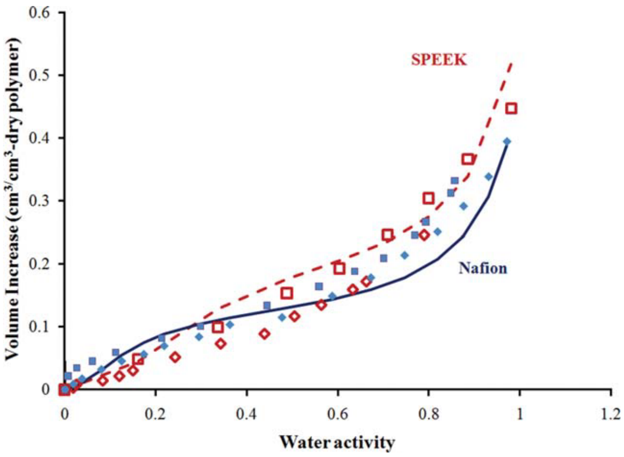

FIGURE 2 Sorption isotherms of water in 1100 EW Nafion and 555 EW SPEEK. Squares are the volumetric expansion, diamonds are from the volume of water sorbed. Blue symbols are Nafion, red symbols are SPEEK. The lines are the least squares fit of the two hydration shell of water sorption presented in the text. (Please refer to the online version for color symbols.)

The excess volume of mixing for water sorption was determined by taking the difference between the volume of water sorbed and the volume change of the polymer after water sorption.[40] The volume of the sorbed water per unit mass of dry polymer, assuming zero excess volume of mixing, is given by eq 2.

$$\frac{V_{\text{sorption}}}{\bar{V}} = \left(\frac{M V_{\text{w}} \rho_{\text{polymer}}}{m_{\text{polymer}}}\right) \tag{2}$$

The linear expansion coefficient for water absorption, ε, is measured by experiment. The volume change due to water absorption assuming isotropic expansion is given by eq 3.

$$\frac{V}{\bar{V}} = (1+\varepsilon)^3 - 1 \tag{3}$$

The excess volume of mixing is the difference of eqs 2 and 3.

RESULTS

Adsorption Isotherms

Water sorption isotherms in EW1100 Nafion and EW555 SPEEK at 80 °C are shown in Figure 2. Sorption isotherms were also obtained at 30 and 60 °C. Both the volume of water sorbed, given by eq 2 and the volume change, given by eq 3, are plotted as functions of water activity. The difference between the volumetric expansion of the polymer and the volume of water sorbed is the excess volume of mixing, which is plotted in Figure 3.

Nafion shows a small positive excess volume of mixing for water sorption. In contrast to Nafion, SPEEK shows a substantial negative excess volume of mixing. The results in Figure 3 also show a change in slope of the excess volume of mixing with water volume corresponding to $\lambda \sim 4$ water/SO_3 for both Nafion and SPEEK. The change in slope of the excess volume of mixing suggests that the sulfonic acid groups are surrounded by a first hydration shell of 4 waters per sulfonic acid group. Even though both polymers appear to form a first hydration shell of 4 waters the packing of the sulfonic acid groups appears to be different. The sulfonic acid groups in SPEEK appear to be associated with free volume which permits the water molecules to be sorbed with almost no change in polymer volume. Water sorption into Nafion requires more volume than the water molecule itself.

The water sorption isotherms were fit by a hydration shell model. Sorption is modeled as a series of water molecules coordinating to the sulfonic acid groups, where W_i* is a sulfonic acid group with *i* water molecules of hydration.

$$\begin{gathered} W(g) + * \overset{K_0}{\rightleftarrows} W* \\ W(g) + W* \overset{K_1}{\rightleftarrows} W_2* \\ \vdots \\ W(g) + W_i* \overset{K_i}{\rightleftarrows} W_{i+1}* \end{gathered} \tag{4}$$

Reaction equilibria may be written for each sequential addition of water as shown in eq 5.

$$\begin{gathered} \frac{x_{W_{i+1}*}}{x_{W_i*} a_{\text{w}}} = K_i = \exp\left\{-\frac{\Delta G_i}{RT}\right\} \\ a_{\text{w}} = \frac{P_{\text{w}}}{P_{\text{w}}^0} \end{gathered} \tag{5}$$

