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Proton Dynamics of Nafion and Nafion/SiO_2 Composites by Solid State NMR and Pulse Field Gradient NMR

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ABSTRACT: Proton mobilities in Nafion and Nafion/SiO_2 composites have been studied using high-resolution solid-state MAS NMR. High-resolution solid-state ^{1}H NMR show that low concentrations of TEOS or short permeation times are necessary to allow complete hydrolysis of TEOS in Nafion. Incomplete hydrolysis of TEOS leaves residual ethyl groups on the surface of silica, which not only reduces the amount of water adsorbed by silica but also blocks the pathway of proton transport in the Nafion/SiO_2 composites. The diffusion coefficients established using PFG NMR show that the best Nafion/SiO_2 composite can be obtained from synthesis with a low concentration of TEOS in a methanol solution. This composite gives a higher diffusion coefficient than pure Nafion under dry conditions, although no differentiation in performance is observed when the membranes are hydrated. ^{29}Si NMR shows that this composite has a high ratio of Q_3/Q_4 sites, consistent with a small particle size and many surface hydroxyl groups. Together, these data demonstrate the role of high-surface-area SiO_2 particles in trapping water and building a pathway for structural (Grotthuss mechanism) proton diffusion. Good proton transport under low relative humidity is the holy grail of the PEM-FC community, and this molecular level study shows how conditions can be iteratively optimized to target desirable structure−property relationships.

1. Introduction

Studies on proton exchange membranes for the applications of fuel cells have been encouraged by the necessity to reduce pollution. As a well-known polymer electrolyte many studies have focused on, Nafion (Dupont trade name) has been given much attention because of its excellent conductivity in the hydrated state.[1,2] However, when this membrane is operated at high temperatures (above 100 °C), the conductivity of the membrane is dramatically decreased due to water loss. Since an elevated temperature has benefit to the fuel cell such as minimizing platinum poisoning and improving the electrode kinetics of the oxygen reduction reaction,[3,4] membranes providing acceptable conductivity at high temperature and low hydration level are desirable. Although increasing the operating pressure can raise the boiling point of water to prevent water loss, this is not efficient due to the energy penalty associated with compressing the reactant gases.[5] A variety of polymer electrolytes have been developed as proton exchange membranes (PEMs).[6,7] These membranes also show a strong conductivity dependence on the state of membrane hydration. It has been demonstrated that addition of inorganic particles to polymers can enhance conductivity.[8] A composite Nafion115/zirconium phosphate membrane displayed better fuel cell performance than pure Nafion115 when the fuel cell was operated at reduced humidity conditions.[9] The proton conductivity of a Nafion/zirconium sulfophenyl phosphate (ZrSPP) composite membrane was reported to reach 0.07 S/cm at 140 °C without additional humidification.[10] Nafion/SiO_2 has also shown better conductivity than pure Nafion at high temperature.[11,12] The improved conductivity of these composites is generally attributed to the surface hydroxyl groups of dopants which retain water at high temperature.[1,13] However, more information on how to obtain well-controlled composites with optimized amounts of dopants and particle size is needed, since these factors play a particularly important role in determining composite performance as a proton exchange membrane.

Solid-state nuclear magnetic resonance (NMR) can provide useful information concerning proton mobility within conducting polymers on the molecular level[14,15] because it is able to probe the local chemical environments. Such information is helpful to give a deeper understanding of the observed differences in proton conductivity. Magic angle spinning (MAS) is used routinely to achieve high resolution of ^{1}H NMR spectra in the solid state. Since dipolar interactions can reveal the relative mobility, methods which can retrieve information about the dipolar interaction removed by magic angle spinning are desirable. The double quantum filtering (DQF) pulse sequence, back-to-back (BaBa),[16,17] has been used to recouple the dipolar coupling between protons and thereby deduce their relative mobility. The intensity of the double quantum coherence (DQC) depends on the product of coupling strength and the excitation time, meaning a DQC 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 spectra due to inefficient excitation. Hence, we can distinguish mobile and rigid protons by comparing MAS NMR with DQF MAS NMR spectra. On the other hand, a longer recoupling (excitation) time is useful to detect weak dipolar couplings which indicate either slowly mobile (i.e., less rigid) protons or dipolar couplings occurring over long distances.

Pulse field gradient (PFG) NMR provides a convenient and noninvasive means for measuring translational motion of protons. Although translational motion can be measured by analysis of spin−lattice relaxation data, the two methods will agree only under certain conditions since the relaxation is also

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sensitive to rotational diffusion, which does not necessarily lead to long-range proton transport.[18] In PFG NMR, the nuclear motion can be measured by the attenuation of a spin echo signal resulting from the dephasing of the nuclear spins due to the combination of the translational motion of the spins and the imposition of spatially well-defined gradient pulses. Since this method can measure motion over millisecond to second time scales, the proton diffusion coefficient obtained by PFG NMR will reflect the proton mobility on the macroscopic level. This information can be used for comparison of various proton exchange membranes.

In this paper, we studied proton mobility in Nafion/SiO_2 composites prepared by in-situ synthesis. Both the concentration of tetraethyl orthosilicate (TEOS) and the permeation time (PT) were varied to investigate how the amount of silica and particle size affects proton dynamics. Homonuclear double quantum pulse (back-to-back) experiments were performed to distinguish strong proton dipolar couplings from weak ones. PFG NMR measurements were obtained for Nafion and Nafion/SiO_2 composites in both the dried and hydrated states. The differences in proton mobility are compared and discussed, in combination with the results of our solid-state NMR measurements.

2. Experimental Section

2.1. Preparation of Samples. Treatment of Nafion 112 was performed as follows. 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 washed in 1 M HCl for 1 h. Finally, it was washed repeatedly in distilled deionized water until the pH of the water was unchanged by the addition of the membrane. Nafion/SiO_2 composite membranes were prepared according to the procedure reported by Deng.[19] The pretreated Nafion was first swollen in MeOH:H_2O (v/v) = 5:1 for 24 h. It was then put in the mixture of methanol, water, and tetraethyl orthosilicate (TEOS) for 24 h to allow permeation of TEOS into Nafion. The concentration of TEOS in mixture was changed to control the amount of silica in the resulting composites. Thus, in this paper Nafion/SiO_2 composites made from different mixture will be shown as Nafion/SiO_2 (a:b:c) in which the ratio is molar ratio of methanol to water to TEOS. For the mixtures in which no methanol is used, a variable permeation time (PT) was used to control the hydrolysis and condensation of TEOS. Three samples made from MeOH:H_2O:TEOS (mol:mol:mol) = 0:1:1 with permeation times of 9 min, 120 min, and 24 h are denoted as Nafion/SiO_2 (0:1:1, PT9 min), Nafion/SiO_2 (0:1:1, PT120 min), and Nafion/SiO_2 (0:1:1, PT24 h), respectively. After the TEOS was allowed to permeate into Nafion, the membrane was dried at 105 °C overnight to remove the excess alcohols and water. Some selected composites were further treated at 170 °C, a temperature at which water physisorbed on silica starts to be driven off.[20] This treatment allowed the study of the interaction of water and silica. 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. For comparison, silica was also made by simply mixing TEOS with 1 M sulfuric acid solution. The molar ratio of TEOS to sulfuric acid solution is 4.5:1. The white powder obtained from this sol−gel process was dried at 105 °C overnight to remove the excess alcohols and water.

