

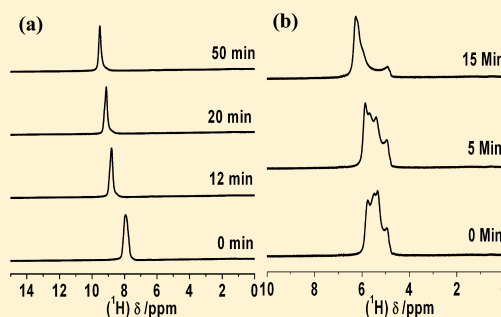
Multinuclear Solid State Nuclear Magnetic Resonance Investigation of Water Penetration in Proton Exchange Membrane Nafion-117 by Mechanical Spinning

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Supporting Information

ABSTRACT: ^1H , ^{17}O , and ^{19}F solid state NMR spectroscopies have been used to investigate water penetration in Nafion-117 under mechanical spinning. It is found that both ^1H and ^{17}O spectra depend on the orientation of the membrane with respect to the magnetic field. The intensities of the side chain ^{19}F spectra depend slightly on the orientation of membrane with respect to the magnetic field, but the backbone ^{19}F spectra do not exhibit orientation dependence. By analyzing the orientation dependent ^1H and ^{17}O spectra and time-resolved ^1H spectra, we show that the water loaded in Nafion-117, under high spinning speed, may penetrate into regions that are normally inaccessible by water. Water penetration is enhanced as the spinning speed is increased or the spinning time is increased. In the meantime, mechanical spinning accelerates water exchange. It is also found that water penetration by mechanical spinning is persistent; i.e., after spinning, water remains in those newly found regions. While water penetration changes the pores and channels in Nafion, ^{19}F spectra indicate that the chemical environments of the polymer backbone do not show change. These results provide new insights about the structure and dynamics of Nafion-117 and related materials. They are relevant to proton exchange membrane aging and offer enlightening points of view on antiaging and modification of this material for better proton conductivity. It is also interesting to view this phenomenon in the perspective of forced nanofiltration.



1. INTRODUCTION

Owing to their environmental friendliness, efficiency, and flexibility, fuel cells as an alternative form of energy sources have been studied vigorously over the past decades. A key component of fuel cells is the proton exchange membrane (PEM). Many types of PEMs have been developed to increase proton conductivity, stability, durability, and robustness, to simplify water management, and to reduce expense. The most used PEM is Nafion,^{1–4} developed by Dupont, mainly owing to its excellent electrochemical and mechanical properties, although its high price has been an issue of concern. Therefore, much effort has been invested to increase its durability so that the expense per unit of energy output can be reduced. This line of research depends on a thorough understanding of the structure and dynamics of Nafion, which, unfortunately, has not been fully achieved yet after many years of extensive investigations. The reason behind this conundrum is because this material is a typical heterogeneous material with multiscale (from 0.1 nm to 1 mm) complexity and involves dynamics over a broad range of time (from fs to years). Its excellent properties are believed to rely on its multiple complexities, although the physical picture remains unclear. New methods and approaches, therefore, are still desired to facilitate a better understanding of this important and complex material.

Hundreds of publications have appeared over the past three decades to characterize this material, to search for alternatives and to improve its performance. Almost the entire arsenal of physical and chemical research has been employed, such as transmission electron microscopy (TEM),⁴ scanning electronic microscopy (SEM),⁵ atomic force microscope (AFM),^{6,7} small-angle X-ray scattering (SAXS),^{8,9} and wide-angle X-ray scattering (WAXS),^{10,11} neutron scattering,^{12,13} cryoporometry,^{14–17} differential scanning calorimetry,¹⁸ complex impedance spectroscopy,^{19,20} infrared spectroscopy (IR),^{21,22} etc. On the basis of these investigations, a number of structure and morphology models for Nafion have been proposed⁴ such as the cluster-network model,¹⁰ rod-like model,^{2,4} sandwich-like model,^{2,4} water-channel model,⁹ etc. However, controversies remain and debate is continuing. On the relationship between its structure and properties of Nafion, solid state NMR^{23–28} has been proved to be a powerful tool for characterizing this complex material with high-speed magic angle spinning (MAS) up to 30 kHz. For example, the highly resolved ^{13}C and ^1H spectra²⁴ provide an atomic level understanding of the mechanical properties of this material and the highly resolved

