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Nanometer-Scale Water and Proton Diffusion Heterogeneities across Water Channels in Polymer Electrolyte Membranes

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Abstract

Nafion, the most widely used polymer for electrolyte membranes (PEM) in fuel cells, consists of fluorocarbon backbones and acidic groups that, upon hydration, swell to form percolated channels through which water and ions diffuse. While the effects of the channel structures and the acidic groups on water/ion transport have been studied before, the surface chemistry or the spatially heterogeneous diffusivity across water channels has never been shown to directly influence water/ion transport. Using molecular spin probes that selectively partition into heterogeneous regions of PEM and Overhauser dynamic nuclear polarization relaxometry, this study reveals that both water and proton diffusivity are significantly faster near the fluorocarbon and the acidic groups lining the water channels compared to within the water channels. The concept that surface chemistry at the (sub-)nanometer scale dictates water and proton diffusivity invokes a new design principle for PEM.

Keywords

electron paramagnetic resonance spectroscopy; Overhauser dynamic nuclear polarization relaxometry; water and proton dynamics; polymer electrolyte membrane; heterogeneous structure

A polymer electrolyte membrane (PEM) placed between a cathode and an anode in a fuel cell, which is a device that converts chemical energy of fuel into electricity through an electrochemical reaction, should be a good conductor for protons but not for electrons and the molecular constituents of the fuel. Nafion's success as PEM stems from the good ionic conductivity through water channels,^[1] as well as high chemical and mechanical stability for a wide operating temperature range between 50°C and 100°C.^[2] Nafion is composed of a

poly(tetrafluoroethylene) backbone with side arms decorated with sulfonic acid groups, as illustrated in Figure S1 of Supporting Information (SI). Nafion is known, upon hydration, to swell to form percolated channels through which water, protons and ions diffuse.^[3] Nafion's hydrophobic domains are known to have ordered helical fibers with crystallinity similar to that of pure poly(tetrafluoroethylene) at elevated temperatures.^[4] However, the exact structure and ordering of the water channels lined by the sulfonic acid groups is still a subject of controversy. Crucially, the channel dimension was found to increase linearly with the water volume fraction^[3] indicating locally flat structures of the channels,^[5] while scattering patterns are consistent with rod-like shapes for hydrated Nafion membrane at water volume fraction < 50%.^[6–8] The structure and connectivity of the water channels has been thought to play an important role in the proton and water diffusivity through Nafion membranes, although a firm relationship between structure and transport function has not been established. At a hydration level of ~20 water molecules per sulfonic acid in Nafion 117, a proton diffusion constant (D_p) of $\sim 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was estimated by proton conductivity measurements, and a water diffusion constant (D_w) of $\sim 6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ found by pulsed field gradient (PFG) nuclear magnetic resonance (NMR) techniques.^[9–12]

Our study takes a new approach by considering the direct influence of Nafion *surface chemistry* on the local D_w and D_p , a factor not considered in the literature to date. Ultimately, maximizing local dynamics should directly enhance the macroscopic proton, ion and water transport through PEM, which in turn is a key determinant of fuel cell efficiency. We quantify the local D_w and D_p within 5–10 Å of spin probes that are partitioned selectively into different local environments of the swollen Nafion membrane. Such measurements became accessible with the development of Overhauser dynamic nuclear polarization relaxometry (ODNP) for ^1H nuclei of water at 9.8 GHz.^[13] ODNP relies on the induced nuclear spin transitions of the proton-bearing species—here, water and protons—by the excitation of nearby electron spin flips of spin probes, as mediated by magnetic dipolar interaction that decays with r^{-6} of the distance r between the electron spin of the spin probe and the nuclear spin of water. Because the theory and interpretation of ODNP is already well established by many researchers^[13–17], they are described in detail in the SI.