2.2. ^{1}H NMR. ^{1}H solid-state NMR experiments were performed on a Bruker AV 500 spectrometer at a ^{1}H Larmor frequency of 500.13 MHz. Both 4 and 2.5 mm diameter rotors were used for Nafion samples spun at 5 and 25 kHz, respectively. In both cases a recycle delay of 3 s and a prescan delay of 4.5 μs were used. The spectra were 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 300−360 K, with the sample temperature corrected to include heating effects arising from the high-speed MAS.[21] The rotor-synchronized DQF MAS spectra were recorded using the back-to-back (BaBa) pulse sequence, with τ_{exc} variable from half a rotor period $\tau_r/2$ to eight rotor periods, $8\tau_r$, and 512 scans.[16]

2.3. ^{29}Si NMR. ^{29}Si solid-state NMR experiments were performed on a Bruker AV 500 spectrometer at a ^{29}Si Larmor frequency of 99.35 MHz. A 4 mm diameter rotor was used for samples spun at 5 kHz. A recycle delay of 180 s was used. It was found that this delay time is long enough since the obtained spectrum does not show observable difference from that by 420 s delay time. The ^{29}Si NMR spectra were acquired with a 90° pulse length of 3.5 μs and referenced to tetrakis(trimethylsilyl)silane (−10.02 and −135.7 ppm for ^{29}Si). 512 scans were averaged for the ^{29}Si NMR spectra.

2.4. PFG NMR. ^{1}H diffusion coefficient experiments were performed on Bruker Avance 400WB spectrometer at a ^{1}H Larmor frequency of 400.13 MHz. Gradient pulse duration, δ, ranged from 1 to 2 ms, and diffusion time, Δ, ranged from 50 to 300 ms. The maximum gradient strength ranged from 50 to 1800 G/cm. For variable temperature measurement, the probe temperature was calibrated using ethylene glycol. A 5 mm Diff30 probe was used with a 60 A (Bruker Great 1/60) amplifier. The predried sample was placed directly into a 5 mm NMR tube for measurement. The uncapped NMR tube with the dried sample was placed in a humidity chamber for 8 days at 50 °C and 90% relative humidity to obtain the hydrated sample. Hydrated samples were capped immediately and analyzed within a few hours of removal from the humidity chamber. The chemical shift of the sulfonic acid proton, which is sensitive to humidity, remained unchanged during measurement once the sample was in the capped NMR tube.

2.5. Proton Conductivity Measurement by Impedance Spectroscopy. A BekkTech four-probe conductivity cell with two platinum foil outer electrodes and two platinum wire inner electrodes was used for proton conductivity measurement. The membrane samples were cut into strips which were 0.3−0.5 cm wide and 2−3 cm long. The thickness of membranes was measured by micrometer. An AUTOLAB PGSTAT30 impedance analyzer was used for impedance spectroscopy. The instrument was used in potentiostatic mode with an ac potential amplitude of 0.01 V over a frequency range of 10−20 000 Hz. The conductivity of membrane was measured in the longitudinal direction. It can be calculated using the following equation

$$\sigma = d/Rlh \tag{1}$$

where σ, d, R, l, and h denote the ionic conductivity, distance between the two inner electrodes, the measured resistance of the membrane, the width of the membrane, and the thickness of the membrane, respectively.[22,23] In order to measure the conductivity of dried samples, membranes were dried at 105 °C for several days and then equilibrated overnight at 35 °C in a sealed oven with desiccants. The hydrated samples were equilibrated overnight at 35 °C and 95% relative humidity in a humidity chamber. This equilibration time was found to be sufficiently long for the four-probe cell configuration, since the membrane is entirely exposed to the environment in the humidity chamber. The conductivity was found to be constant within 1% over several days in the controlled environment. The water content of these samples was measured to determine number of water molecules per sulfonic acid group for comparison of proton diffusion coefficients. For dried samples, the water content can be determined from the first weight loss in a thermal gravimetric analysis (TGA) study. The water content of hydrated samples was measured by the weight difference of dried samples and hydrated samples, with the weights of the dried samples normalized for their known water contents.

3. Results and Discussion

3.1. Nafion/SiO_2 Composites: Influence of Concentration of TEOS. Figure 1 shows ^{1}H MAS NMR spectra of SiO_2, Nafion, and Nafion/SiO_2 prepared from different concentrations

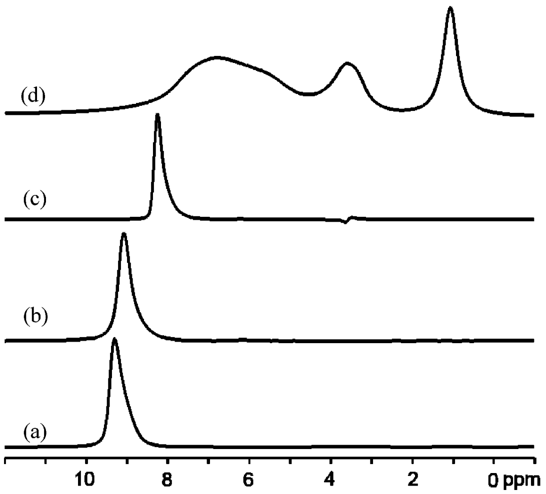

Figure 1. ^1H MAS NMR of SiO_2, Nafion, and Nafion/SiO_2 composites made with different concentrations of TEOS and 24 h of permeation time. All samples were treated overnight at 105 °C: (a) SiO_2 made from mixture of TEOS and 1 M $H_2SO_{4(aq)}$, MAS = 5 kHz; (b) Nafion, MAS = 5 kHz; (c) Nafion/SiO_2 (23:1:1), MAS = 5 kHz; (d) Nafion/SiO_2 (2.3:1:1), MAS = 25 kHz.

of TEOS and 24 h of permeation time. The high-frequency proton resonance shown in Figure 1a is assigned to the residual sulfuric acid protons. Because of the complete hydrolysis of TEOS under these conditions, no residual ethyl group signals were observed. The absence of Si−OH proton signal in this spectrum could be attributed to the insignificant amount of surface Si−OH groups compared with the large number of sulfuric acid protons. The only peak shown in Figure 1b is assigned to the sulfonic acid protons of Nafion. After silica was doped into Nafion, water adsorbed on the silica surface forms hydrogen bonds with Si−OH groups. This water shifts the sulfonic acid proton resonance to a lower chemical shift, as shown in Figure 1c.

Proton resonances from Si−OH groups were not observed in this composite, as only a small amount of silica was formed from the initial low concentration of TEOS. When a higher concentration of TEOS was used to dope silica into Nafion, new peaks were observed in Figure 1d. The peaks at 1.0 and 3.5 ppm are assigned to CH_3 and CH_2 groups of the residual ethyl groups of incompletely hydrolyzed TEOS, respectively. The broad resonance spanning from 5 to 8 ppm in Figure 1d is assigned to hydrogen-bonded $-SO_3H$ and Si−OH protons. The wide range of local environments in the membrane causes significant spectral overlap. The broad resonance at 4 ppm is assigned to water physisorbed on silica. Similar spectra have been reported in the literature for silicates, in which a resonance at 4 ppm is assigned to physisorbed water and broad resonances ranging from 2 to 8 ppm are attributed to silanol protons in various hydrogen-bonding environments.[24−26]

Comparing Figure 1a with Figure 1c,d, we find that full hydrolysis of TEOS can be achieved in a mixture of sulfuric acid and TEOS without polymer and in Nafion membranes when the concentration of TEOS is very low. When the concentration of TEOS is as high as that in Figure 1d, an incomplete hydrolysis of TEOS is observed. This is caused by the steric effect of the polymer microstructure in the Nafion/SiO_2 composite. When Nafion is immersed in methanol and water, the competing hydrolysis and condensation reactions favor the former, allowing full hydrolysis of TEOS. When the concentration of TEOS is increased, the condensation reaction dominates over full hydrolysis of TEOS, leading to a fast growth of silica particle size. Since the sulfonic acid group is restricted by the pendent side chain of Nafion, the mobility of H^+ and SO_3 in Nafion will be lower than that in free sulfuric acid. Additionally, the increasing silica particle size will decrease its mobility. Both factors inhibit the complete hydrolysis of residual ethyl groups in the membrane composites when the concentration of TEOS is high.