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^{19}F chemical shifts on the backbone and side chain shed light on the mechanism of its high proton conductivity.²⁶ Two-dimensional ^{13}C – ^{13}C correlation spectra with unprecedented resolution have also been obtained^{25,26,28} which reveal some important findings relevant to the property of this material. More recently, high resolution ^7Li solid state NMR spectra unveil fine structures of nanopores and channels that are closely related to the proton conductivity of the material.²⁹ Furthermore, high resolution NMR microimaging^{30,31} with spatial resolution down to tens of micrometers has been carried out on this material, revealing a number of novel structural and dynamic properties of this material. Theoretical and computational investigations have aided our understanding of this material, including fluid dynamics simulation,^{32–35} theoretical analysis based on equilibrium statistical mechanics,³⁶ Monte Carlo simulation,³⁷ molecular dynamics simulation,^{4,38–46} *ab initio* quantum chemistry computation,^{47,48} etc.

With these studies, much information on the structure, dynamics, electrochemical, and mechanical properties of Nafion has been amassed and a much deeper understanding of this material has been reached.^{4,9,10,40,41} The structure and morphology models^{4,9,10} are helpful for finding approaches to improving its properties or increasing its durability.^{49,50} The proposed proton transport mechanism^{40,41} in this material provides important guidelines for developing alternative, less expensive proton exchange membranes in the future. This material has also been used as a favored model of complex systems and numerous new physical phenomena have been discovered in it, such as the surprising hydration effect on proton transport,⁵¹ anomalous diffusion,⁵² a new mode of collective motion of nanochannels,⁵³ etc.

In this work, we report yet another new phenomenon on Nafion. ^1H spectra acquired using both static samples with different orientations and spinning samples with different levels of hydration show that water can penetrate into normally inaccessible regions in this material after a period of spinning. The effects of spinning speed and time are demonstrated. It is found that water is driven closer to the acidic sites as a result of mechanical spinning, suggesting a new approach to improving the performance of this material. The implication of these findings to Nafion structure, proton transport, degradation, and aging is discussed. These results are also worthwhile if water penetration by mechanical spinning is viewed in terms of forced nanofiltration.

2. MATERIALS AND METHODS

2.1. Membrane Preparation. Nafion-117 membrane with a thickness of 0.18 mm was purchased from DuPont. The membrane was cut along the machine direction into small pieces of size $20 \times 30 \text{ mm}^2$ and boiled in distilled water with 3% H_2O_2 at 80°C for 1 h, then washed in boiling distilled water for 1 h, and finally placed in a dilute solution of sulfuric acid for 1 h. All membranes were dried at temperatures of 60°C for 10 h. In the subsequent experiments, the membranes were then cut uniformly into $2 \times 15 \text{ mm}^2$ size, so that all the membranes were uniaxially oriented. In this paper, we used both “dry” (nearly 30% RH) and hydrated (kept in DD water and nearly 100% RH) samples, denoted “dry” and “hyd”, respectively, in the following sections. We mention that here dry Nafion does not mean there is no water in it, but the number of water molecules is far smaller than that of sulfonate groups.

2.2. NMR Experiments. The NMR studies were carried out on a Varian Unity Inova solid-state 500 MHz NMR spectrometer (magnetic field 11.7 T). To study the orientation dependence effect, the membrane was positioned in the rotor, with different orientations, viz., membrane plane parallel (named as “P”) and perpendicular (named as “V”) to the magic angle direction. Figure 1 shows the schematic diagram of