The average level of hydration of each sulfonic acid is given by eq 6. This general form had previously been presented by Datta and coworkers.[24,41,42] Choi and Datta considered two special cases of eq 6; (1) all equilibrium constants were the

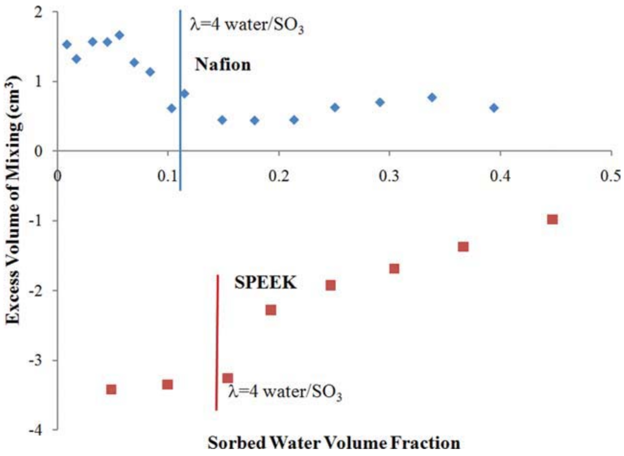

FIGURE 3 Excess volume of mixing of water in 1100 EW Nafion and 555 EW SPEEK at 80 °C. The vertical lines show the volume of water corresponding to 4 water molecules per sulfonic acid group.

TABLE 1 Water Sorption Equilibrium Constants for Nafion and SPEEK

	Nafion		SPEEK	
Temperatures (°C)	K_0	K_1	K_0	K_1
60	6.1	0.91	3.9	0.93
80	5.9	0.86	3.8	0.88

same; and (2) the equilibrium constants decayed exponentially with coordination number.[42]

$$\lambda = \frac{\sum_{i=0}^{\infty} iN_i}{\sum_{i=0}^{\infty} N_i} = \frac{\sum_{n=0}^{\infty} n a_{\mathrm{w}}^{n} \left[\prod_{i=0}^{n} K_i\right]}{\sum_{n=0}^{\infty} a_{\mathrm{w}}^{n} \left[\prod_{i=0}^{n} K_i\right]} \tag{6}$$

On the basis of the change in excess volume of mixing, we suggest a more appropriate model is a first solvation shell of n_1 water molecules that coordinate to sulfonic acid with equilibrium constant K_0, and the water molecules that sorb beyond the first shell have a weaker adsorption energy associated with an equilibrium constant K_1.

$$\begin{aligned} K_i &= K_0 \qquad 1 \le i \le n_1 \\ K_i &= K_1 \qquad n_1 < i \end{aligned} \tag{7}$$

The average number of sorbed water molecules for this three parameter adsorption isotherm is given by eq 8.

$$\lambda = \frac{\sum_{i=1}^{n_1} i(K_0 a_{\mathrm{w}})^i + (K_0 a_{\mathrm{w}})^{n_1} \left[\frac{n_1}{1-K_1 a_{\mathrm{w}}} + \frac{1}{(1-K_1 a_{\mathrm{w}})^2}\right]}{\sum_{i=1}^{n_1} (K_0 a_{\mathrm{w}})^i + (K_0 a_{\mathrm{w}})^{n_1} \left[\frac{1}{1-K_1 a_{\mathrm{w}}}\right]} \tag{8}$$

The sorption isotherms for Nafion and SPEEK in Figure 2 have been fit by least squares to eq 8; n_1 was constrained to integral values. The best fit was for $n_1 = 4$ for both SPEEK and Nafion; the values of K_0 and K_1 at 60 and 80 °C are summarized in Table 1.

