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Solid-State NMR Study of Two Classic Proton Conducting Polymers: Nafion and Sulfonated Poly(ether ether ketone)s

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ABSTRACT: Proton mobilities in Nafion and sulfonated poly(ether ether ketone) (S-PEEK) have been studied using high-resolution solid-state ^{1}H NMR under fast magic angle spinning (MAS). These studies demonstrated proton exchange between sulfonic acid groups and water within both Nafion and S-PEEK. Variable temperature experiments were used to determine the activation energy for proton transport in pure Nafion, found to be 11.0 kJ/mol, which is lower than those determined for S-PEEKs with different degrees of sulfonation. Increasing proton exchange rates with increasing temperature indicate the expected dependence of proton mobility on temperature. A rotor-synchronized homonuclear double quantum filter sequence (BaBa) was used to disclose the nature of the H-bonding interactions in the two polymers, from which a model of the proton interactions in the polymers is developed.

Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising new power sources for both portable and stationary applications, ranging from portable electronics and vehicles to industries and residences.[1] Membranes currently used in PEMFCs are sulfonated perfluorinated polymers such as Nafion (shown in Figure 1) designed by Dupont or Nafion-like polymers supplied by Dow.[2] These membranes have good proton conductivity and long-term stability. However, the high cost of perfluorinated polymers limits the large-scale commercialization of PEMFCs. Another drawback for these membranes is methanol crossover which occurs when they are used in direct methanol fuel cells (DMFC).[3] This leads to a decreased fuel cell performance due to depolarization of the oxygen reducing cathode.[4] The problem caused by methanol crossover can be relieved to some extent by doping with various inorganic fillers.[5,6] Dopants such as silica and zirconium phosphate that have surface hydroxyl groups are preferred since these groups are assumed to retain water even at temperatures higher than 100 °C. Data on the interactions between Nafion acid protons and protons of hydroxyl group of dopants is elusive and yet important to understanding the performance of these composites. Such data can be provided by solid-state NMR studies.

Sulfonated aromatic polyether ether ketones (shown in Figure 1) have been studied as an alternative to Nafion due to the good mechanical properties, thermal stability, and conductivity exhibited by this polymer.[4,7,8] These properties have been shown to depend on the degree of sulfonation of the polymer. Although a high degree of sulfonation degrades the mechanical properties of humidified S-PEEK, it does give improved proton conductivity under high relative humidity conditions. This is a typical juxtaposition of polymer electrolyte membranes: good conductivity is achieved at the expense of structural integrity. Such problems motivate the efforts to understand the molecular-level processes at work in the proton transport mechanism and thereby contribute to the development of new materials.

Many studies on these proton-conducting materials have been carried out by impedance spectroscopy measurements,[9−11] which provide standard proton conductivity data. Such studies probe proton mobility indirectly, through a measurement of a bulk property of the material. Small-angle X-ray scattering (SAXS)[12,13] and small-angle neutron scattering (SANS)[14] have been used to obtain details on the structures of membranes; however, dynamic information about proton mobility is not available from these methods.

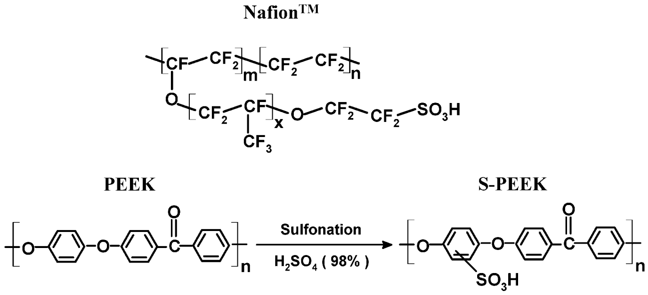

Figure 1. Schematic chemical structures of Nafion and S-PEEK.

Solid-state NMR can provide useful information concerning proton mobility of conducting polymers on the molecular level[15,16] because it is able to probe local chemical environments. Such information is helpful to give a fundamental understanding of the observed differences in proton conductivity. Chemical surroundings are determined from the proton chemical shift, and relative proton mobilities can be compared using the solid-state ^{1}H NMR line widths as a function of temperature.

For a powder sample, the ^{1}H NMR spectrum exhibits noticeably broadened peaks due to the random orientation of molecules and very strong ^{1}H−^{1}H homonuclear dipolar coupling in a rigid polymer. Fast magic angle spinning (MAS) is used to average the dipolar couplings on the time scale of the rotor period and thereby achieve significant line narrowing. Since the strength of dipolar interactions can be used to determine the relative mobility of protons, methods which can selectively retrieve information about the dipolar interaction removed by MAS are desirable. Double quantum filtering (DQF) pulse sequences, such as back-to-back (BaBa),[17,18] allows us to recouple the dipolar couplings between protons which are rigid on the time scale of the pulse sequence and which are close to each other in space. For two given nuclei in a compound,

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the dipolar coupling is very sensitive to the distance between nuclei as shown in eq 1

$$D_{ij} = \frac{(\mu_0/4\pi)\hbar\gamma_i\gamma_j}{r_{ij}^{\ 3}} \tag{1}$$

$$H_{D_{ij}} = D_{ij}(3\cos^2\theta - 1)(2I_{iz}I_{jz} - I_iI_j)/2 \tag{2}$$

where D_{ij} is the dipolar coupling constant, γ_i and γ_j are the magnetogyric ratio of the two spins, and r_{ij} is the distance between them. In the dipolar Hamiltonian $H_{D_{ij}}$ given in eq 2, θ is the angle of the dipolar coupling interaction to the magnetic field, indicating the sensitivity of the dipolar coupling to motional averaging.[19] Thus, the observation of a weak dipolar coupling will be due to either fast tumbling of molecules (termed the residual dipolar coupling) or a long distance between nuclei. The BaBa sequence is used here to detect proton interactions and gauge their relative mobilities. The intensity of the double quantum coherence (DQC) depends on the product of coupling strength and the excitation time, meaning DQCs based on strong dipolar coupling will be efficiently excited in a short recoupling time. Mobile protons which generate weak or no dipolar coupling will be absent from the DQF MAS NMR spectrum due to inefficient excitation of the DQC. Hence we can ascertain the relative mobilities of protons by comparing ^{1}H NMR with ^{1}H DQF NMR. By extending the length of the recoupling (excitation) time, the DQF sequence can be used to detect weak dipolar couplings which are partially dynamically averaged by local mobility or where the dipolar coupling occurs over a long distance.[17]