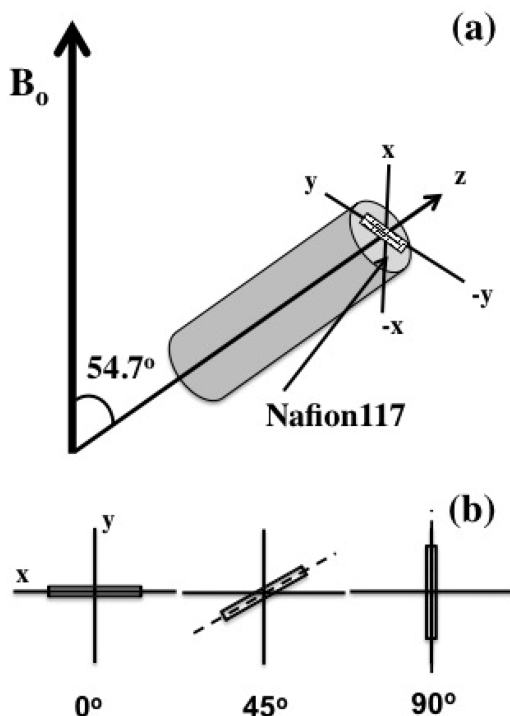


Figure 1. (a) The schematic diagram of the Nafion-117 membrane position in the rotor. (b) The top view of membranes in different orientations. The rotor is spun in different rates in the rf coil, and the membrane is rotated only in the x – y plane. z is the magic angle axis.

membrane positioning in the rotor. ^1H spectra were recorded with static and spinning samples. The spinning speeds used were 3, 6, and 12 kHz. The other acquisition parameters were the following: single pulse excitation with a pulse width, 3 μs ; recycle delay, 1 s; number of transients, 64. Natural abundance ^{17}O NMR spectra of water were recorded with static samples in different orientations using a single pulse of width 3 μs , a recycle delay of 0.2, and 100 000 scans. All experiments were carried out at ambient temperature (25°C).

3. RESULTS AND DISCUSSION

Figure 2 shows static ^1H NMR spectra of dry and hydrated Nafion-117 membranes with three different orientations with respect to the applied magnetic field, B_0 . From the orientation dependent ^1H static spectra, the variations of chemical shift (δ), line width ($\Delta\delta$), and line shape are shown distinctly. The chemical shift (δ) difference between 0 and 90° orientations is larger than 5 ppm for both dry and hydrated samples. Due to a higher mobility of water molecules in the hydrated Nafion-117 membrane, both the overall spectral width and the line width ($\Delta\delta$) of the narrow peak are smaller than that in the dried membrane. For each sample, the largest line width appears at the VP orientation. If many membranes with different orientations are simultaneously placed in the rotor for

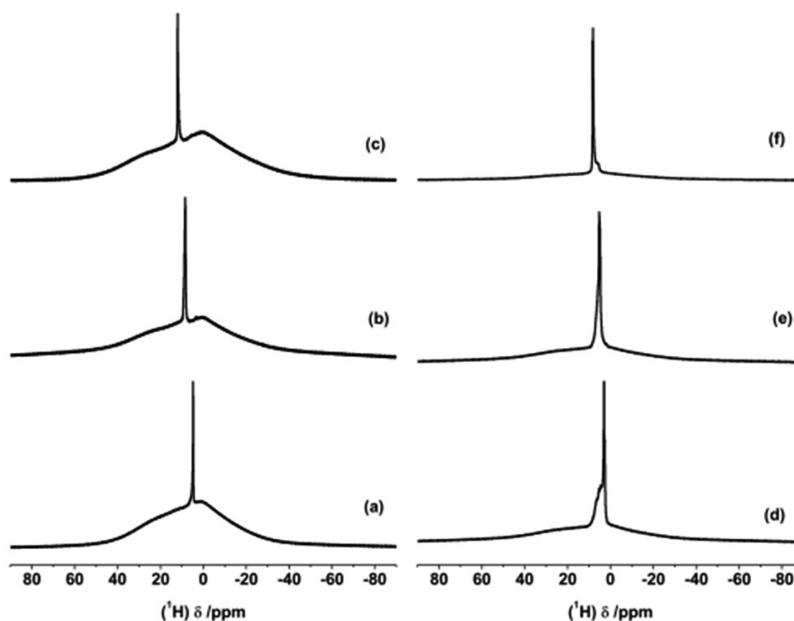


Figure 2. ^1H static NMR spectra of different orientations for Nafion-117 membrane with respect to magnetic field. Dried membranes (left side, a–c); hydrated membranes (right side, d–f). Parts (a) and (d) are aligned in “P” orientation; parts (b) and (e) are aligned in “VP” orientation; parts (c) and (f) are aligned in “V” orientation (for writing convenience, angle “0°” is named as “V”, angle “45°” as “VP”, and angle “90°” as “P”).

recording the spectrum, a broad spectrum would arise, as shown in the Supporting Information where the spectra correspond to various numbers of membranes placed in the rotor, each with a different orientation.