Both Nafion and SPEEK data were fit with $n_1 = 4$, corresponding to a tetrahedral coordination of waters around the sulfonic acids in the first hydration shell. The values of K_0 and K_1 were insensitive to temperature. K_0 values and were larger for Nafion than for SPEEK, while the values of K_1 were very similar for SPEEK and Nafion. These results suggest that water in the first hydration shell is more strongly associated with the sulfonic acid in Nafion. The similar values of K_1 for Nafion and SPEEK suggest that the energies of association for the second hydration shell and beyond are similar for SPEEK and Nafion. The concept of hydration shells has been proposed by several previous investigations to account for both water sorption, and changes in water transport in Nafion.[17–19,43,44]

The hydration shell isotherm gives a semiquantitative fit to the data. It matches the plateau in water uptake at intermediate water activity and large increase in water uptake at high water activity. The model assumes that all the sulfonic acid groups are in identical environments within the ionomer, but because both these ionomer have random distribution of the sulfonic acid groups, we expect a distribution of interaction energies which cannot be fully captured with two equilibrium constants K_0 and K_1. The model could be made to fit the data better by including more variation of the equilibrium constants for each water of hydration, but the increased complexity of such a model would obscure the physical insight from the model.

Proton Conductivity

Proton conductivities for 1100EW Nafion and 555EW SPEEK at 60 and 80 °C as functions of water activity are shown in Figure 4. For 100-μm thick films, the smallest conductivity measureable was 2×10^{-5} S/cm; this limit was a consequence of the total resistance from the membrane (~100 Ω – 1 MΩ) exceeding the internal resistance of the voltmeters (~1 MΩ) used to measure the voltages across each leg of the voltage divider.

When equilibrated with saturated vapor the conductivities of the 1100 EW Nafion and 555 EW SPEEK are nearly the same. However, the conductivity of Nafion is much greater than that of SPEEK at lower water activity. The proton conductivity of Nafion increases exponentially from $\sigma < 2 \times 10^{-5}$ S/cm at $a_{\mathrm{w}} = 0$ to $\sigma = 10^{-2}$ S/cm at $a_{\mathrm{w}} = 0.2$. In contrast, the proton conductivity of SPEEK is $<10^{-5}$ S/cm for $a_{\mathrm{w}} \le 0.4$ and increases exponentially to $\sigma = 10^{-2}$ S/cm at $a_{\mathrm{w}} = 1.0$.

Protons are conducted through the hydrophilic domains of the polymer electrolytes. The Gierke model suggests that water sorption swells the hydrophilic domains and establishes percolation paths for water and proton diffusion through the polymer matrix. The percolation model suggests

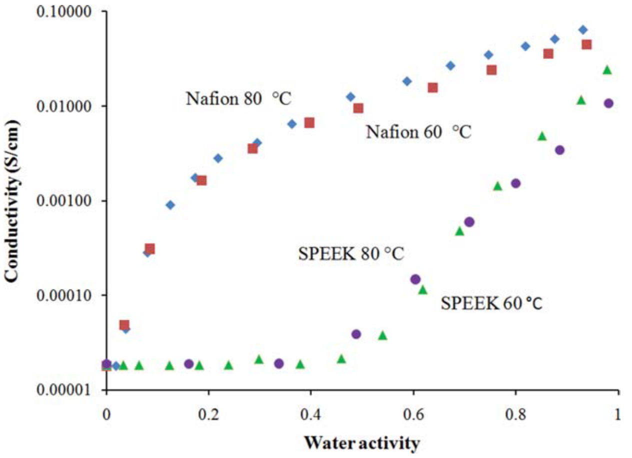

FIGURE 4 Proton conductivities of 1100 EW Nafion and 555EW SPEEK at 60 and 80 °C as functions of water activity. The constant value of 2×10^{-5} S/cm shown for SPEEK at $a_{\mathrm{w}} < 0.4$ is the smallest value of conductivity we could measure. The conductivity of SPEEK is $<10^{-5}$ S/cm.