To achieve selective partitioning of spin probes by their different affinities to specific regions or surfaces of the water channels in Nafion, we strategically employed nitroxide derivatives such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, stable free radical), 4-hydroxy-TEMPO, 4-carboxy-TEMPO, and 4-amino-TEMPO as spin probes (chemical formulae shown in Figure S2 of SI). All four nitroxide derivatives are soluble in water, of which 4-hydroxy- and 4-carboxy-TEMPO are thought to predominantly reside in the water phase, while 4-amino-TEMPO has a primary amine group that is positively charged at $\text{pH} < 7$, and should readily bind to the negatively charged sulfonic acid groups. TEMPO, while water soluble, is thought to be the most hydrophobic probe that may approach the fluorocarbon backbone polymer wall. Nafion samples swollen in an aqueous solution containing the nitroxide derivative of choice were prepared, as described in the Experimental Section in SI. The continuous wave (cw) electron paramagnetic resonance (EPR) spectra of these fully hydrated Nafion samples are shown in Figure 1a). They are scaled for the maximum EPR intensity to be 1. The cw EPR spectra of 4-hydroxy- and 4-

carboxy-TEMPO are indistinguishable and represent typical spin probes with significant rotational freedom. The cw EPR spectra for TEMPO yield a much broader linewidth, while a single broad peak is observed for 4-amino-TEMPO. This observation of the coalescence of the three peaks that originate from the hyperfine coupling of the electron spin to the $I = 1$ spin of the ^{14}N nucleus of TEMPO's nitroxide moiety, into one broad peak implies either that the local magnetic field variation is larger than the electron spin- ^{14}N hyperfine coupling and/or that the majority of these nitroxide radicals are within close proximity ($< 10 \text{ \AA}$) to one another. The observation of distinct cw EPR spectra strongly suggests that the different nitroxide derivatives reside in distinctly different local environments within the swollen Nafion membrane.

Figure 1b) shows the EPR spectrum of 4-hydroxy-TEMPO imbibed into Nafion at different hydration levels. For a fully hydrated Nafion, the signal-to-noise ratio was sufficiently high for EPR spectral simulation to quantify the spin label's rotational correlation time. The result of the simulation (performed with Easyspin-4.5.1) shows that the dynamics of 4-hydroxy-TEMPO can be characterized with a single average rotational correlation time, τ_r , of $\sim 1.4 \text{ ns}$, implying that 4-hydroxy-TEMPO is moving rather freely in its local environment. As Nafion is gradually dehydrated, empirically achieved with a set amount of dehydration time at 60°C (see the legend of Figure 1b) for dehydration duration), a new spectral signature appears, indicating less-mobilized 4-hydroxy-TEMPO whose amplitude increases with longer dehydration duration, as marked with an arrow in Figure 1b) at the lower magnetic field region.^[18–21]

The EPR spectrum of TEMPO imbibed in fully hydrated Nafion in Figure 1c) can be simulated with a longer $\tau_r \sim 2.2 \text{ ns}$ compared to that of 4-hydroxy-TEMPO, with the result shown in the inset. As with 4-hydroxy-TEMPO, the broad spectral component becomes stronger as the sample is dehydrated, as marked with an arrow in Figure 1c). All spectra of TEMPO in Nafion, at various hydration levels, are visibly broader than those of 4-hydroxy-TEMPO in Nafion. Such spectral broadening can be due to slower mobility of TEMPO, and/or due to stronger dipolar broadening between proximal electron spins from higher local TEMPO concentration. The contribution of motional vs. electron-electron spin dipolar broadening can be verified by acquiring cw EPR spectra of the same samples at low temperature (Figure S3 in SI), where the contribution from molecular motion is eliminated. The consistently broader spectral features of TEMPO compared to 4-hydroxy-TEMPO in hydrated Nafion frozen at 8.5 K unambiguously identify a dipolar contribution to this broadening, in addition to motional broadening present at ambient temperature. Importantly, the different local spin concentration found in Nafion, hydrated from solutions of initially equal spin probe concentration, shows that there are differential intrinsic driving forces for the absorption of 4-hydroxy-TEMPO vs. TEMPO into the water channels. Both, 4-hydroxy-TEMPO and 4-carboxy-TEMPO experience repulsion between the (partial) negative charge of their hydroxyl or carboxyl oxygen and the sulfonic acid group, while TEMPO does not. We suggest that TEMPO resides predominantly within the water channel core, judging by the only moderately retarded spin probe motion from the EPR spectrum, however with much higher local concentration than 4-hydroxy-TEMPO. It is also possible that a greater fraction

of TEMPO is present at the channel-fluorocarbon interface compared with 4-hydroxy- and 4-carboxy-TEMPO.