The orientation dependence indicates that the membranes show slight anisotropy of susceptibility. Similar observation on Nafion and other PEM was reported before.^{54,55} However, a full investigation of this phenomenon and particularly its significance to membrane performance have never been conducted, to the best of our knowledge. It would be interesting to find out whether we can take advantage of this phenomenon to tap some new information about the structure, dynamics, and properties of Nafion and, probably, other PEMs. Consequently, we further carried out sample spinning experiments. Shown in Figure 3 are the ^1H MAS NMR spectra of dry

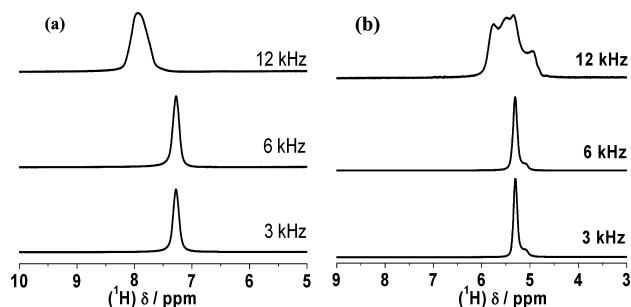


Figure 3. ^1H MAS NMR spectra of dry (a) and hydrated (b) Nafion-117 membranes at different spinning speeds (spinning rates are marked in the figure).

and hydrated Nafion-117 membranes with different spinning rates (3, 6, and 12 kHz). It is found that the center of gravity of the spectra is largely unchanged by spinning speed, but the line width increases significantly with spinning speed. The hydrated sample shows a much larger line width increase than the dry sample. This is clear evidence that water is forced into regions that are inaccessible in a static sample. When more water is

available for hydrated membrane, more regions are invaded. The integral intensity of the spectrum is a good measure of the newly acquired territories of water by the force of mechanical spinning. At 12 kHz for the hydrated sample, for instance, water can reach about 4 times the volume that it can access in a static membrane.

In general, for a given sample whose structure is not affected by spinning, the MAS spectrum shows a narrower line width than the static one because of the time-averaged dipolar interactions between protons. In our case, the internal structure of the samples was affected by sample spinning, so MAS spectra not only show narrower spectra with respect to that of the static samples, but they also produce some anomalies: the spectrum of the hydrated sample may be wider than that of the “dry” one; the spectral line width at shorter spinning time is wider than that at longer spinning times. The second observation rules out the possibility that the spectral change is caused by water evaporation owing to sample spinning.

Because it only takes about 1 min to acquire a ^1H MAS NMR spectrum, we can obtain “time resolved” MAS spectra of Nafion. Figure 4 demonstrates the feasibility of this idea and reveals a striking phenomenon: the chemical shift, line width,

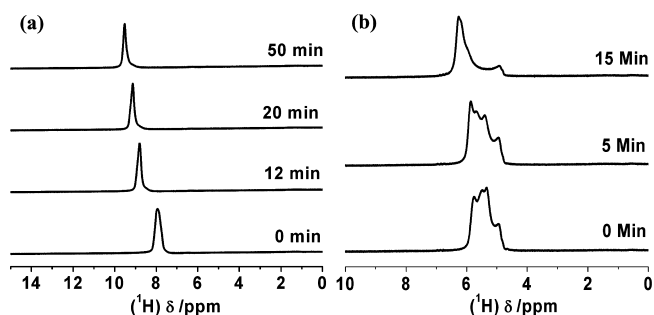


Figure 4. ^1H MAS NMR spectra of dry (a) and hydrated (b) Nafion-117 membranes after they were spun at 12 kHz for different times as indicated in the diagram.