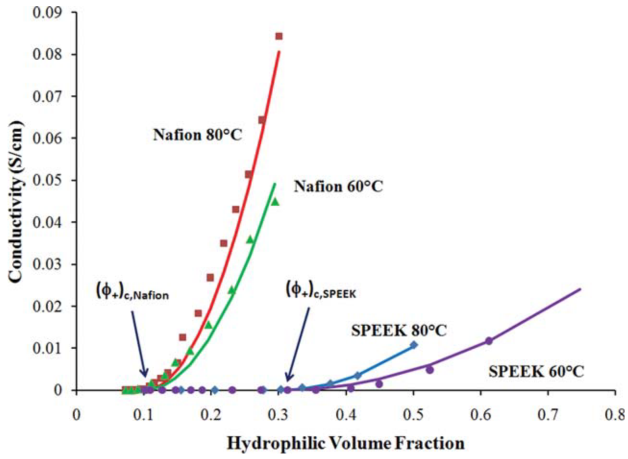

FIGURE 5 Proton conductivities of 1100 EW Nafion and 555 EW SPEEK at 60 and 80 °C as functions of hydrophilic volume fraction. The onset of the quadratic rise with volume fraction is identified as the critical fraction for percolation. The solid lines are fits to the data $\sigma = \sigma_0(\phi_+ - (\phi\_)_c)^2$. Values of σ_0 and $(\phi_+)_c$ are listed in Table 2.

that there is a threshold amount of sorbed water at which proton conductivity turns on and then increases with water activity. The water sorption data from Figure 2 was combined with the conductivity measurements to identify the percolation threshold. Equation 9 is the volume fraction of the hydrophilic domains, (ϕ_+); this is given by the sum of the volume of the sulfonic acid groups and the volume of sorbed water divided by the swollen volume of the polymer.

$$\phi_+ = \frac{\frac{\rho_{\text{polymer}}\bar{V}_{SO_3}}{EW} + \frac{V_{\text{sorption}}}{V}}{(1+\varepsilon)^3} \tag{9}$$

The molar volume of the sulfonate group is ~40 cm^3/mol.[45] Figure 5 plots the conductivity as a function of the hydrophilic volume fraction of the polymer on a linear scale. The percolation thresholds for proton conductivity are readily identified as the onset for rapid increase in the proton conductivity: $(\phi_+)_{c,\text{Nafion}} = 0.1$ and $(\phi_+)_{c,\text{SPEEK}} = 0.3$. The conductivity data have been fitted by quadratic functions, $\sigma_p = \sigma_0\ (\phi_+ - (\phi_+)_c)^2$ which is the expected functional dependence predicted by percolation theory.[46–51] The large difference in the critical condition for percolation between Nafion and SPEEK suggest the hydrophilic domains in the two polymers have different microstructures.

DISCUSSION

Water sorption and proton conductivity data show similarities and differences between Nafion and SPEEK which may provide insight into the structure of these two polymers. Water adsorption isotherms for Nafion and SPEEK were fit by a hydration shell model with a first hydration shell of 4 water molecules. The proton conductivity increased quadratically with increasing water activity above the percolation volume threshold for both Nafion and SPEEK. The data showed two major differences in water sorption and proton conductivity between Nafion and SPEEK.

1. Water sorption in Nafion had a positive excess volume of mixing, while water sorption in SPEEK had a large negative excess volume of mixing.
2. The hydrophilic volume fraction percolation threshold for proton conductivity is much lower in Nafion than in SPEEK.

These differences in macroscopic properties results suggest that there are differences in the hydrophilic domain microstructures of Nafion and SPEEK.

The spherical cluster model of hydrophilic domains proposed by Gierke has been the common starting point to account for the transport and mechanical properties of polymer electrolyte membranes.[16,17] This model is based on analogy to inverse micelles of hydrophilic groups in a hydrophobic solvent.[52–54] To minimize the repulsive interaction energy between the hydrophilic domains (sulfonic acid groups and water) and the hydrophobic matrix, the hydrophilic groups are assumed to form spherical clusters.[55–63] As water is sorbed the spheres expand and begin to touch each other. At the percolation threshold, the hydrophilic clusters form a continuous path through the matrix, and the proton conductivity increases exponentially with the volume fraction of hydrophilic domains.