In this paper we studied proton mobility in Nafion, Nafion composites, and S-PEEK with different degrees of sulfonation. Several samples exposed to different relative humidities (RH) were used to understand proton interactions between water and sulfonic acid groups. Homonuclear DQF experiments are performed to distinguish strong dipolar couplings from weak couplings. The differences in proton mobility are compared and discussed.

Experimental Section

Preparation of S-PEEK. S-PEEK with different degrees of sulfonation were made as follows: 20 g of commercial PEEK (Victrec Co.) was dissolved in 300 mL of 98% H_2SO_4 at room temperature. In intervals of tens of hours, samples were taken periodically from the previous mixture and added to ice water under strong agitation. To remove any residual acid, the polymer precipitate was washed until a constant pH was obtained. After that, it was dried first at room temperature for 2 days and then at 343 K for 2 days. Finally, polymer beads of 1−2 mm diameter were obtained; the color of the beads varied with the degree of sulfonation. The degree of sulfonation of S-PEEK was determined using solution NMR. For these studies, samples of S-PEEK were dissolved in DMSO-d_6. For solid-state NMR measurements, powder samples are preferred to facilitate rotor spinning. Powders were prepared by grinding previously dried S-PEEK in liquid nitrogen. Afterward, the powder samples were treated at 353 K in an oven for dried samples. The humidified samples were prepared by storing S-PEEK in a humidity chamber (model 9000, VWR) at 323 K for 24 h. The relative humidity of the chamber was set at 50% or 100% to control the amount of water in hydrated S-PEEK.

Preparation of Nafion Composites. Treatment of Nafion 112 was performed in two ways. Method I: Nafion 112 was first washed in 1 M NaOH for 1 h, and then it was washed in distilled deionized water for another hour, during which time the water was refreshed four times. Subsequently, the membrane was again washed in 1 M HCl for 1 h. Finally, it was washed in distilled deionized water until a constant pH was obtained. Method II: Nafion 112 was first washed in 3% H_2O_2 for 1 h and then washed in distilled deionized water for another hour, again changing the water four times. Subsequently, it was again washed in 1 M H_2SO_4 for 1 h. Finally, it was washed in distilled deionized water until a constant pH was obtained. The dried Nafion samples were prepared by drying the treated Nafion membranes at 353 K from 2 days to 1 week.

SiO_2−Nafion composite membranes were prepared according to the procedure reported by Deng.[20] Nafion treated by method I was first swollen in MeOH:H_2O (v/v) = 5:1 for 24 h. It was then immersed in TEOS:H_2O (mol/mol) = 1:1 for 9 min to allow permeation of TEOS into Nafion. After that, it was dried at 353 K overnight to remove the excess alcohols. The polymerization of TEOS to silica is an acid-catalyzed process. Since the sulfonic acid groups within Nafion are the only source of acid, it is assumed that the silica is formed within the Nafion membrane. ZrP−Nafion composite membranes were prepared following the procedure reported by Costamagna.[21] Nafion treated by method II was first swollen in boiling MeOH:H_2O (v/v) = 1:1 for 2−3 h. Subsequently, the material was washed in 1 M zirconyl chloride solution at 353 K for 1 h. To remove excess zirconium chloride, it was quickly rinsed in distilled deionized water and then put in 1 M H_3PO_4 at 353 K overnight. Finally, it was washed in distilled deionized water and dried at 353 K overnight.

^{1}H NMR. ^{1}H solution NMR experiments were carried out on a Bruker AV 200 spectrometer at a ^{1}H Larmor frequency of 200.13 MHz. The 3% S-PEEK solution was prepared by dissolving polymer beads in DMSO-d_6. TMS was added as the internal standard. NMR data were acquired with a 90° pulse length of 6.35 μs at room temperature.

^{1}H solid-state NMR experiments were performed on a Bruker AV 500 spectrometer at a ^{1}H Larmor frequency of 500.13 MHz. Rotor diameters of 4 and 2.5 mm rotor were used for Nafion samples and S-PEEK samples, respectively. The former rotor was spun at 5 or 10 kHz and the latter at 25 kHz. In both cases a recycle delay of 3 s was used. The spectra are referenced to adamantane (1.63 ppm for ^{1}H). Solid-state ^{1}H NMR spectra were acquired with a 90° pulse length of 2.5 μs. Variable temperature experiments were performed in the range of 300−360 K, with the sample temperature corrected to include heating effect arising from the high-speed MAS.[22] The ^{1}H line width as a function of temperature reflects changes of spin−spin relaxation time (T_2) with temperature, which is used to fit the activation energy for proton transport in this work. Because of inhomogeneity of the applied magnetic field B_1, the effective T_2 is denoted as T_2* in terms of the observed line width.[23] Since the chemical shift of sulfonic acid proton, which is humidity sensitive, does not show any noticeable shift within 2 days once samples were put in the rotor, this suggests that the humidity of samples in the rotor does not change during that time. Thus, the humidification of the samples is maintained during measurement.