and line shape all depend on time. As the spinning time increases, the chemical shift moves to the left by almost 1 ppm, meaning the shielding on water protons is reduced as a result of spinning. Taking into account the structure of Nafion, we suppose that water is driven closer to the acidic regions in Nafion, probably closer to the sulfonate sites. Also interesting is that the line widths for both samples are smaller at longer spinning times. Comparing this result with Figure 3, we may assume that water is initially driven to many regions, but as spinning time increases, these regions become more and more homogenized by spinning and they are more “acidic”. It implies that water exchange between acidic and other regions is accelerated. This is an interesting finding and worth discussion about its implication to proton transport. It is well-known that proton transport in Nafion proceeds via sulfonate sites.^{4,41} When more water is close to sulfonate sites, proton transport may be enhanced. Therefore, it is possible to use mechanical spinning to modify Nafion or other PEM and increase their proton conductivity.

The longitudinal relaxation times measured at different orientations and different hydration levels on static and spinning samples are summarized in Table 1. It shows that

Table 1. ^1H NMR T_1 Relaxation Times for the Nafion-117 Membrane in Different Orientations

orientation	T_1 (ms)	
	dry	hyd
static-V	33.9	123.8
static-VP	31.2	124.2
static-P	33.3	119.0
3 kHz	40.4	95.3
6 kHz	46.2	91.3
12 kHz	82.0	87.1

T_1 only slightly depends on the orientation, which is easily understood because the anisotropy of the samples is small. However, T_1 varies significantly with hydration level. At higher hydration levels until saturation, T_1 can be multiplied, indicating that the rotational diffusion increases when more and more water is introduced into the membrane so that the majority of water behaves like “free” water. We notice that, as shown in the table, T_1 decreases with spinning speed. Because the possibility of dehydration caused by sample spinning is ruled out, this means that water molecules are driven to less “free” regions. It is well-known that water molecules in Nafion tend to be attracted to sulfonate groups.^{4,40} This provides compelling support to the picture of water penetration. We do not report $T_{1\rho}$ results because $T_{1\rho}$ is much smaller than T_1 and its change is much smaller than that of T_1 .

^{17}O spectra also show anisotropy, as shown in Figure 5. The relatively high resolution spectra were acquired with small-flip angle excitation and short recycle delay time so that tens of thousands of FIDs could be added up to achieve satisfactory sensitivity. Although the time needed for acquiring an ^{17}O spectrum does not allow us to observe the spinning time dependence of chemical shift or line width, the orientation effect is clearly observed for the ^{17}O spectrum at 12 kHz spinning rate, as shown in Figures 5 and 6c. The average ^{17}O chemical shifts of the MAS spectra indicate that water molecules move to more acidic regions, consistent with ^1H results. In addition, because of the much less dipolar interactions between ^{17}O spins or between ^{17}O and ^1H , the

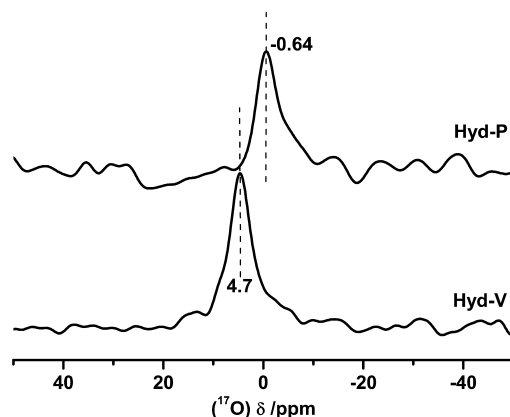


Figure 5. Natural abundance ^{17}O MAS NMR spectra (12 kHz) for hydrated Nafion-117 membranes at different orientations.