The threshold for percolation depends on the shape of the objects.[46,48,64] It has been proven that for randomly dispersed spherical clusters in a matrix the percolation threshold for conduction, ϕ_c, occurs at a volume fraction of 0.28–0.3.[46] The percolation threshold for rods and ellipsoids is less than that for spheres and depends on the aspect ratio of the particles. Above the percolation threshold the conductivity should increase as a power law, $\sigma = (\phi - \phi_c)^\alpha$, where the exponent is a universal constant dependent on the dimensionality of the network. For three-dimensional networks $\alpha \approx 2$.[46]

If the sulfonic acid groups aggregate as spherical domains, then they should sorb sufficient water to achieve a hydrophilic volume fraction of 0.3 for conduction paths to span an infinite matrix of the polymer electrolyte. This is true for spherical inclusions in a continuum independent of the size of the domains. Whether each sulfonic acid group defines spherical domains 1 nm apart, or if there are spherical clusters of 100 sulfonic acid groups spaced 5 nm apart, the percolation threshold is only dependent on the critical volume fraction of the hydrophilic domains. The percolation

TABLE 2 Proton Conductivity Parameters for 555 EW SPEEK and 1100 EW Nafion

Ionomer	Temperature (°C)	σ_0 (S/cm)	$(\phi_+)_c$
1100 Nafion	60	1.3	0.1
1100 Nafion	80	2	0.1
555 SPEEK	60	0.12	0.3
555 SPEEK	80	0.26	0.3

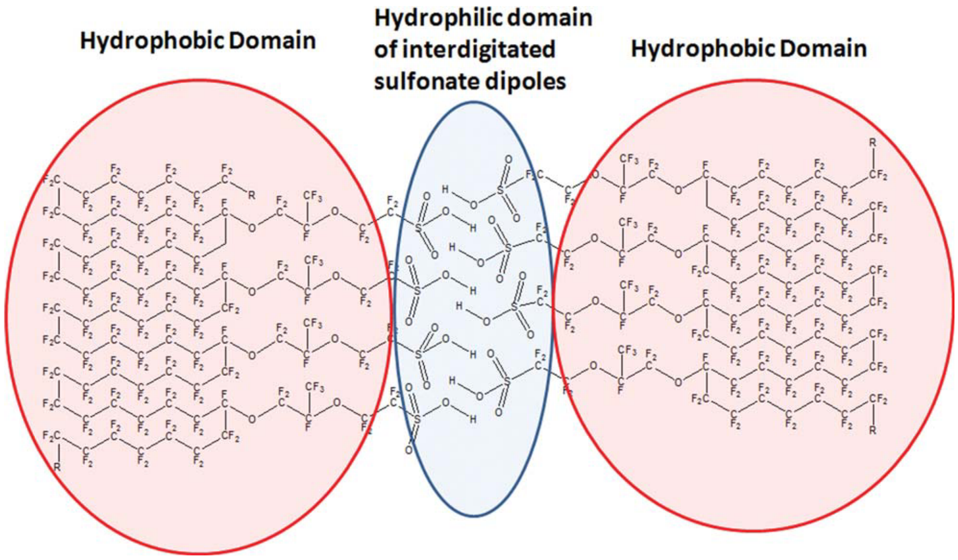

FIGURE 6 Schematic of lamellar structure of Nafion at zero water content. The sulfonic acid groups are attached to the end of a flexible side chain which facilitates the microphase separation into lamella with interdigitated sulfonic acid groups.

threshold $(\phi_{+})_c = 0.10$ for Nafion indicates that the hydrophilic clusters cannot be spherical.

The Gierke model attempted to account for the percolation at low volume fraction by introducing narrow hydrophilic channels that connected the spherical clusters. We suggest a more physically reasonable explanation is that the hydrophilic domains in Nafion are not spherical. Cylindrical rods or flat plates will percolate at lower volume fractions.[48] We suggest that the percolation threshold is indicative of the hydrophilic domain shape.

The conductivity data shows that the percolation threshold for SPEEK is ~0.3, which is expected for spherical domains. Above the percolation threshold the proton conductivity increases quadratically with hydrophilic volume fraction. This is expected based on the critical exponent for diffusion and electrical conductivity in random heterogeneous media.[46] Zhao et al. have recently measured the diffusivity of water in Nafion, and it also increases quadratically with hydrophilic volume fraction.[40] Benziger and coworkers have also shown that mechanical properties of Nafion (e.g., tensile modulus, yield stress, stress relaxation rate, creep rate) also display large changes at a hydrophilic volume fraction of 0.1.[30,33]