The rotor-synchronized DQF MAS spectra were recorded by using the back-to-back (BaBa) pulse sequence, with variable excitation times, τ_{exc}, from τ to 8τ and 512 scans.[24]

The deconvolution of S-PEEK ^{1}H MAS NMR spectra was performed by both Bruker Topspin 1.2 and MestRe-C software to determine line widths of sulfonic acid proton and aromatic proton resonances. Error bars of E_a within 1% were determined by comparing the goodness of fit from the two routines. Since the difference in activation energies determined for different samples, prepared at different times, is less than 4%, this is taken as the error bar for each measurement.

Results and Discussion

Determining the Degree of Sulfonation. Two examples of ^{1}H NMR spectra of S-PEEK samples dissolved in DMSO-d_6 are shown in Figure 2. The degree of sulfonation can be determined quantitatively by ^{1}H NMR.[25] The presence of the sulfonic acid group increases the deshielding effect for proton H_A in Scheme 1, causing the H_A resonance to move to a higher chemical shift compared with protons H_B and H_C. Therefore, a

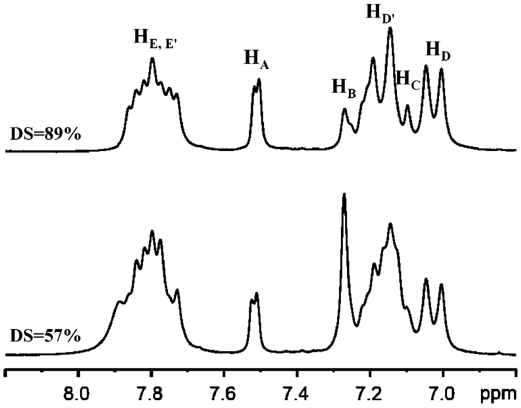


Figure 2. Solution-state ^{1}H NMR spectra of sulfonated PEEK (S-PEEK). Chemical shifts are assigned as annotated in Scheme 1.

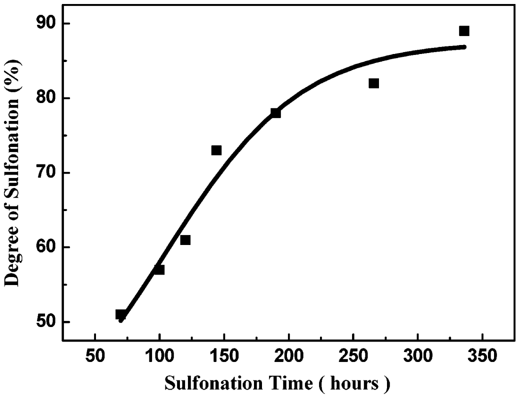
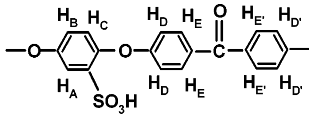


Figure 3. Degree of sulfonation of S-PEEK as a function of sulfonation time. The curve is included as guide for the eye.

Scheme 1. Structure of S-PEEK



distinct signal for H_A can be observed from NMR spectra. The ^{1}H NMR signal for the sulfonic acid group cannot be recorded directly since the sulfonic acid proton is highly mobile. Nevertheless, the number of the H_A is exactly equal to that of the sulfonic acid protons. Thus, if the degree of sulfonation (DS) is defined as a ratio of sulfonated units to total units, the DS can be calculated as follows:[25]

$$\mathrm{DS} = \frac{100 \times \mathrm{area}_{\mathrm{H_A}}}{[\mathrm{area}_{\mathrm{H_{B,C,D,D',E,E'}}} + 2 \times \mathrm{area}_{\mathrm{H_A}}]/12} \qquad (3)$$

The DS calculated from the ^{1}H NMR spectra of seven S-PEEK samples is plotted in Figure 3. In our experiments, when the sulfonation time increases from 70 to 336 h, the DS changes from 51% to 89%. Because of differences in experimental conditions, such as the concentration of PEEK in H_2SO_4 and the reaction temperature, Huang reported S-PEEK with higher DS but shorter sulfonation time.[26]

Proton Exchange between Water and Sulfonic Acid Group. Figure 4 shows a series of ^{1}H solid-state NMR spectra of Nafion treated under different conditions. After Nafion was fully acidified and heated (b), the broad peak at 9.7 ppm indicates that the only protons remaining are from the sulfonic acid group and they are immobile. When the sulfonic acid protons were replaced with Na^+ in Nafion treated with NaOH(aq), a narrow peak at 4.0 ppm, similar to the chemical shift of pure water, is observed (a).[27] On the basis of these two assignments, it follows that the narrow resonance at 6.7 ppm observed for the fully acidified and hydrated Nafion membrane (c) likely represents fast proton exchange between water and the sulfonic acid group. Similar fast proton exchange has been also reported by Fyfe[28] and Fraissard.[29]

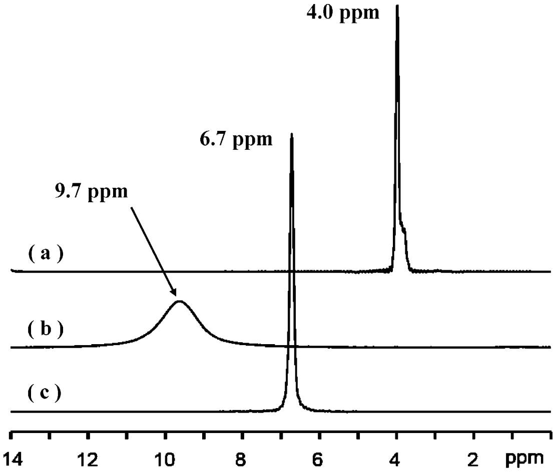


Figure 4. Solid-state ^{1}H MAS NMR at 5 kHz for Nafion 112 treated by (a) NaOH(aq), (b) fully acidified and heated at 80 °C for 12 h, and (c) fully acidified and hydrated.