Notably, 4-amino-TEMPO appears as a single, exchange-broadened, peak whose shape and peak-to-peak width of 20 Gauss is not altered with different hydration levels, as shown in Figure 1d). From this we conclude that 4-amino-TEMPO is adsorbed to the sulfonic acid groups of Nafion, while the majority of the sulfonic acid groups exposed to the water channel lie within 10 Å proximity to one another.^[3] The observation that the characteristic single-line EPR spectrum of 4-amino-TEMPO in Nafion does not change with dehydration is highly interesting, as it implies the sulfonic acid groups are arranged on a locally flat surface, so that the lateral distance between them is unaltered upon dehydration that induces the water channels to gradually collapse.^[5] Such coalescence of the nitroxide's three hyperfine lines into a single line due to strong dipolar coupling has been observed in poly(vinyl ether) thin film with TEMPO covalently attached to the polymer side chains.^[22] Also, nitroxides in some organic solvents with carbon-coordinating oxygen, such as tetrahydrofuran or ether, have shown a single line^[23–25] EPR spectrum, where the 3 hyperfine peaks are constantly exchanged.

Having identified that different nitroxide derivatives probe different local environments in Nafion, the next question is whether the local water diffusivity spatially varies with the nitroxide's location. This can be assessed by ODNP measurements. In fully hydrated Nafion, the majority of NMR signal at the ¹H Larmor frequency of ~14.8 MHz at 0.35 T comes from the ¹H of water molecules. Constant irradiation with an external microwave at the electron spin Larmor frequency of ~9.8 GHz at an external field of 0.35 T, induces the enhancement of the ¹H NMR signal amplitude through hyperpolarization and shortens the spin lattice relaxation time of ¹H. Such *enhancement* of ¹H NMR signal and *change* in ¹H relaxation times are driven by the dipolar interaction between proximal electron and ¹H spins that induces an electron-¹H transition upon irradiation at ~9.8 GHz, when the relative motion of ¹H-bearing water to the electron spin bearing nitroxide has a correlation time comparable to the inverse electron Larmor frequency. As dipolar coupling decays with r^{-6} , 99% of the nuclear spin transition occurs within 10 Å from the electron spin and the closer spins are more effectively polarized. As described in detail in SI, we compute a coupling constant, ξ , from the ¹H NMR signal enhancement and change in relaxation rates that describes the extent of electron-¹H dipolar relaxation. ξ is a unit-less parameter in which the spin probe concentration dependence is factored out as it is the ratio of relaxivity terms.^[13] As the efficiency of the dipolar electron-¹H coupling depends on the relative dynamics of the ¹H-bearing molecules, here the water and protons, it contains information about the distance between the electron and nuclear spins and their diffusion constants, while the closest electron-¹H distance is unaltered in fully hydrated systems. The quantitative relation between ξ and the water/proton dynamics depends on the specific model employed to describe their motion, but generally ξ increases with faster dynamics, as faster dynamics implies effective transfer of electron spin polarization to ¹H spin. Given the electron Larmor frequency of 9.8 GHz at 0.35 T, ODNP probes the diffusion process at ~100 ps timescale and across 10 Å length scale^[13, 15], and thus provides dynamics information at different time and length scales than PFG NMR.