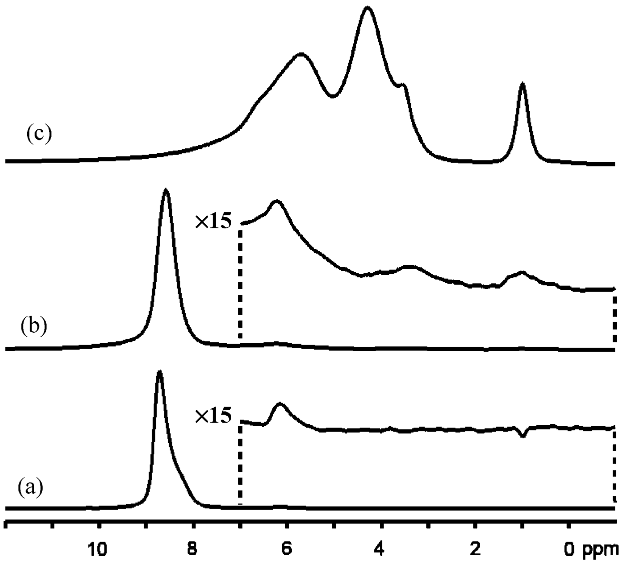

Figure 2. ^1H MAS NMR of Nafion/SiO_2 (0:1:1) composites made using different permeation times. All samples were treated overnight at 105 °C: (a) Nafion/SiO_2 (PT9 min), MAS = 5 kHz; (b) Nafion/SiO_2 (PT120 min), MAS = 5 kHz; (c) Nafion/SiO_2 (PT24 h), MAS = 25 kHz.

3.2. Nafion/SiO_2 Composites: Influence of Permeation Time. ^1H MAS NMR spectra of Nafion/SiO_2 (0:1:1) prepared by varying the permeation time are shown in Figure 2. As expected, when the permeation time is decreased from 24 h to either 120 or 9 min, the ^1H NMR spectra of the composites are dominated by a sulfonic acid proton resonance. However, if we take a closer look at the two spectra, we can still observe the proton signal of Si−OH, as shown in the expanded plots in Figure 2a,b. In addition, Figure 2b also shows weak proton signals for the residual ethyl group from TEOS (near 1.0 and 3.5 ppm). Since these signals are not observed in Figure 2a, this means that there are virtually no residual ethyl groups of TEOS in Nafion/SiO_2 (0:1:1, PT9 min) compared with the Si−OH groups. The presence of residual ethyl groups from TEOS will have two negative effects on proton conductivity of the composites. One is to reduce the number of surface hydroxyl groups by occupying the surface of the silica. This ultimately decreases the amount of water adsorbed by the silica particles, thereby minimizing the targeted water-binding action of the composite. The other is to block the proton channels of the composite due to the larger volume occupied by ethyl groups compared with hydroxyl groups. This result demonstrates that a short permeation is preferable to allow hydrolysis of TEOS to silica, while maintaining a high surface area, ensuring that ethyl groups are fully hydrolyzed and can escape from the membrane. These conditions will positively influence proton mobility within Nafion/SiO_2 composite.

3.3. Nafion/SiO_2 Composites: Influence of Relative Humidity. The unambiguous assignment of ^1H resonances for H_2O/OH/H^+ groups in these systems is difficult. With reference to literature studies of related SiO_2-based materials, and using our knowledge of the treatment conditions of the composites, we attempt a logical interpretation of the observed changes as a

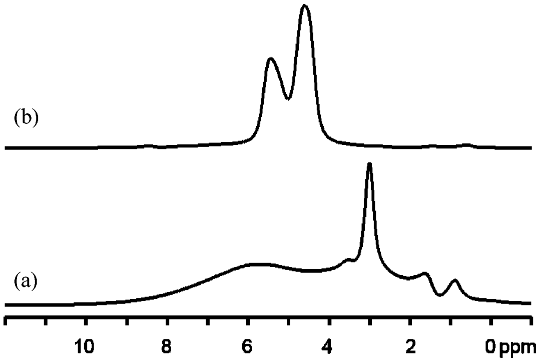

Figure 3. ^{1}H MAS NMR of Nafion/SiO$_2$ (0:1:1) composites with PT = 24 h at 25 kHz: (a) treated at 105 °C for 24 h and then at 170 °C for 24 h; (b) sample from (a) is hydrated in oven for 96 h at 50 °C and relative humidity of 90%.

function of temperature/humidity. Figure 3 shows spectra of Nafion/SiO$_2$ (0:1:1, PT24 h) treated by drying or hydration. Comparing with Figure 2c, two new peaks at 1.6 and 3.0 ppm are readily observed in Figure 3a, and the resonance assigned to physisorbed water (4.3 ppm) has disappeared from the spectrum. The peak at 1.6 ppm is assigned to isolated (non-hydrogen-bonded) Si−OH groups.[21,27,28] The other peak at 3.0 ppm is assigned to rapidly exchanging, weakly hydrogen-bonded hydroxyls (including those of both water and silanols).[29,30] Other studies have attributed the resonances at 3 ppm to water on significantly dehydrated surfaces and those at 4.5−5.0 ppm to water on strongly hydrated surfaces, as reviewed by Turov et al.[31] It has been reported that, for silica gels, physisorbed water starts to be driven off at about 170−175 °C.[20,32] Since this composite was dried at 170 °C for 24 h before NMR measurement, loss of physisorbed water is expected, which accounts for the absence of a physisorbed water signal. On the other hand, physisorbed water must be very immobile at room temperature because it was not removed even when the drying temperature was as high as 105 °C, as seen in Figure 2c. At 170 °C, not only is the physisorbed water eliminated, but water strongly hydrogen bonded with Si−OH is also partially removed. This causes some isolated Si−OH groups to appear with a peak at 1.6 ppm. At the same time, the percentage of hydrogen-bonded Si−OH groups decreases, which results in a smaller but broader peak.