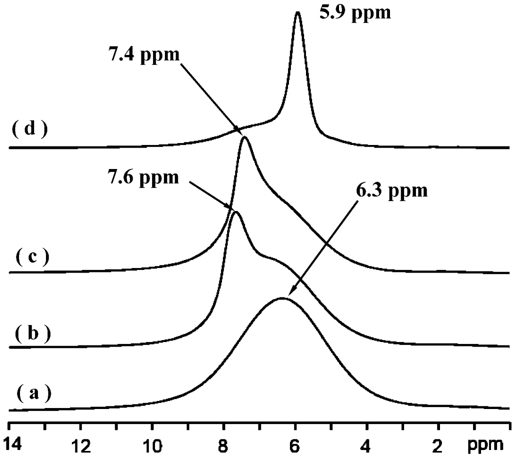


Figure 5. Solid-state ^{1}H MAS NMR at 25 kHz for PEEK and S-PEEK (DS = 57%): (a) PEEK, (b) dried S-PEEK, (c) S-PEEK (24 h in RH = 50%), and (d) S-PEEK (24 h in RH = 100%).

Figure 5 shows a series of ^{1}H solid-state NMR spectra for PEEK and a series of S-PEEK powders treated under differing relative humidity conditions. PEEK itself (a) shows a single, broad aromatic resonance. Dried S-PEEK (b) gave a broad resonance (393 Hz) for the acidic protons at 7.6 ppm. After it was treated in relative humidity (RH) equal to 50% for 24 h, the water content was slightly increased, which moved this resonance to 7.4 ppm (c). The line width narrowed slightly to 372 Hz. When a higher RH equal to 100% was applied for an equivalent time (d), a further increase in water content shifts the resonance to 5.9 ppm accompanied by line narrowing to 261 Hz. Compared with the small fluctuation of line width of aromatic proton less than 3%, the significant decrease in the line width of the sulfonic acid proton indicates increasing proton mobility resulting from rapid proton exchange with water molecules and thus indicates a mechanism for proton diffusion that occurs independent of polymer backbone dynamics.

Careful comparisons of the ^{1}H solution-state NMR spectra and ^{1}H solid-state NMR spectra allow us to deduce not only

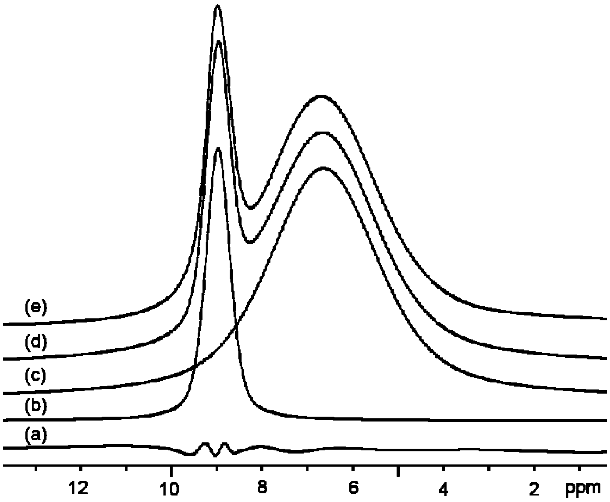


Figure 6. Deconvolution of ^1H MAS NMR of dried S-PEEK (DS = 73%): (a) difference between simulated and experimental, (b) sulfonic acid proton, (c) aromatic proton, (d) experimental spectrum, and (e) simulated spectrum from NMR software MestRe-C.

the degree of sulfonation but also the amount of water associated in the membranes. The acidic proton resonance in the solid-state spectra is consistently larger than what should be attributed to the sulfonic acid proton alone at a given degree of sulfonation. Therefore, the excess proton intensity is assigned to trapped water molecules and is seen to increase as expected, as a function of humidification. Accurate spectral deconvolution is essential to both this analysis and the previous observations regarding the aromatic polymer backbone. Therefore, an example deconvolution is presented in Figure 6, showing the two resonances, their sum, and the minimal residual signal observed following subtraction of the fitted and experimental data.

Activation Energy for Proton Transport in Nafion and S-PEEK. Figure 7a shows the dependence of the proton chemical shift on temperature for a dried Nafion sample. As the temperature increases, the effective hydrogen bond strength of the sulfonic acid protons becomes weaker. This moves the chemical shift toward lower frequency. As well, higher temperature leads to a faster proton exchange rate between the sulfonic acid group and surrounding water molecules and causes the resonance to narrow. The same trend was found for the Nafion composites of SiO_2−Nafion in Figure 7b and ZrP−Nafion in Figure 7c.

In the case of SiO_2−Nafion, there are strong hydrogen-bonding sites available which may trap extra water molecules in the composite. These hydrogen bonds take the form of Si−OH groups located on the surfaces of silicon oxide nanoparticles.[30,31] It was reported that the physisorbed water in silica gels, such as water molecules bound to Si−OH groups, starts to be driven off and surface silanol groups condense at around 443 K.[32] Since our composite was treated at 353 K, water molecules bound to surface Si−OH groups will remain. The single peak shown in Figure 7b is the resonance of sulfonic acid proton exchanging with water adsorbed on silica surface.[33] The chemical shift of this resonance is lower than that of pure Nafion treated under equivalent conditions.

In the case of ZrP−Nafion, the inorganic component, zirconium phosphate, is a well-known proton conductor.[34] In this layered compound, the acid P−OH groups belonging to adjacent layers remain close to each other and allow proton transport in the interlayer region even under anhydrous conditions. It has been demonstrated that ZrP−Nafion membranes can reabsorb water at 403 K from the vapor phase that was lost at 413 K.[21] This indicates that zirconium phosphate in the nanopores of the Nafion can reduce the rate of evaporation of water in Nafion. Thus, after our sample was treated at a lower temperature of 353 K, it is probable that there are still water molecules left in the membrane which move the sulfonic acid ^1H resonance to lower chemical shift relative to Nafion treated under equivalent conditions. It has also been confirmed by the thermogravimetric analysis (TGA) (not shown here) that the ZrP−Nafion composite has a higher water content per sulfonic acid group than pure Nafion.