The measured ξ values, for the nitroxide derivatives residing at different locations in the hydrated Nafion are listed in Table 1. ξ values obtained with 4-hydroxy-TEMPO and TEMPO are similar with $\sim 2 \times 10^{-3}$. This is very small compared to $\sim 57 \times 10^{-3}$ obtained with 4-amino-TEMPO. This significant difference is highly interesting as 4-amino-TEMPO was identified to bind to sulfonic acid groups, while 4-hydroxy-TEMPO/TEMPO survey the freely diffusing water in the water-filled channels. The translational correlation time, τ , computed by employing a force-free hard sphere diffusion model,^[15] is 280 ps (see Eqs. (3) and (4) in SI) for water moving near 4-amino-TEMPO, which is considerably smaller than 2.2 μ s for water near 4-hydroxy-TEMPO or TEMPO. For reference, both values are still significantly smaller than the longitudinal and transverse relaxation times for ^1H of water in swollen Nafion, which range from a few to hundreds of milliseconds.^[26, 27] This reassures that the modulation in ξ is not influenced by the intrinsic nuclear spin relaxation, but by the dynamics of water. From $\tau = 280$ ps, D_w for water molecules near sulfonic acid can be computed (see Eq. (5) in SI) to be $5.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, which is comparable to $D_w \sim 6 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ found by PFG NMR for swollen Nafion with ~ 20 water molecules per sulfonic acid.^[9] In contrast, from $\tau = 2.2 \mu$ s, D_w for water molecules in the central region of the water channel is computed to be $6.8 \times 10^{-14} \text{ m}^2\text{s}^{-1}$, i.e. smaller by four orders of magnitude. Thus, while nearby water is virtually immobile in terms of translational motion, 4-hydroxy-TEMPO is freely rotating with $\tau_r \sim 1.4$ ns as deduced from EPR lineshape analysis. In contrast, 4-amino-TEMPO adsorbed to the sulfonic acid group surveys much faster water diffusivity nearby, which we suggest is due to its vicinity to an extended hydrophobic fluorocarbon surface surrounding the water channels. The fluorocarbon backbone exposes a surface that offers no intrinsic attraction or coordination for water other than through the sulfonic acid and the oxygen of the polymer side chains. Therefore, water molecules adjacent to such surface experience a smaller energy barrier for diffusion, yielding faster surface water diffusivity. The translational water diffusion is likely further enhanced by 4-amino-TEMPO strongly binding to, and thus neutralizing the negative charges of sulfonic acid groups that otherwise are responsible for surface-water attraction. This means 4-amino-TEMPO is on the one hand altering the property of the surface probed, while on the other hand offering the opportunity to probe intrinsic effects of the fluorocarbon on water diffusivity. Although it has been known that water near sulfonic acid groups and in the middle of water channels exchange within < 1 ms time scale^[28], given the ~ 100 ps time scale and 10 Å length scale that ODNP probes, the contributions from the dynamics of water near the surface and in the middle of the water channels do not mix. The exchanged water molecules at the surface that were in the channel core milliseconds earlier now diffuse according to the environment that the surface water experiences. Thus what ODNP measures with 4-amino-TEMPO probes is the dynamics of water near sulfonic acid groups and with 4-hydroxy-TEMPO the dynamics of water in the middle of the water channels.

In order to further elucidate the role of the sulfonic acid groups and the hydrophobic fluorocarbon on water mobility, we chose an experimental design that exploits a non-paramagnetic structural analog of 4-amino-TEMPO, 4-amino-2,2,6,6-tetramethylpiperidine (triacetonediamine, shown in Figure S2 in SI) that similarly occupies the sulfonic acid groups. Pretreated Nafion was sequentially put into a solution of 33 mM triacetonediamine solution and 33 mM 4-hydroxy-TEMPO solution. In this way, 4-hydroxy-TEMPO is

imbibed into the water channel after triacetonediamine had a chance to bind to sulfonic acid groups. When compared with the spectrum without triacetonediamine, the population of the less-mobile component (indicated by an arrow) increases significantly (see Figure 2), yielding similar spectral feature as with TEMPO in partially dehydrated Nafion, as shown in Figure 1c).