The weakly hydrogen-bonded hydroxyls at 3.0 ppm could be due to protons which are rapidly exchanging with water trapped within tiny cavities formed in silica particles. In an analogous study, the improved water retention of Nafion/zirconium phosphate composites was attributed to capillary condensation effects induced by zirconium phosphate doped in Nafion.[5] In the present case, the strong capillary condensation effect prevented the weakly bonded water from being eliminated even at temperatures as high as 170 °C. After this composite was treated for another 24 h at the same temperature, the NMR spectrum (not shown here) indicates that the percentages of both strongly and weakly hydrogen-bonded Si−OH groups decrease, while the percentage of isolated Si−OH groups increases. This also supports the hypothesis that hydrogen-bonded Si−OH groups changed into isolated Si−OH groups after the loss of water. The hydrated sample shown in Figure 3b only presented two peaks which should be assigned to hydrogen-bonded Si−OH groups (5.6 ppm) and physisorbed water (4.5 ppm). Since a large amount of water is present in the sample treated at 50% relative humidity, the residual ethyl groups cannot be observed from this sample due to their very low relative concentration. However, once the sample is dried again, the resonances of the ethyl groups become observable in the ^{1}H NMR spectrum, confirming therefore the loss of this signal under hydration is simply an issue of relative intensity and not a completion of the hydrolysis reaction.

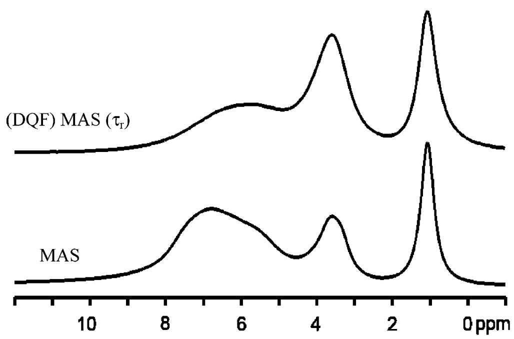

Figure 4. ^{1}H MAS and DQF MAS NMR spectra of Nafion/SiO$_2$ (2.3:1:1) composite dried at 105 °C for 24 h, MAS = 25 kHz. τ_r indicates the number of rotor periods of recoupling used in the DQF sequence (one in this case).

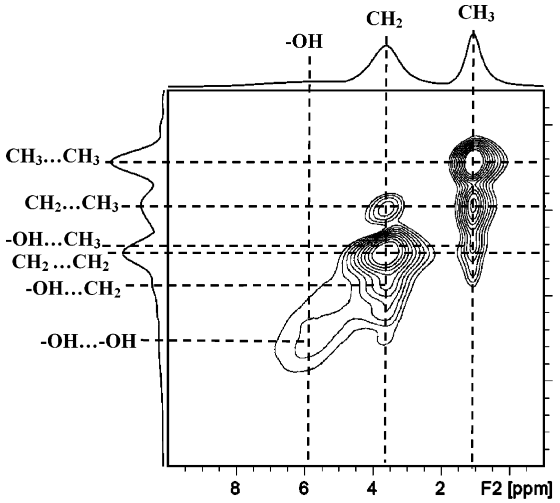

Figure 5. ^{1}H 2D DQ correlation MAS NMR of Nafion/SiO$_2$ (2.3:1:1) composite dried at 105 °C for 24 h, MAS = 25 kHz, $\tau_{exc} = \tau_r$.

3.4. Immobile Protons Detected by DQ MAS NMR of Nafion/SiO$_2$. Since DQF MAS NMR measurements provide information on the relative mobility of protons, it is used to distinguish immobile protons from mobile ones in Nafion/SiO$_2$ composites. Results of Nafion/SiO$_2$ (2.3:1:1) composite prepared from an intermediate concentration of TEOS are chosen to represent this information. Figure 4 and Figure 5 show the 1D and 2D ^{1}H DQ correlation MAS NMR spectra of Nafion/SiO$_2$ (2.3:1:1), respectively. It is clear that the residual ethyl group of TEOS is not mobile since it did not disappear from the DQF MAS spectra when the recoupling time was increased from $\tau_r/2$ to $8\tau_r$ (see, e.g., spectrum for τ_r shown in Figure 4). This proves that the ethyl group is from incompletely hydrolyzed TEOS rather than from free TEOS, since the ethyl group of free TEOS would be mobile even if the TEOS was trapped in silica. In DQF MAS NMR spectra, the presence of the Si−OH resonance indicates that some of these hydroxyl groups are not mobile, which is consistent with ^{1}H CRAMPS dipolar dephasing experiments in which silanol groups show strong dipolar interactions.[26,27] Not surprisingly, the strong dipolar coupling between ethyl protons was observed in the 2D DQ correlation MAS spectrum as well, shown in Figure 5. Strong dipolar coupling between protons of the ethyl group and Si−OH was also observed. This implies that the residual ethyl groups are spatially close to Si−OH groups. Since these Si−OH groups

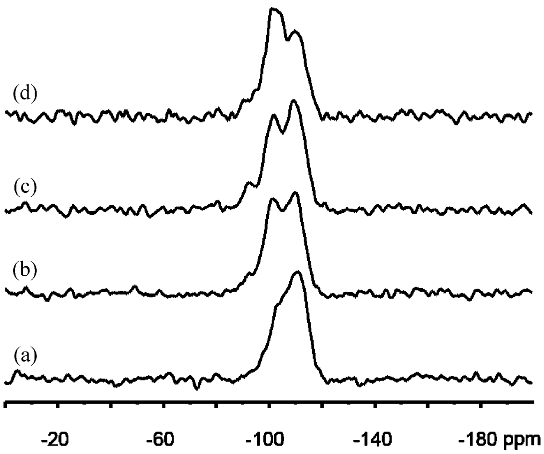

Figure 6. ^{29}Si MAS NMR of SiO$_2$ and Nafion/SiO$_2$ composites dried at 105 °C for 24 h, MAS = 5 kHz: (a) SiO$_2$ from TEOS and H$_2$SO$_{4(aq)}$; (b) Nafion/SiO$_2$ (0:1:1, PT = 120 min); (c) Nafion/SiO$_2$ (0:1:1, PT = 24 h); (d) Nafion/SiO$_2$ (2.3:1:1, PT = 24 h).

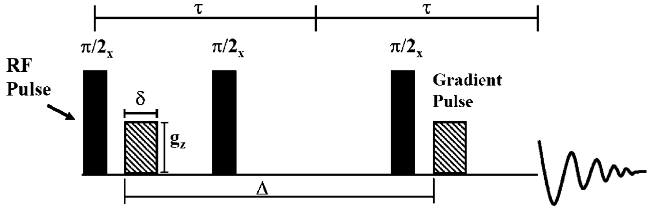

Figure 7. Stimulated echo (STE) pulse sequence. The applied gradient pulses cause dephasing for spins which experience translational motion.