Not surprisingly, S-PEEKs with different degrees of sulfonation also showed temperature-dependent proton chemical shifts and line widths, consistent with the weakening relative strength of hydrogen bonding with increasing temperature. More interestingly, the amount of water retained in S-PEEK increases with increasing degrees of sulfonation. This is seen both in the decreasing line width with increasing DS seen in Figure 8 a,b and by comparing the integrated acidic proton intensities in these materials. Compared with the line width of the sulfonic acid proton resonance (344 Hz at 310 K) of S-PEEK (DS = 61%) in Figure 8a, a narrower line width of the sulfonic acid proton resonance (256 Hz at 310 K) for S-PEEK (DS = 73%) in Figure 8b indicates that the sulfonic acid protons in the latter are more mobile than those in the former. The ratio of the number of water molecules per sulfonic acid proton, denoted as nH_2O/SO_3H, in both dried and hydrated S-PEEKs can be estimated from peak areas of the sulfonic acid proton peak and aromatic proton peak of solid-state ^1H NMR of S-PEEKs, by comparison with the degree of sulfonation established by ^1H solution-state NMR studies above. The obtained nH_2O/SO_3H values for dried and hydrated S-PEEKs are presented in Table 1. It is important to note that as the degree of sulfonation of the polymer increases, the amount of associated water retained in the membrane will increase proportionally. Therefore, higher proton mobility would be expected from humidified S-PEEK with higher DS, consistent with the trend of macroscopic proton conductivity that higher DS gives better proton conductivity.[35,36]

The influence of polymer backbone motion on the sulfonic acid proton dynamics has also been considered. Since the aromatic proton resonance always shows an invariable line width for S-PEEKs with variable DS treated under different relative humidity, which is 1480 ± 40 Hz, this implies that the motions of polymer chain for measured S-PEEK samples do not change with DS and relative humidity. Thus, in this study the contribution of polymer chain motion to proton mobility can be ignored, compared with the motion of sulfonic acid protons. A more accurate measurement of polymer chain motion will be performed by examining the influence of dynamics on the ^{13}C chemical shielding anisotropies.[37]

The line width trends of the acidic protons can be analyzed using the Arrhenius equation. As shown in eq 4, the change in line width is proportional to the inverse of T_2*, the spin−spin relaxation time. Equation 5 shows how activation energy can be obtained from line width,[38] where E_a is the activation energy for proton transport and τ_c is the correlation time of the motion.

$$\Delta\nu_{\mathrm{FWHM}} = \frac{1}{\pi T_2{}^*} \tag{4}$$

$$\tau_c = \frac{1}{\Omega} \approx \pi T_2^* = \tau_o e^{\left(\frac{-E_A}{RT}\right)} \tag{5}$$

Figure 9 shows an example of an Arrhenius plot for dried S-PEEK (DS = 73%). Activation energies for Nafion and its

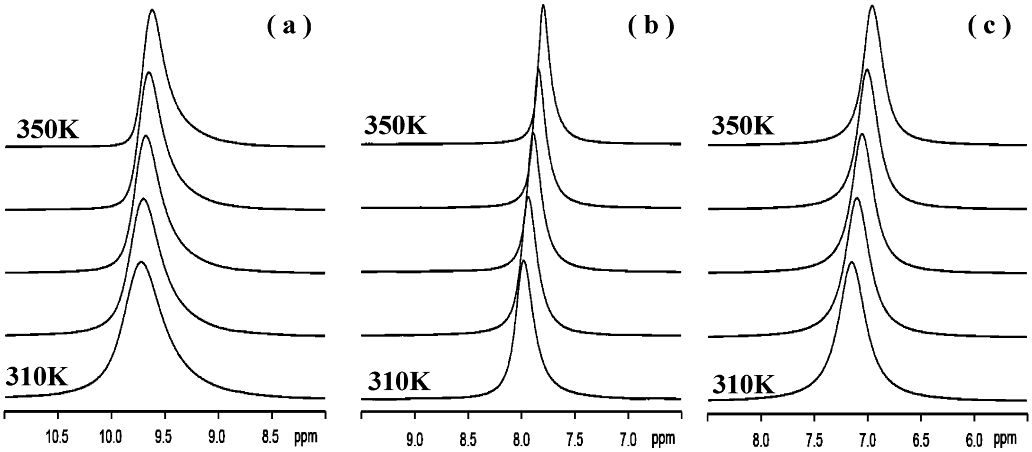


Figure 7. Solid-state ^1H MAS NMR at 5 kHz for (a) dried Nafion, (b) dried SiO_2−Nafion, and (c) dried ZrP−Nafion.

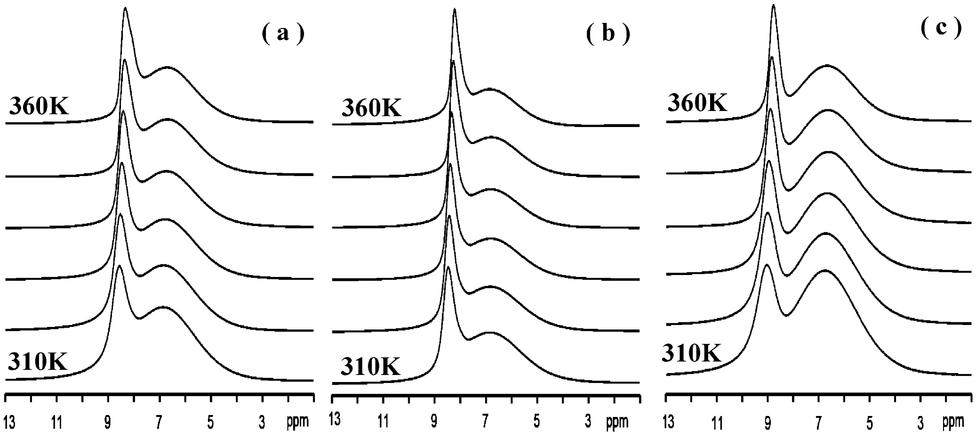


Figure 8. Solid-state ^1H MAS NMR at 25 kHz for (a) humidified S-PEEK (DS = 61%), (b) humidified S-PEEK (DS = 73%), and (c) dried S-PEEK (DS = 73%).