The percolation threshold for proton conductivity data suggests that the hydrophilic domains in Nafion and SPEEK have different topologies. The percolation threshold in SPEEK is consistent with spherical clusters, but the percolation threshold for Nafion suggests some kind of oblate structure. Gebel suggested that Nafion arranges into inverted micellar structures.[65,66] He assumed that the micelle structures were spheres at low water content, analogous to surfactant molecules in solution. Micelle structures are normally determined by the projected areal size ratio of the polar head group to the hydrophobic tail.[67] When the head group has a large projected area compared to the tail the micelle is predicted to be spherical to minimize the interfacial area of contact between the hydrophilic and hydrophobic domains. When the projected areal sizes of the head and tail are equal, the expected micellar structure is expected to be lamellar sheets, for example, bilayers of polar groups sandwiched between the hydrophobic tails. The sulfonic acid group in Nafion is about the same size as the perfluoro alky ether (PFAE) chain to which it is attached. At low water content, we suggest the preferred packing would be lamella with sheets of sulfonic acids sandwiched between layers of PFA as indicated in Figure 6. The flexible PFAE side chain provides sufficient flexibility to allow lamella to form. Water sorption will cause the lamella to swell leading to contacts between domains forming creating percolation paths.

The location of the sulfonic acid group in SPEEK is different from Nafion. The sulfonic acid group is attached directly to a phenyl ring along the backbone of the polymer. There is little flexibility to allow the phase separation as suggested for Nafion in Figure 6. At best, bonding between interdigitated sulfonic acid groups could occur if the spacing of the sulfonic acid groups were regular. It is more likely that the repulsive interactions between the polar sulfonic acid group and the nonpolar phenyl groups of the PEEK backbone would create free volume surrounding the sulfonic acid. Water molecules that hydrate the sulfonic acid group will occupy that free volume. Since sorbed water can occupy free volume surrounding the sulfonic acid, the polymer does not need to swell to accommodate water which causes the large negative excess volume of mixing for water sorption.

A conceptual packing of the sulfonic acid groups in SPEEK is shown in Figure 7. The sulfonic acid groups are suggested to either be isolated or in small clusters of two or three interacting sulfonic groups. The small number of sulfonic acid groups in a cluster would sorb water in spherical hydration shells. The spherical nature of the hydrophilic domains in

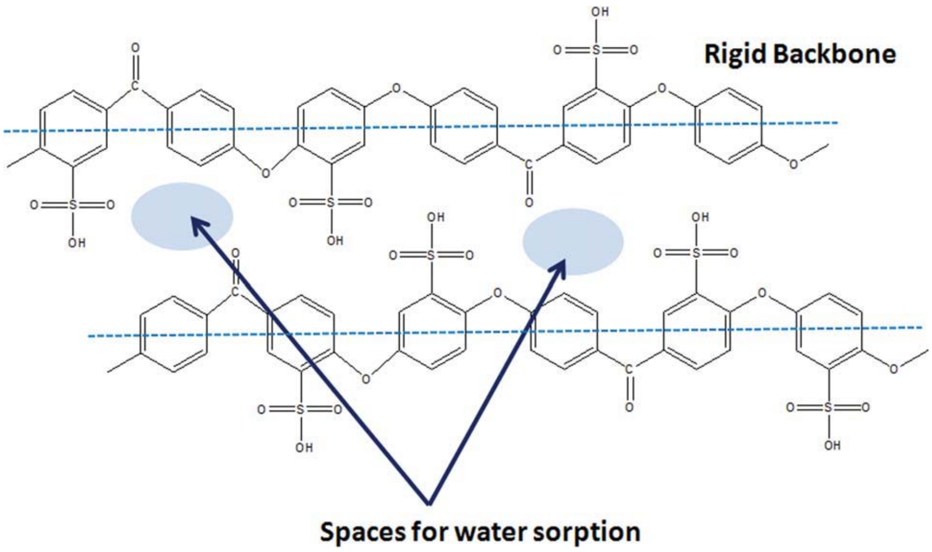

FIGURE 7 Schematic of packing sulfonic acid groups in SPEEK. The random position of the sulfonic acid groups and minimal flexibility of the PEEK backbone results in small clusters. The poor packing leaves free volume where water sorbs with little change in the bulk polymer volume.

SPEEK would result in a percolation threshold at volume fraction of 0.3.