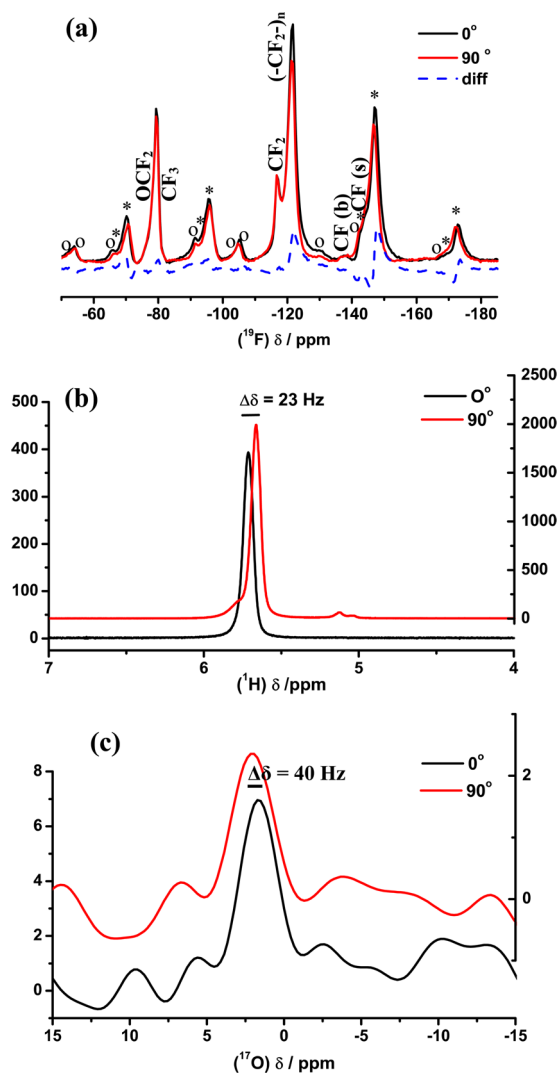


Figure 6. NMR spectra for hydrated Nafion-117 membrane cut into two different directions: (1) machine direction (marked as “0°”, black color) and (2) transverse direction (marked as “90°”, red color) at 12 kHz spun rate. (a) ^{19}F (pulse width 3.5 μs , recycle delay 2 s, and 64 scans); (b) ^1H (pulse width 3 μs , recycle delay 1.5 s, and 64 scans); (c) ^{17}O (pulse width 1.5 μs , recycle delay 150 ms, and 25 000 scans). Side bands of the backbone $(-\text{CF}_2-)_n$ resonances are marked by “*”, and side group resonances are marked by “o”.

susceptibility effect on ^{17}O spectra is much less. Therefore, the ^{17}O result provides an additional argument that the spectra change is not a consequence of susceptibility change.

Because ^{19}F is on the membrane (the backbone and side chains of polymer) and ^1H and ^{17}O are on water molecules, it is interesting to see whether there is a difference between the spectra of different nuclear species and the difference between backbone and side chains. To compare the orientation effect and chemical shift change of the sample spinning speed at 12 kHz with different nuclear species, the hydrated Nafion membrane for different nuclei was cut, both in the machine direction and the transverse direction with identical size and hydration level, and the corresponding NMR spectra are shown in Figure 6. The ^{19}F spectrum is similar to that of Chen and Schmidt-Rohr.²⁶ Actually, our assignment is based on their work. However, our spectrum has a lower resolution because of slower sample spinning speed. In the ^{19}F NMR spectra (shown in Figure 6a), two signals are overlapped at -79 ppm ($-\text{CF}_3$, $-\text{OCF}_2$), and the peak at -117 ppm corresponds to the side chain group ($-\text{CF}_2$), while peaks at about -121 and -119 ppm correspond to the backbone ($-\text{CF}_2$)_n of the membrane. For the two orientations, the intensities of the side chain are almost the same, but the intensities of the backbone are slightly different. Because both chemical shift anisotropy and proton–proton homogeneous dipolar interaction (which is of many-body type interaction involving in principle an infinite number of spins) contribute to the peak intensities, a numerical simulation of the central and side bands is not feasible. However, the spectral characteristics are useful for our purpose. The intensities of spinning side bands are also slightly affected by the orientational effect, as shown by the blue dashed line in Figure 6a. This indicates that an orientational effect also exists for the sidebands of the ^{19}F spectrum in high speed spinning samples. Because both the chemical shifts and intensities of backbone peaks are not affected by sample spinning, this suggests that the chemical environment of the backbone is not changed. The slight change of the sideband intensities, however, suggests that the side chains are affected by spinning. This is consistent with the structural model of hydrated Nafion where water molecules are close to the sulfonate groups. To contrast the difference between ^{19}F from membrane and ^1H and ^{17}O from water, the ^1H and ^{17}O NMR spectra of the same samples with the same spinning speed are illustrated in Figure 6b and c. Chemical shift differences between two membranes are clearly observed (23 Hz for ^1H , 40 Hz for ^{17}O).