Table 1. Activation Energy of Proton Transport for S-PEEK with Variable DS

S-PEEKs with variable DS	DS = 61%	DS = 73%	DS = 82%
dried samples			
E_a (kJ/mol)	20.1 ± 0.8	20.8 ± 0.8	27.3 ± 1.1
nH_2O/SO_3H	1.7 ± 0.1	1.6 ± 0.1	1.9 ± 0.1
samples hydrated at RH = 20% and 50 °C for 24 h			
E_a (kJ/mol)	18.3 ± 0.7	13.9 ± 0.6	12.8 ± 0.5
nH_2O/SO_3H	2.6 ± 0.1	2.6 ± 0.1	2.8 ± 0.1

composites are presented in Table 2. Those for S-PEEKs with variable DS treated under different relative humidity are shown in Table 1.

In Table 2 the activation energy for hydrated pure Nafion obtained by NMR (11.0 kJ/mol) correlates very well with the macroscopic conductivity measurements (9.34 kJ/mol).[21] The dried pure Nafion shows an activation energy higher than hydrated Nafion due to the significantly lower water content of the dried Nafion membrane. This is consistent with the presumed vehicle mechanism of proton transport in Nafion and its composites. As the number of water molecules or "vehicles" is reduced, the activation energy for proton transport increases steeply. Analogously, the connectivity of the hydrogen-bonding network is reduced in the dried sample: as the domains become isolated, the probability of structural proton transport is also reduced.

Compared with dried pure Nafion, both dried SiO_2−Nafion and dried ZrP−Nafion give lower activation energies for proton hopping. This is attributed to the greater number of water molecules retained in the Nafion composites, which help to enhance mobility of the sulfonic acid protons. It is important to emphasize again that these activation energies arise from NMR measurements of proton dynamics and, as such, are extremely local, molecular probes of proton mobility. This is in contrast with impedance measurements, which give macroscopic pictures but lack molecular-level detail. Both composites

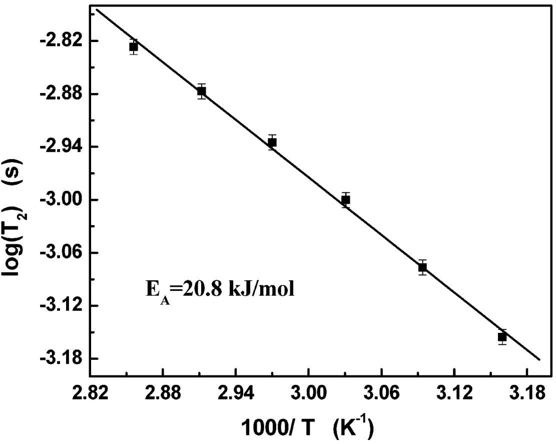


Figure 9. Activation energy for proton mobility in dried S-PEEK (DS = 73%) by linear fitting to the Arrhenius equation.

Table 2. Activation Energy of Proton Transport for Nafion and Nafion Composites

Nafion and composites	Nafion (hydrated in H_2O)	Nafion (dried)	SiO_2−Nafion (dried)	ZrP−Nafion (dried)
E_a (kJ/mol)	11.0 ± 0.4	16.4 ± 0.7	12.2 ± 0.5	10.3 ± 0.4

show significantly reduced activation energies for proton hopping relative to pure, dried Nafion. This indicates that at the molecular level, the inorganic fillers are playing their intended roles; providing excess mobile protons to the hydrogen bonding network. Moreover, the enhancement is more substantial for ZrP− Nafion than for SiO_2−Nafion, suggesting that ZrP, a known proton conductor, contributes to proton mobility of ZrP−Nafion. This synergistic contribution of the inorganic "filler" was part of the motivation for choosing this composite.[39]

In comparing S-PEEKs with different degrees of sulfonation, higher activation energies were determined for dried S-PEEK with higher DS in Table 2. As expected, the hydrated samples show decreased activation energy with increasing degree of sulfonation. To our knowledge, activation energies for pure S-PEEKs are not reported in the literature. For comparison, the activation energy determined by impedance measurements for fully hydrated composites of S-PEEK (DS = 70%) is roughly 15 kJ/mol,[4] which is comparable to our results.

To compare activation energies of S-PEEKs, the residual water in these samples has to be considered. As seen in Nafion, the observed chemical shift of the sulfonic acid proton is influenced by the exchange with residual water molecules. In dried S-PEEK, the low value of $n\mathrm{H_2O/SO_3H}$ decreases the mobility of sulfonic acid proton due to the stronger hydrogen bonding. Therefore, within the same domain size of polymer, the greater number of sulfonic acid groups in polymers with higher DS will limit proton mobility and increase the activation energy for proton transport in dried samples.

S-PEEK samples listed in Table 2 were hydrated at RH = 50% for 24 h, causing a slight increase in the water content of these materials. In these slightly hydrated S-PEEKs, although the value of $n\mathrm{H_2O/SO_3H}$ does not increase much, the number of water molecules within the same domain size of polymer will increase drastically as the degree of sulfonation increases. This facilitates the water molecules exchange among sulfonic acid groups by providing an increasingly continuous network for proton conductivity and allowing Grotthus mechanism diffusion.