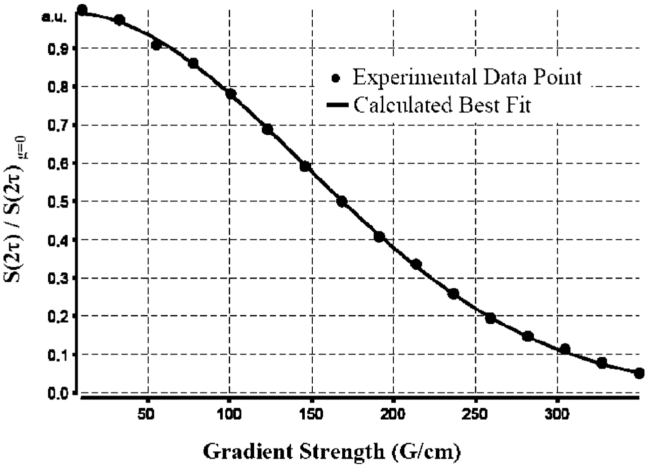

Figure 8. Example of fitted PFG NMR data. The sample is dried Nafion/SiO$_2$ (23:1:1). The fitted diffusion coefficient is 2.55 × 10^{-7} cm^2/s at 305 K.

always are on the surface of silica, some of the residual ethyl groups have to be on the silica surface. Those residual ethyl groups located on the silica surface can still be hydrolyzed once an acid catalyst is available. Thus, acidifying the composite can finally complete the hydrolysis of these residual ethyl groups. Figure 5 also shows strong proton dipolar coupling between Si−OH groups. The strong proton dipolar coupling between Si−OH groups suggests that Si−OH groups are spatially close to each other as well. This proximity is important for allowing a hopping mechanism of proton transport. Water molecules hydrogen bonded with these Si−OH groups will be able to have proton exchange with each other because of the short distance between these bonding sites. Nevertheless, since this composite was treated at 105 °C for 24 h before NMR measurement, water molecules left in the composite would not be expected to undergo proton exchange with each other at room temperature. The reduced intensity of the Si−OH resonance relative to the CH$_2$/CH$_3$ resonances in the 2D DQ correlation spectrum as compared to the MAS spectrum indicates a weaker coupling, possibly attributable to local mobility. If the composite is subjected to an operating temperature above 105 °C, proton exchange among water would be expected. This is also the motivation for doping silica to improve proton conductivity of Nafion.

3.5. ^{29}Si MAS NMR. ^{29}Si solid-state NMR is a well-established means of determining the coordination environments of ^{29}Si nuclei. From this information, we can deduce the number of surface hydroxyl groups in the various samples and optimize the synthetic conditions to favor high surface area materials. A silicon atom which is bonded to three other silicon atoms through oxygen can be shown as HO−Si−(O−Si)$_3$ and is generally denoted as Q$_3$, giving a chemical shift of ∼−100 ppm. Similarly, Si−(O−Si)$_4$ is denoted as Q$_4$ and has a chemical shift of ∼−110 ppm.[33−35] It is clear that the higher ratio of Q$_3$ to Q$_4$ indicates a higher surface area and therefore smaller average size of silica particles for the same total amount of SiO$_2$. Thus, ^{29}Si MAS NMR of Nafion/SiO$_2$ composites can provide qualitative information regarding the silica particle size.

^{29}Si MAS NMR of SiO$_2$ and Nafion/SiO$_2$ composites are shown in Figure 6. There is no silicon resonance observed at −80 ppm in all ^{29}Si spectra, confirming that there is no unreacted TEOS in these samples. Based on the data shown in Figure 6a, the majority of silicon nuclei in the silica made from TEOS and sulfuric acid are in the form of Q$_4$. This indicates that a full condensation reaction has occurred among the TEOS molecules and that the average silica particle size is large. The Nafion/SiO$_2$ composite prepared using a short permeation time (120 min) gives an increased ratio of Q$_3$ to Q$_4$ as shown in Figure 6b, which suggests smaller silica particles in the composite compared with neat SiO$_2$. This is likely due to the restricted motion of silica in water channels of Nafion. It has been reported that the diameter of water channels in hydrated Nafion is as large as 5 nm.[36] Compared with silica made from a mixture of TEOS and sulfuric acid, such a narrow channel will certainly restrict the motion of the precursor units within the membrane. Therefore, the condensation reaction among these silica units will be limited. This maintains a large number of surface hydroxyl groups of silica. Thus, more silicon atoms have the Q$_3$ coordination environment in the composite. Nevertheless, when a longer permeation time is allowed (24 h), the ratio of Q$_3$ to Q$_4$ decreases slightly, as shown in Figure 6c. This may be attributed to the condensation reaction dominating over the hydrolysis reaction of TEOS. Interestingly, this composite also shows a peak at −90 ppm, which is attributed to silicon in the form of (HO)$_2$−Si−(O−Si)$_2$, denoted as Q$_2$. The Q$_2$ sites of silicon could be also due to the restricted condensation reaction between newly formed small silica particles, since the initially formed silica particles would be large and further prevent the fast motion of the subsequently formed small particles. As expected, because of the reduced concentration of TEOS, the composite Nafion/SiO$_2$ (2.3:1:1) shows an even higher ratio of Q$_3$ to Q$_4$, as shown in Figure 6d, which suggests a further decrease in the condensation among silica particles. This is desirable because silica with more surface hydroxyl groups will provide more sites to retain water. Ramani reported that an enhanced conductivity of Nafion/phosphotungstic acid composite membrane by up to 35% was obtained when the additive particle size was reduced by nearly 2 orders of magnitude from 1 to 2 μm to 30 nm.[37] The ratios of Q$_3$ to Q$_4$ calculated from

Table 1. Ratio of Q_3 to Q_4 in SiO_2 and Nafion/SiO_2 Composites

samples	SiO_2 (TEOS and H_2SO_4)	Nafion/SiO_2 (0:1:1) PT = 120 min	Nafion/SiO_2 (0:1:1) PT = 24 h	Nafion/SiO_2 (2.3:1:1) PT = 24 h
Q_3:Q_4	1:4.2	1:1.2	1:1.6	1:0.7

the deconvoluted spectra for these samples are shown in Table 1 for reference.

On the basis of the ^{29}Si NMR results, we target samples that have the maximum number of Q_3 sites or, equivalently, a high concentration of surface OH groups. We also note that samples with even lower concentrations of silicate gave very weak ^{29}Si NMR signals but did not provide quantifiable spectra. Nevertheless, the same trend is expected.

3.6. PFG NMR for Proton Diffusion Coefficient Measurement. The pulse field gradient NMR experiment provides a measure of the translational motion of protons in the membrane. By comparing a select set of samples, where high numbers of surface hydroxyl groups are present (i.e., those with low permeation times or low concentrations of TEOS used in the sample preparation), we can determine the influence of those surface hydroxyl groups on water retention and proton transport within the dried vs humidified membranes. These data are compared to the performance of Nafion itself under equivalent conditions.

The pulse sequence applied for PFG NMR measurement in this study is shown in Figure 7. A pair of symmetrically spaced field gradient pulses is superimposed onto a standard spin echo sequence. This is known as the stimulated echo (STE) pulse sequence. The predicted dependence of the observed signal attenuation on gradient strength is[18]

$$E(2\tau) = \frac{S(2\tau)}{S(2\tau)_{g=0}} = \exp(-\gamma^2 g^2 D\delta^2(\Delta - \delta/3)) \qquad (2)$$

where $S(2\tau)$ is the observed signal intensity with applied gradient pulse g, $S(2\tau)_{g=0}$ is the signal intensity observed in the absence of an applied gradient, γ is the nuclear gyromagnetic ratio, D is the self-diffusion coefficient, δ is a pulse width of applied gradient, and Δ is the separation in time between the leading edges of the two gradient pulses (also referred to as the "diffusion time"). In this study, a series of spectra are obtained at increasing gradient strengths, holding all other parameters constant. The diffusion coefficient is obtained by fitting the peak intensity data vs the applied gradient strength, as shown in Figure 8.