On the basis of the above results, we propose a physical picture about this phenomenon: water can be forced to penetrate into exotic regions of Nafion by mechanical spinning; as water invades into new regions, some of the originally isolated pores and channels are opened by the centrifugal force of water. In this perspective, proton transport may be improved because more pathways are available and new “shortcuts” may be formed for conducting protons. A narrower line width at longer spinning time also indicates that water is driven closer to sulfonate sites. This suggests a novel route to improving the performance of Nafion and other PEM, which is under our investigation.

In addition to the positive support of our physical picture from line shape and relaxation times of both ^1H and ^{17}O species, we may consider other possible explanations because, besides the possibility of dehydration we ruled out above, there are other causes that might explain our results. However, these other possibilities can be ruled out: (1) Susceptibility effect:

Susceptibility is the classical average of the quantum mechanical dipolar interactions among the spins. In our samples, the dominant dipolar interaction comes from protons. Susceptibility is certainly changed when the sample is spun because dipolar interaction is modulated by sample spinning. However, because the microscopic origin of susceptibility is dipolar interaction, it has a simple property—the stronger the dipolar interaction, the larger the susceptibility effect. In our results, the “dry” samples have stronger dipolar interactions than hydrated samples. Therefore, “dry” samples would have shown a larger susceptibility effect. However, the changes of line shape and chemical shift are larger for hydrated samples. Moreover, susceptibility is smaller when dipolar interaction is weaker; this means susceptibility is smaller when the spinning speed is higher because dipolar interaction is more averaged out by spinning. Our results show the opposite: the larger line width for hydrated samples at higher speed. More importantly, susceptibility cannot explain the chemical shifts moving upfield with increasing spinning speed. Consequently, susceptibility cannot explain our results. (2) Sample heating: Actually, sample heating would cause a narrower spectrum because, at higher temperature, the anisotropies of both chemical shift and the dipolar interaction are reduced. (3) Changes in relaxation: Relaxation time did change with spinning speed, as shown in Table 1 for both “dry” and hydrated samples. Relaxation change does contribute to the change of line shapes. However, relaxation time cannot explain the upfield shift of the center of gravity of the peaks. Therefore, we conclude that our results of ^1H , ^{17}O , and ^{19}F chemical shift, spectral line shape, and relaxation time can only be explained with the model we proposed.

The results may also provide us with some insights about aging or degradation and proton transport in the membrane. On one hand, water penetration into new regions resembles water invasion resulting from aging. On the other hand, water penetration may affect proton conductivity. On the basis of these observations, we hypothesize that water penetration caused by mechanical spinning can increase the connectedness of the nanopores and nanochannels in Nafion, while aging induced water invasion cannot have this effect and probably does the opposite. We note that the resemblance between water invasion caused by sample spinning and aging is about the outcome rather than about the microscopic cause. In fact, the resemblance is limited to physical degradation caused by, e.g., swelling or thermal effects (temperature gradient, expansion inhomogeneity, etc.), although the chemical shift change owing to degradation is similar to that owing to sample spinning, both becoming larger (more acidic). However, the relaxation time for a spinning hydrated sample decreases with spinning speed, whereas the relaxation time would increase for swollen Nafion because rotational and translational diffusion rates will be increased^{56,57} as a result of the larger pores and channels after swelling.⁵⁸

In the perspective of forced nanofiltration, these results display an intricate effect of the macroscopic centrifugal force generated by mechanical rotation on the microscopic intermolecular interactions. Water molecules driven by mechanical rotation move to new regions, but they, on average, are close to the acidic sites, as indicated by the chemical shift data. It is largely because of the hydrophilic interactions between water and sulfonate groups. On one hand, this suggests that some sulfonate groups are buried in an unspun membrane. On the other hand, this also shows that water

exchange is enhanced by mechanical spinning. It is unclear whether the activation energy is lowered or not, but the effect of mechanical spinning on nanofiltration is undoubtedly a worthwhile subject of research.