A comparison of dried Nafion with dried S-PEEKs indicates an obvious difference of proton mobility when their water content is low. This is consistent with results reported by Alberti where it is stated that Nafion is the best proton conductor at low relative humidity and differences of proton conductivity become smaller and vanish when the relative humidity is close to 100%.[34,35]

Detection of Immobile Protons in Nafion and S-PEEK. DQF MAS NMR spectra differ from normal MAS NMR spectra in that resonances are only observed for protons having strong dipolar couplings. Thus, peaks which disappear from the DQF MAS NMR spectrum can be correlated with protons with very weak dipolar coupling. Weak or residual dipolar couplings may still be detected by extending the recoupling time for efficient excitation of double quantum coherence. In Figure 10a the resonance corresponding to protons of sulfonic acid groups and associated water molecules in dried Nafion shows a strong dipolar coupling, detected most intensely when the recoupling time is short (τ_r), and decaying as the recoupling time is extended, as expected for strongly coupled spins.[17] The estimated $n\mathrm{H_2O/SO_3H}$ for this sample is about 1.5 ± 0.1 based on comparisons with literature values.[29] In Nafion, the flexible side chains can reorient to shorten the distance between sulfonic acid groups. Thus, strong dipolar couplings are detected for sulfonic acid proton of rigorously dried Nafion and are attributed to strongly H-bonded acid−H_2O complexes. In Figure 10b the proton resonance in a less rigorously dried polymer is not observed at short recoupling times. The appearance of this peak at recoupling times of $4\tau_r$ and longer indicates that the residual dipolar coupling among these protons is nevertheless strong enough to be detected in the membrane. This is indicative of increasing proton mobility in the membrane. The $n\mathrm{H_2O/SO_3H}$ in this sample is estimated to be 2.0 ± 0.1 based on our TGA studies and is consistent with values in the literature.[29] As expected, humidified Nafion did not exhibit peaks attributable to dipolar coupled protons in DQF MAS NMR spectrum even when the recoupling time was extended up to $8\tau_r$. The particularly weak dipolar coupling suggests very mobile protons which are attributed to rapid proton exchange between sulfonic acid protons and mobile water molecules. These three stages represent a three points along a continuum of increasing humidification (illustrated in Figure 12), corresponding with increasing proton transport within the hydrogen-bonding network. The connectivity between domains allows for structural, or Grotthus, mechanism diffusion to participate together with vehicular proton transport.

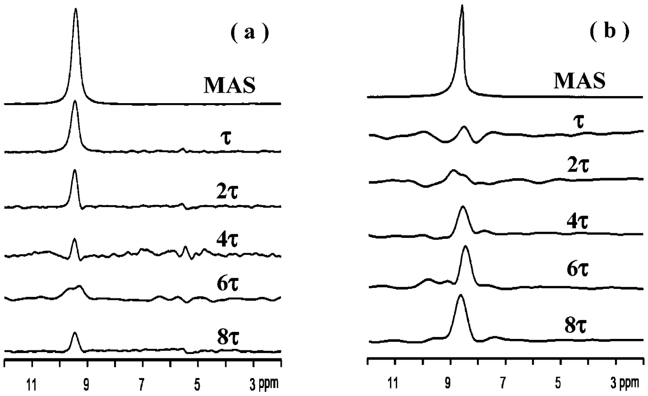


Figure 10. ^{1}H DQF MAS NMR of dried Nafion spun at 10 kHz, τ = 0.1 ms: (a) dried at 353 K for 1 week and (b) dried at 353 K for 2 days.

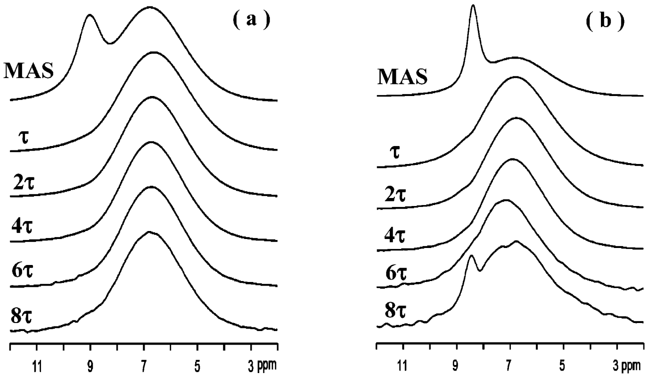


Figure 11. ^{1}H DQF MAS NMR of S-PEEK spun at 25 kHz, τ = 0.04 ms: (a) dried S-PEEK (DS = 73%) and (b) humidified S-PEEK (DS = 73%).

Backbone mobility has been discounted as a significant influence on proton transport in S-PEEK in the temperature ranges considered here. Nevertheless, there are key differences between the polymer backbones in the two polyelectrolytes of interest here. The flexible backbone and long side chains in Nafion as compared to the rigid aromatic backbone and lack of side chains in S-PEEK play significant roles in the nature of the hydrogen-bonding domains found in the two polymers. For Nafion, the distance between sulfonic acid protons on the same polymer backbone or spatially adjacent ones is short, on account of the flexibility of the long side chain.