The lamella structure suggested for Nafion in Figure 6 has plate-like hydrophilic domains. The plates will percolate through the hydrophobic matrix at much lower volume fraction. Small angle X-ray scattering data for hydrated SPEEK and Nafion that show the spacing between hydrophilic domains is ∼5 nm for Nafion but only 1 nm for SPEEK.[13,20,68–73] These spacing increases slightly with water content, but the 5 and 1 nm spacing persists from low to high water content. The models shown in Figures 6 and 7 are consistent with SAXS data for Nafion and SPEEK. These models also account for the difference in excess volume of mixing for water sorption and for the difference in percolation threshold for proton conductivity.

The shapes of the hydrophilic clusters in Nafion and SPEEK may evolve with water sorption. As water molecules cluster around the sulfonic acid group in Nafion, they would make the polar head groups larger than the hydrophobic tails, which would be expected to induced curvature. Cylindrical and spherical micelles might be anticipated as the water content increases. The detailed SAXS data for Nafion at high water contents indicates rod-type structures.[70,71]

The use of different shape particles to improve electrical and thermal conduction of composite materials is well known. However, we have not seen any reports that have considered the effects of domain shape on the proton conductivity in polymer electrolytes. Differences in percolation thresholds for polymer electrolytes could be essential in developing new membranes for PEM fuel cells to operate at reduced relative humidity. There is a much greater penalty to pay in terms of proton conductivity at reduced relative humidity when the percolation threshold is 30 vol % as seen for SPEEK compared to 10 vol % seen for Nafion. The surfactant nature of Nafion makes it well suited to form lamellar and rod shaped domains that can provide percolation pathways at reduced water content. SPEEK does not appear to have a structure that would make it suited to function at low activity. We suggest that when searching for new polymers to replace Nafion one may wish to consider what size and shape of hydrophilic domains might form.

CONCLUSIONS

Water sorption and proton conductivity have been compared for 1100EW Nafion and 555EW SPEEK. Water sorption is described by a hydration shell isotherm, with a first hydration shell of 4 water molecules. The water in the first hydration shell is more strongly associating in Nafion than in SPEEK. Water sorption in Nafion occurs with a small positive excess volume of mixing. Water sorption in SPEEK has a large negative excess volume of mixing.

Proton conductivities were similar in both Nafion and SPEEK at high water activity. At low water activity, Nafion has greater proton conductivity. Proton conductivity increases quadratically with hydrophilic volume fraction above the percolation threshold, 30 vol % in SPEEK and 10 vol % in Nafion. The differences in percolation thresholds for proton conduction and excess volumes of mixing for water sorption indicated different structures of the hydrophilic domains in Nafion and SPEEK. It is suggested that SPEEK has spherical hydrophilic domains and Nafion has rod- or plate-like hydrophilic domains.

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NOMENCLATURE

a_w	water activity
i	number of water molecules added to the polymer
K_i	equilibrium constant of number i water molecule added
K_0	equilibrium constant of first hydration shell
K_1	equilibrium constant beyond first hydration shell
n_1	water molecules in the first hydration shell
P	equilibrium pressure in the container of water sorption measurement cell (kP_a)
P_w	partial pressure of water vapor (kP_a)
P_w^0	saturate pressure of water vapor (kP_a)
R	gas constant
T	temperature (K)
$V_{\mathrm{waterinjected}}$	volume of injected water in the container of water sorption measurement cell (cm^3)
V_{vessel}	volume of the container (cm^3)
V_w	molar volume of water (cm^3/mol)
V_{soption}	volume fraction of sorbed water (cm^3)
$\overline{V}$	volume of dry polymer (cm^3)
$\overline{V}_{\mathrm{SO3}}$	molar volume of SO_3 group (cm^3/mol)
V	volumetric expansion of polymer (cm^3)
W_i^*	sulfonic acid group with i water molecules of hydration
$x_{W_i^*}$	molar fraction of W_i^*
$*$	sulfonic acid group
ε	linear expansion coefficient
ΔG	Gibbs free energy of water sorption (kJ/mol)
λ	number of water molecules per sulfonic acid group
σ	proton conductivity (S/cm)
ϕ_+	molar fraction of hydrophilic domains in the swollen polymer
$(\phi_+)_c$	critical molar fraction of hydrophilic domains in the swollen polymer

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