The ξ value between 4-hydroxy-TEMPO and water increases from 2×10^{-3} to 6×10^{-3} for Nafion pretreated with triacetonediamine. Given that the amine moiety of triacetonediamine and 4-amino-TEMPO have an equivalent effect on blocking the sulfonic acid groups, it is notable that the ξ value for 4-amino-TEMPO with 57×10^{-3} ($D_w = 5.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) is still dramatically larger than 6×10^{-3} ($D_w = 1.3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$) found for 4-hydroxy-TEMPO in the presence of triacetonediamine. Thus, the 3 – 4 orders of magnitude higher water diffusivity, D_w , measured with 4-amino-TEMPO compared to 4-hydroxy-TEMPO, cannot be simply due to a global effect of charge compensation on water dynamics in Nafion, but must be a genuine surface effect resulting in water diffusivity near the surface to be dramatically faster than within the water channel core. Protons bound to sulfonic acid groups may also contribute to the ^1H NMR signal and ODNP enhancements, although the contribution from water is dominant given their higher population. By changing the solvent from H_2O to D_2O , the population ratio of proton bound to the sulfonic acid group over the hydrogen of water can be dramatically increased, if the lifetime of bound proton is long enough to sustain a significantly high bound proton population near the sulfonic acid groups, although protons will be eventually exchanged with the deuteron of D_2O . The EPR spectra of all nitroxide derivatives in Nafion hydrated with D_2O are indistinguishable from those with H_2O (Figure S4 in SI), implying similar rotational motion and local environments for the nitroxide derivatives in the Nafion membranes hydrated with both solvent isotopes.

Table 1 summarizes the measured ξ for Nafion swollen in D_2O , whereby the ξ values was estimated from ODNP enhancement values measured at the highest microwave power. The ODNP enhancement could not be accurately extrapolated to the maximum value due to inherent limits in signal sensitivity given the very low concentrations of ^1H -bearing species (details can be found in the caption of Figure S5 in the SI). Thus, these reported ξ values systematically represent lower bounds—even so, dramatically larger values are found for 4-amino-TEMPO and 4-hydroxy-TEMPO in Nafion hydrated with D_2O compared to with H_2O . The nominally indistinguishable ξ value found for TEMPO in D_2O and H_2O is likely due to the most severe sensitivity limitation found for ODNP measurements with TEMPO in D_2O . The actual ξ in D_2O will be larger, if extrapolated to higher microwave powers, but was not possible given limitations of low ^1H signal to noise ratio of samples whose ^1H populations are largely exchanged with ^2D , requiring exceedingly long experimental time. Again, the proton diffusion dynamics near sulfonic acid groups, as probed by 4-amino-TEMPO, is dramatically faster than within the water channels, and at the same time faster than water diffusivity. The enhanced proton mobility observed with 4-hydroxy-TEMPO in D_2O compared to in H_2O likely arises from a small fraction of 4-hydroxy-TEMPO probing the protons bound to sulfonic acid groups. The estimated D_p for the proton near the sulfonic acid groups from the $\xi \sim 270 \times 10^{-3}$ measured with 4-amino-TEMPO is $\sim 2.8 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, which is a value comparable to $D_p \sim 2 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ estimated from conductivity

measurements at ~20 water molecules per sulfonic acid^[9] While the absolute proton mobility is smaller than in bulk water, not surprisingly, the proton over water diffusivity measured with 4-amino-TEMPO in Nafion yields $D_p/D_w \sim 5$ comparable to what is known to be $D_p/D_w = \sim 7$ in bulk water with $D_p \sim 1.7 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ ^[29-31] and $D_w \sim 2.4 \times 10^{-9} \text{ m}^2\text{s}^{-1}$.^[31, 32] In contrast, D_p/D_w is only ~ 2 for the central region of the water channels as measured with 4-hydroxy-TEMPO.