A fundamental requirement of a PFG NMR experiment is that the diffusional attenuation must be significant relative to attenuation caused by relaxation of the observed nuclei. Determination of diffusion coefficients by PFG NMR measurement will be difficult or infeasible if relaxation is too rapid. Boyle[38] reported that iron contamination in Nafion caused significantly shortened relaxation time (T_1 on the order of 10 ms for 1100 EW Nafion), which made the PFG NMR experiment of Nafion impractical in their studies. On the basis of well-purified, protonic forms of Nafion, Zawodzinski found that T_1 relaxation times vary from 80 to 200 ms for Nafion 117 membranes and reduce with decreasing water content in the membrane.[39] In our experiments, the T_1 relaxation times ranged from 130 to 580 ms, and the hydrated samples showed longer T_1 relaxation times than dried samples as well.

The proton diffusion coefficients obtained by PFG NMR are shown in Table 2. For pure Nafion, the hydrated sample shows a proton diffusion coefficient around 37 times higher than the dried ones. Zawodzinski reported proton diffusion coefficients for Nafion117 of 4.4 × 10^{-6} and 5.8 × 10^{-6} cm^2/s when H_2O/SO_3H is 9 and 14, respectively.[39] By comparison, H_2O/SO_3H in our hydrated Nafion is found to be in the range between 10 and 13, as noted in Table 4. In Table 2, the dried Nafion/SiO_2 composites made from high concentration of TEOS (such as MeOH:H2O:TEOS = 0:1:1) have lower diffusion coefficients than pure Nafion, but composites made from low concentrations of TEOS (such as MeOH:H_2O:TEOS = 23:1:1, 1:0.5:0.005, and1:0.26:0.026) show higher diffusion coefficients than pure Nafion.

Table 2. Proton Diffusion Coefficient of Nafion and Nafion/SiO_2[a]

samples	dried ($\times 10^{-7}$ cm^2/s)	hydrated ($\times 10^{-7}$ cm^2/s)
Nafion	1.32 ± 0.02	48.3 ± 0.2
Nafion/SiO_2 (0:1:1, PT9 min)	0.96 ± 0.02	41.7 ± 0.2
Nafion/SiO_2 (0:1:1, PT120 min)	0.097 ± 0.002	43.8 ± 0.2
Nafion/SiO_2 (23:1:1)	2.15 ± 0.02	46.7 ± 0.2
Nafion/SiO_2 (1:0.5:0.005)	1.82 ± 0.02	47.4 ± 0.2
Nafion/SiO_2 (1:0.26:0.026)	1.65 ± 0.02	48.3 ± 0.2

[a] Error bars reported here are based upon repeat measurements with different diffusion times.

Doping silica in Nafion will have two opposing effects on proton mobility of Nafion/SiO_2. The first effect is to help Nafion to retain water by forming hydrogen bonds between water and hydroxyl groups of silica. This is desirable. The second is to block the pathway of proton transportation by silica. This is undesirable. The diffusion coefficients of Nafion/SiO_2 listed in Table 2 imply competition of the two effects. A sketch shown in Figure 9 is used to display the difference in Nafion/SiO_2 prepared from low and high concentrations of TEOS. For composites made from high concentrations of TEOS, the silica particles are relatively large since the condensation reaction of silica is facile, which has been proven by our ^{29}Si MAS NMR data (see section 3.5). In such a case, the negative effect will play a dominant role in changing the proton diffusion coefficient. Moreover, for the a composite made from a high concentration of TEOS with a permeation time of 120 min, the very low diffusion coefficient could be due to not only the increased silica particle size but also the residual ethyl groups which have been shown by our ^{1}H NMR spectra. In this case, the negative effect will be overwhelming. Since the Nafion/SiO_2 composites made from low concentrations of TEOS have been shown to have smaller silica particle size and no residual ethyl groups, the positive effect will be dominant in these composites. This composite would have well connected pathway for proton hopping, which contributes to higher proton diffusion coefficient.

TGA measurements, available in the Supporting Information, provide information about the total amount of silica in the composites. Nafion/SiO_2 (0:1:1, PT120 min), Nafion/SiO_2 (0:1:1, PT9 min), and Nafion/SiO_2 (23:1:1) have 2.8%, 1.2%, and 1.0% mass percentage of silica, respectively, after taking into account of residual mass percentage of Nafion (1.7%). Clearly, Nafion/SiO_2 (0:1:1, PT120 min) has the highest weight percentage of silica. Shortening the permeation time reduces the total amount of silica in Nafion/SiO_2 (0:1:1, PT9 min) but still slightly exceeds the amount of silica made with a long permeation time and a low concentration of TEOS, as in Nafion/SiO_2 (23:1:1). On the basis of the TGA results and diffusion coefficient data, the composite made from the lower concentration of TEOS should have the smallest silica particle size, which should

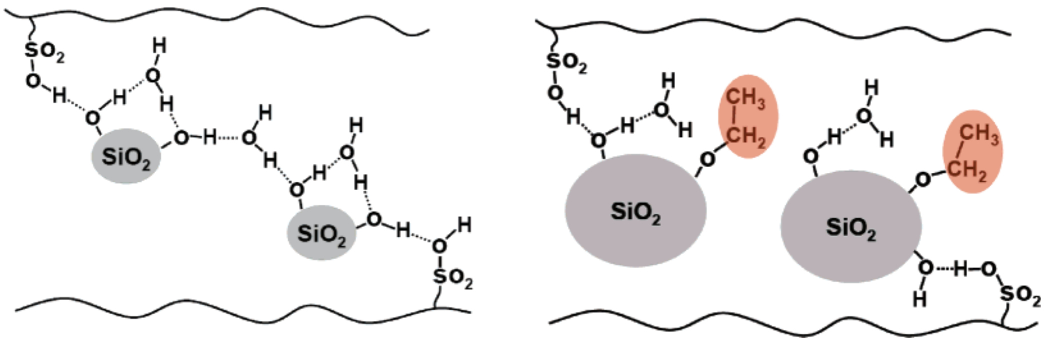

Figure 9. Schematic representation of the structure of dried Nafion/SiO$_2$ composites prepared from low concentration TEOS (the left) and high concentration TEOS (the right). The residual ethyl groups are highlighted.

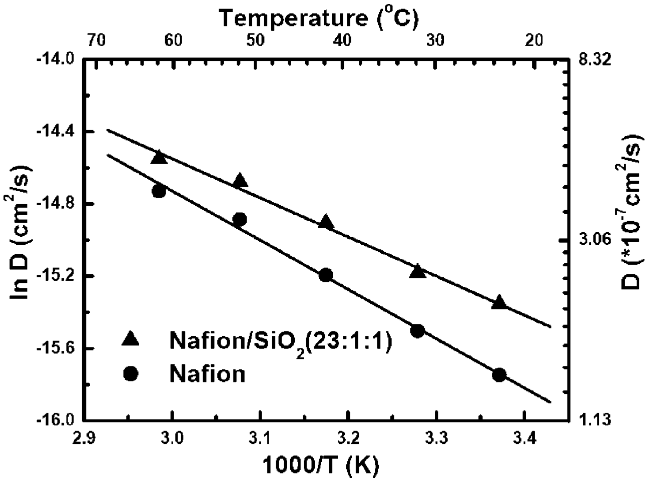

Figure 10. Arrhenius plot of proton diffusion for Nafion and Nafion/SiO$_2$ composites.