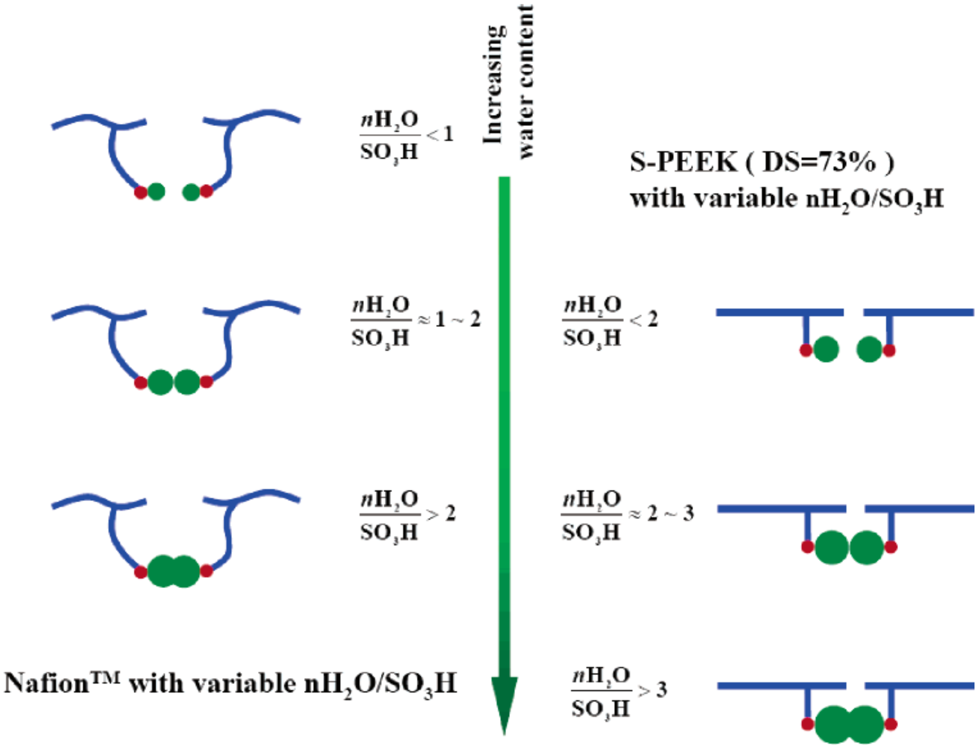


Figure 12. A model illustrating the hydrogen bonding between sulfonic acid protons and water molecules in Nafion and S-PEEK. The blue lines, red balls, and green balls represent the polymer chains, sulfonic acid protons, and water clusters in polymer, respectively. The figures on the left represent Nafion, with a flexible polymer backbone and side chains, whereas the figures on the right represent the more rigid S-PEEK polymer, without side chains. From top to bottom, the relative humidity of the membranes increases, as shown schematically by the increasing size of the acidic proton/water clusters. At the highest relative humidity, these hydrogen-bonded domains overlap and provide a conduit for long-range proton transport.

Compared with dried Nafion, a clear difference has been observed for dried S-PEEK (DS = 73%), as seen in Figure 11a. Namely, there is no observable dipolar coupling among the sulfonic acid protons, even when the recoupling time is extended to $8\tau_r$. The possibility of close packing between adjacent polymer chains could give short distance between sulfonic acid protons. However, since no coupling was observed in the dried membrane, the protons must be either isolated or extremely mobile. Because of the absence of long side chains in S-PEEK, proton distance between sulfonic acid groups in dried samples must be long irrespective of whether they are on same polymer backbone or spatially adjacent ones. Thus, the hydronium ions formed by complexing of water molecule and sulfonic acid proton are isolated. The fast rotation of these ions around any of O−H bonds greatly averages the dipolar coupling between protons of hydronium ion and could explain the weakness of the dipolar coupling in the dried S-PEEK sample. It is important to note that the hydronium ion rotation will not contribute long-range proton transport in the absence of a continuous H-bonding network. After this sample was humidified slightly, the dipolar coupling become strong enough to be detectable when the recoupling time is $8\tau_r$ (Figure 11b). Since humidification of S-PEEK will increase the mobility of the sulfonic acid group, the dipolar coupling would be intuitively expected to decrease. The observed increase in the coupling strength is attributed to the growth of the hydrogen-bonding network beyond local SO_3H groups and their associated ∼2−3 water molecules (Table 2) to a more extended, but still strongly H-bonded, network. The formation of this network is considered to be essential to long-range proton transport and continues to grow with increasing humidification. Again, under 100% humidification, no detectable dipolar couplings were observed in the DQF spectra. A model illustrating the hydrogen bonding between sulfonic acid protons and water molecules in Nafion and S-PEEK is shown in Figure 12. In Nafion, flexible side chains (blue) allow for close proximity between different sulfonic acid groups (red) and associated water molecules (green). This makes it possible to form a hydrogen-bonded network when nH_2O/SO_3H is about 1−2. Higher water content, $nH_2O/SO_3H > 2$, increases proton mobility, which decreases dipolar coupling. In S-PEEK, the sulfonic acid groups (red) are too far apart due to the lack of side chains and the relative rigidity of the aromatic backbone (blue). When $nH_2O/SO_3H < 2$, there is no hydrogen-bonded network formed, and rotation of hydronium ion (green) averages proton dipolar coupling, which makes it undetectable. When nH_2O/SO_3H is about 2−3, a hydrogen-bonded network is formed. In the meantime, the increased water mobility makes the proton dipolar coupling very weak. Thus, it is expected that a further increased water content $nH_2O/SO_3H > 3$ causes proton dipolar coupling undetectable due to the high mobility of the water molecules.

The model resulting from this study gives a concise differentiation between the conductivity of Nafion and S-PEEK based on the responses of these two materials, under varying degrees of humidification, to the DQF pulse sequences. This molecular level understanding of proton conductivity has been lacking in the discussions of membrane candidates, which are more typically characterized exclusively by macroscopic conductivity measurements obtained using impedance spectroscopy.

Conclusions

Proton exchange between water and sulfonic acid groups has been confirmed by high-resolution solid-state NMR for both Nafion and S-PEEK. The proton mobility depends on not only water content but also temperature. Compared with dried S-PEEK, a lower activation energy for proton transport in dried

Nafion suggests that S-PEEK is a competitive proton conductor under low-humidity conditions. The small difference in activation energy between pure Nafion and ZrP−Nafion indicates that ZrP is a promising additive for Nafion composites. A model is proposed for the proton−proton contacts in Nafion and S-PEEK on the basis of their respective $^1H-^1H$ dipolar couplings. These data were obtained using a homonuclear double-quantum filtered NMR sequence, which allows the molecular level structure and dynamics to be explored.

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