The results of this work demonstrate that water, as a probe of the structure and dynamics of Nafion, can be employed in a new manner. To have a better understanding of this phenomenon and tap the potential of applying it to improve the performance of PEM, more work is certainly needed. The future work includes the shortening of experimental time for acquiring ^{17}O spectra, e.g., by using ^{17}O enriched water or polarization transfer, so that the time variation of the chemical shift change can be better resolved. Because ^2D is a spin-1 quadrupole nucleus, it would be interesting to see the spectral and relaxation changes of this spin by using deuterated water. Variable temperature experiments may also provide extra information on the structural and dynamic changes induced by water penetration. AC impedance and probably imaging experiments will be carried out because we have evidence that the spinning induced change is persistent, as shown in Figure 7,

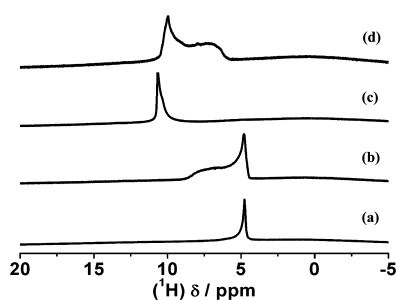


Figure 7. ^1H static spectra of Nafion-117 “dry” membranes in different orientations measured before and after spinning at 12 kHz for a period of 1 h: (a) dry-P without spinning; (b) dry-P after spinning; (c) dry-V without spinning; (d) dry-V with spinning.

where the static spectra acquired after the samples were spun at 12 kHz for a period of 1 h show a very different line shape from that of the samples that were not spun. This opens a new possibility of modifying Nafion to improve its proton conductivity and possibly other characteristics. Undoubtedly, it is worth studying the possible change of the polymer framework in Nafion as a result of water penetration via ^{19}F – ^1H or ^{19}F – ^{13}C correlation spectra, for instance. The translational diffusion coefficient and diffusion tensor of water in Nafion after mechanical spinning may also be measured with magnetic gradient field experiment and microimaging.

4. CONCLUSION

In summary, this work reveals some new behaviors of water in Nafion. Both ^1H and ^{17}O solid state NMR spectra of “dry” and hydrated Nafion membranes show a strong orientation dependence, while the chemical shifts of the ^{19}F spectra do not exhibit orientation dependence, although the sideband intensities of side chains show slight changes. These results are best explained with the picture that water can penetrate into the regions in Nafion-117 that are normally inaccessible to water. Other possibilities such as sample dehydration, susceptibility, thermal effect, and change of relaxation behavior can be safely ruled out as we argued in previous sections. As the spinning time increases or the spinning speed increases, the chemical shift, line width, and line shape change, suggesting that the

longer time the sample is spun at higher speed, the more regions water can penetrate into. Water exchange is found to be accelerated as a result of mechanical spinning. Water penetration caused by mechanical spinning is shown to be persistent. These results demonstrate a new approach of using water to probe the structure and dynamics of Nafion-117 and related materials. From the line shape and chemical shift changes, it is tentative to infer that some originally isolated or blocked nanopores and channels are opened or streamlined. If this picture is correct, then mechanical spinning may become a new and simple method to improve proton transport in proton exchange membrane. This may also be used to slow down the aging of a membrane by reopening the collapsed and blocked nanopores and nanochannels. It implies that a proton exchange membrane may be modified by injecting water at high pressure. The phenomena observed in this work are also interesting in the perspective of forced nanofiltration.

■ ASSOCIATED CONTENT

Supporting Information

The static ^1H NMR spectra of dry membranes in different orientations are shown in Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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