Table 3. Activation Energy of Proton Transport for Nafion and Nafion Composites

fully dried samples	PFG NMR derived E_a values (kJ/mol)	solid-state NMR derived E_a values (kJ/mol)
Nafion	22.6	15.7 ± 0.6
Nafion/SiO$_2$ (0:1:1, PT9 min)	20.9	12.2 ± 0.5
Nafion/SiO$_2$ (23:1:1)	18.0	N/A

minimize the effect of blocking pathways for proton transportation. The number of surface hydroxyl groups in dried Nafion/SiO$_2$ composite has a significant influence on the proton diffusion coefficient. Therefore, minimizing the concentration of SiO$_2$, while maximizing the number of surface OH sites, as in sample Nafion/SiO$_2$ (23:1:1), provides the best pathway for proton conductivity.

In contrast, no significant difference can be seen between hydrated Nafion and hydrated Nafion/SiO$_2$ composites. This is attributed to the high proton mobility in expanded water channels in hydrated samples. Compared with water added by hydration, under high relative humidity, water adsorbed on silica surface will not contribute much to the proton mobility of Nafion/SiO$_2$ composites since the proton diffusion coefficient in this instance is determined primarily by the water from hydration. Under this condition, the silica dopant in Nafion will merely be an obstacle for proton transportation, leading to decreased diffusion coefficients of Nafion/SiO$_2$. However, because of rapid vehicle transport in the fluid phase of the expanded water channels and the relatively small filled silica particles, the dopant cannot lower the diffusion coefficient significantly, even for the composite prepared with 120 min of permeation time. From this behavior, we infer that proton transport in dried Nafion/SiO$_2$ composite has a Grotthuss hopping mechanism different from that in the hydrated composite. In the dried composites, the proton transport is achieved by proton hopping on the surface of silica. Thus, well-distributed small silica particles can enhance the efficiency of proton hopping. In the hydrated composite, the proton transport is dominated by vehicle transport and completed by reorganization of hydrogen bonds between H$^+$ and water molecules. Kreuer points out that the Grotthuss mechanism is increasingly dominated by the vehicle mechanism as temperature increases.[40] Similarly here, the vehicle mechanism becomes increasingly important with increasing relative humidity. The existence of silica particles changes the pathway of proton migration and makes it somewhat longer but does not significantly influence transport. The length scale of proton diffusion (d) can be given by

$$d = \sqrt{2D\Delta} \tag{3}$$

where D is the diffusion coefficient and Δ is the diffusion time shown in the STE pulse sequence. For the dried samples, d is between 0.4 and 1.9 μm. Because of similar diffusion time, the sample with higher diffusion coefficient shows longer length scale of motion. For the hydrated samples, d is between 9 and 17 μm. The difference of length scale of motion for the hydrated samples results from different diffusion time, which was varied between Δ of 50 and 300 ms. Nevertheless, no obvious difference of diffusion coefficients is observed for the same sample when the diffusion time, Δ, is varied. The above d values for both dried and hydrated samples are apparently much greater than the size of water channels in the hydrated Nafion, which can be up to 5 nm.[36] This implies that proton diffusion is not constrained by the diameter of the channels even under dried conditions, but rather that the protons move readily along the channels, or from particle to channel wall, in the presence of silica particles with hydrophilic surfaces.

Since the diffusion coefficient is temperature dependent, variable temperature measurements with PFG NMR can demonstrate how the diffusion coefficients changes with temperature. The corresponding activation energy of proton diffusion can then be obtained by fitting the equation $D = D_0 \exp(-E_a/RT)$, where D is the diffusion coefficient, D_0 is a preexponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the temperature. Figure 10 shows the natural log plot from which the activation energies were derived for Nafion and Nafion/SiO$_2$ (23:1:1), which are 22.6 and 18.0 kJ/mol, respectively. The lower activation energy shown by the Nafion/SiO$_2$ (23:1:1) composite indicates that proton mobility of these composites is less sensitive to temperature change. The activation energies determined by PFG NMR are summarized in Table 3, along with some of the data obtained from variable solid-

Table 4. Conductivity of Nafion and Nafion/SiO_2 at 35 °C

	dried		hydrated	
samples	σ (S/cm)	$H_2O/-SO_3H$	σ (S/cm)	$H_2O/-SO_3H$
Nafion	3.7×10^{-4}	3.1	6.0×10^{-2}	12.6
Nafion/SiO_2 (0:1:1, PT9 min)	2.4×10^{-5}	3.1	5.7×10^{-2}	12.7
Nafion/SiO_2 (0:1:1, PT120 min)	1.1×10^{-5}	2.6	4.9×10^{-2}	10.5
Nafion/SiO_2 (23:1:1)	4.9×10^{-4}	2.8	5.1×10^{-2}	11.8

state NMR line width calculations. The composite made from a low concentration of TEOS gives a lower E_a than that made from a high concentration of TEOS, although the difference is not very large. An interesting observation is that the composite made from a high concentration of TEOS shows a lower activation energy than pure Nafion, even though pure Nafion exhibits higher diffusion coefficients at all temperatures measured. The lower activation energy shown by both Nafion/SiO_2 (0:1:1, PT9 min) and Nafion/SiO_2 (23:1:1) composites indicates that proton mobility of these composites is less sensitive to temperature. In our previous studies, an activation energy for proton transport has been obtained by linear fitting of the change of ^1H line width with temperature in solid-state NMR.[41] These solid-state NMR-derived activation energies are also included in Table 3. The large difference between the values derived from the two different methods is attributed to the fact that PFG NMR measures the proton motion over the millisecond to second time scale, whereas solid-state NMR does so over the microsecond time scale. In the case of motion over long time scale (i.e., PFG NMR), the activation energy obtained will include the energy of proton motion used for crossing longer length scales in the membrane, i.e., in and out of channels, similar to grain boundary effects in microcrystalline solids. Therefore, it is reasonable that PFG NMR measures a higher E_a than solid-state NMR.

3.7. Proton Conductivity of Nafion and Nafion/SiO_2 Composites. Although PFG NMR experiments can provide information on proton translation motion in the electrolyte, this technique is not able to distinguish protons dissociated from sulfonic acid groups from those associated with sulfonic acid groups which do not contribute to proton conductivity, according to the Nernst–Einstein equation.[42] Proton conductivity data measured by impedance spectroscopy is the industrially accepted method for evaluation of the conductivity of Nafion and Nafion/SiO_2 composites. The obtained results are shown in Table 4. The measured number of water molecules per sulfonic acid group is shown in this table for comparison as well.

The proton conductivity of hydrated Nafion is in good agreement with values reported by others.[22,43] Similar to PFG NMR results, the hydrated samples do not show much conductivity difference which may be attributed to the similar, high, number of water molecules per sulfonic acid group. In contrast, the dried samples present significant conductivity differences, of as much as 1 order of magnitude, although the number of water molecules per sulfonic acid group in dried samples is very similar. The conductivity data are consistent with interpretation of NMR and PFG data above, where the enhancement of performance upon introduction of the silica is achieved under dry conditions for the composites formed with dilute concentrations of TEOS, and short permeation times. Higher concentrations of TEOS in the preparation give rise to more blocked channels, as reflected in the lower conductivity values for composites formed without methanol ((0:1:1, PT9 min) and (0:1:1, PT120 min)). This is a confirmation of observed trends, in which bulk conductivity measurements indicate impediments to long-range transport, such as blocked channels (this case), or grain boundaries, as observed in polymers with a propensity to form crystalline regions.[44] Thus, the combination of PFG NMR and impedance spectroscopy allows us to derive a complete picture of the processes governing the function of the materials.

4. Conclusions

Solid-state NMR measurements show that increasing the concentration of TEOS or extending the permeation time for synthesis of Nafion/SiO_2 composites will cause incomplete hydrolysis of the ethyl groups of TEOS. The residual ethyl groups are located on the surface of silica, which blocks the pathway for proton transportation and therefore lowers the proton conductivity. For synthesis with a high concentration of TEOS, a short permeation time needs to be used to avoid the issue of residual ethyl groups present in the membrane composite. Diffusion coefficient data obtained by PFG NMR show that the best Nafion/SiO_2 composite can be obtained from synthesis with a low concentration of TEOS in methanol solution. Although all Nafion/SiO_2 composites in this study give the same or slightly lower diffusion coefficients than pure Nafion in the hydrated state, composites made from low concentrations of TEOS display higher diffusion coefficient than pure Nafion in the dried state. The same trend has been observed from conductivity measurements. This result suggests that Nafion/SiO_2 composites synthesized using the right procedures may hold promise for use as proton exchange membranes working at elevated temperature and reduced relative humidity.

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Supporting Information Available: TGA data for the Nafion/SiO_2 composites. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Alberti, G.; Casciola, M. *Solid State Ionics* **2001**, *145*, 3–16.
(2) Slade, R. C. T.; Hardwick, A.; Dickens, P. G. *Solid State Ionics* **1983**, *9–10*, 1093–1098.
(3) Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B. *J. Membr. Sci.* **2001**, *185*, 73–81.
(4) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Chem. Mater.* **2003**, *15*, 4896–4915.
(5) Costamagna, P.; Yang, C.; Bocarsly, A. B.; Srinivasan, S. *Electrochim. Acta* **2002**, *47*, 1023–1033.
(6) Sumner, M. J.; Harrison, W. L.; Weyers, R. M.; Kim, Y. S.; McGrath, J. E.; Riffle, J. S.; Brink, A.; Brink, M. H. *J. Membr. Sci.* **2004**, *239*, 199–211.
(7) Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. *J. Membr. Sci.* **2000**, *173*, 17–34.
(8) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin, V. *Nature (London)* **2000**, *408*, 447–449.
(9) Yang, C.; Srinivasan, S.; Bocarsly, A. B.; Tulyani, S.; Benziger, J. B. *J. Membr. Sci.* **2004**, *237*, 145–161.
(10) Kim, Y.-T.; Song, M.-K.; Kim, K.-H.; Park, S.-B.; Min, S.-K.; Rhee, H.-W. *Electrochim. Acta* **2004**, *50*, 645–648.
(11) Wang, H.; Holmberg, B. A.; Huang, L.; Wang, Z.; Mitra, A.; Norbeck, J. M.; Yan, Y. *J. Mater. Chem.* **2002**, *12*, 834–837.
(12) Antonucci, P. L.; Arico, A. S.; Creti, P.; Ramunni, E.; Antonucci, V. *Solid State Ionics* **1999**, *125*, 431–437.
(13) Mauritz, K. A.; Payne, J. T. *J. Membr. Sci.* **2000**, *168*, 39–51.

(14) Graf, R.; Demco, D. E.; Hafner, S.; Spiess, H. W. *Solid State Nucl. Magn. Reson.* **1998**, *12*, 139−152.
(15) Hickman, B. S.; Mascal, M.; Titman, J. J.; Wood, I. G. *J. Am. Chem. Soc.* **1999**, *121*, 11486−11490.
(16) Schnell, I.; Spiess, H. W. *J. Magn. Reson.* **2001**, *151*, 153−227.
(17) Brown, S. P.; Schnell, I.; Brand, J. D.; Mullen, K.; Spiess, H. W. *J. Mol. Struct.* **2000**, *521*, 179−195.
(18) Price, W. S. *Concepts Magn. Reson.* **1997**, *9*, 299−336.
(19) Deng, Q.; Moore, R. B.; Mauritz, K. A. *Chem. Mater.* **1995**, *7*, 2259−2268.
(20) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33−72.
(21) Brus, J. *J. Sol-Gel Sci. Technol.* **2002**, *25*, 17−28.
(22) Sumner, J. J.; Creager, S. E.; Ma, J. J.; DesMarteau, D. D. *J. Electrochem. Soc.* **1998**, *145*, 107−110.
(23) Sone, Y.; Ekdunge, P.; Simonsson, D. *J. Electrochem. Soc.* **1996**, *143*, 1254−1259.
(24) Chuang, I. S.; Kinney, D. R.; Maciel, G. E. *J. Am. Chem. Soc.* **1993**, *115*, 8695−8705.
(25) Kinney, D. R.; Chuang, I. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1993**, *115*, 6786−6794.
(26) Liu, C. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 5103−5119.
(27) Bronnimann, C. E.; Zeigler, R. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 2023−2026.
(28) Hwang, S.-J.; Uner, D. O.; King, T. S.; Pruski, M.; Gerstein, B. C. *J. Phys. Chem.* **1995**, *99*, 3697−703.
(29) Trebosc, J.; Wiench, J. W.; Huh, S.; Lin, V. S. Y.; Pruski, M. *J. Am. Chem. Soc.* **2005**, *127*, 3057−3068.
(30) Grunberg, B.; Emmler, T.; Gedat, E.; Shenderovich, I.; Findenegg Gerhard, H.; Limbach, H.-H.; Buntkowsky, G. *Chem.*−*Eur. J.* **2004**, *10*, 5689−5696.
(31) Turov, V. V.; Leboda, R. *Adv. Colloid Interface Sci.* **1999**, *79*, 173−211.
(32) Deng, Q.; Moore, R. B.; Mauritz, K. A. *J. Appl. Polym. Sci.* **1998**, *68*, 747−763.
(33) Babonneau, F.; Thorne, K.; Mackenzie, J. D. *Chem. Mater.* **1989**, *1*, 554−558.
(34) Wu, C. G.; DeGroot, D. C.; Marcy, H. O.; Schindler, J. L.; Kannewurf, C. R.; Liu, Y. J.; Hirpo, W.; Kanatzidis, M. G. *Chem. Mater.* **1996**, *8*, 1992−2004.
(35) Young, S. K.; Jarrett, W. L.; Mauritz, K. A. *Polymer* **2002**, *43*, 2311−2320.
(36) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535−4585.
(37) Ramani, V.; Kunz, H. R.; Fenton, J. M. *J. Membr. Sci.* **2005**, *266*, 110−114.
(38) Boyle, N. G.; McBrierty, V. J.; Douglass, D. C. *Macromolecules* **1983**, *16*, 75−80.
(39) Zawodzinski, T. A., Jr.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. *J. Phys. Chem.* **1991**, *95*, 6040−6044.
(40) Kreuer, K. D. *Chem. Mater.* **1996**, *8*, 610−641.
(41) Ye, G.; Janzen, N.; Goward, G. R. *Macromolecules* **2006**, *39*, 3283−3290.
(42) Atkins, P. *Physical Chemistry*, 6th ed.; Oxford University Press: New York, 1999.
(43) Wang, H.; Holmberg, B. A.; Huang, L.; Wang, Z.; Mitra, A.; Norbeck, J. M.; Yan, Y. *J. Mater. Chem.* **2002**, *12*, 834−837.
(44) Goward, G. R.; Schuster, M. F. H.; Sebastiani, D.; Schnell, I.; Spiess, H. W. *J. Phys. Chem. B* **2003**, *106*, 9322−9334.

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