Proton and deuteron can exchange fast. Therefore, if H^+ is replaced by D^+ , and incorporated into HDO or H_2O , the measured ξ should have remained equal as in H_2O or slightly decreased, as the mobility of HDO is nearly the same as H_2O ,^[33] while the abundant D_2O and D^+ diffuses 1.2–1.5 times slower than H^+ and H_2O in bulk.^[29, 34, 35] Thus, the observation of an increased ξ for 4-amino-TEMPO and 4-hydroxy-TEMPO in D_2O unequivocally demonstrates that a significant fraction of proton remains bound to the sulfonic acid groups, not readily exchanged by deuteron, and that these bound proton species diffuse > 5 times faster than water. The existence of tightly bound, yet highly mobile protons offer experimental support to the Grotthuss type mechanism for cooperative proton transport in Nafion membranes.^[36] However, it is unclear whether this is the exclusive mechanism, or whether there is also a fraction of proton transport facilitated by water molecules (Vehicle mechanism).

We conclude that distinctly heterogeneous water and proton diffusivity clearly correlates with spatial and chemical heterogeneities of the water channels in Nafion membranes, such as regions comprising near the sulfonic acid groups, the fluorocarbon surface and the water channel core, as pictorially summarized in Figure 3. Our findings suggest that the local water diffusivity, and hence the water transport, can be significantly enhanced by decreasing the charged sulfonic acid group density and accompanied increase of the accessible fluorocarbon surface area. However, reducing the number of sulfonic acid groups that retard the water diffusion can also decrease the water and proton uptake, by reducing the hydrophilic region and electro-osmotic drag, which in turn may affect the membrane stability, as well as decrease proton conductivity.^[37] Crucially, this study reveals why the specific surface chemistry of Nafion membranes should be a key design element, besides channel structure, for optimizing water and proton transport. Furthermore, the experimental access to local and surface water diffusivity with site, domain and phase selectivity will serve as an important toolbox in the study of a large array of heterogeneous materials, where adsorption and transport to and out of active sites are critical to their function, with heterogeneous catalysts and fuel cell PEM being prominent materials of upmost significance.

Experimental Section

General experimental procedures and data analysis methods can be found in the Supporting Information.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Hsu WY, Gierke TD. *J. Membr. Sci.* 1982; 13:307.
2. Mauritz KA, Moore RB. *Chem. Rev.* 2004; 104:4535. [PubMed: 15669162]
3. Gierke TD, Munn GE, Wilson FC. *J. Polym. Sci., Part B: Polym. Phys.* 1981; 19:1687.
4. Starkweather HW Jr. *Macromolecules.* 1982; 15:320.
5. Kreuer K-D, Portale G. *Adv. Funct. Mater.* 2013; 23:5390.
6. Gebel G. *Polymer.* 2000; 41:5829.
7. Rubatat L, Rollet AL, Gebel G, Diat O. *Macromolecules.* 2002; 35:4050.
8. Schmidt-Rohr K, Chen Q. *Nature Mater.* 2008; 7:75. [PubMed: 18066069]
9. Zawodzinski TA Jr, Neeman M, Sillerud LO, Cottesfeld S. *J. Phys. Chem.* 1991; 95:6040.
10. Kreuer K-D. *Chem. Mater.* 2014; 26:361.
11. Li J, Park JK, Moore RB, Madsen LA. *Nat. Mater.* 2011; 10:507. [PubMed: 21685901]
12. Zhao Q, Majsztrik P, Benziger J. *J. Phys. Chem. B.* 2011; 115:2717. [PubMed: 21370837]
13. Hodges MW, Cafiso DS, Polnaszek CF, Lester CC, Bryant RG. *Biophys. J.* 1997; 73:2575. [PubMed: 9370451]
14. Abragam, A. *Principles of Nuclear Magnetism.* London: Oxford University Press; 1961.
15. Freed JH. *J. Chem. Phys.* 1978; 68:4034.
16. Overhauser AW. *Phys. Rev.* 1953; 92:411.
17. Solomon I. *Phys. Rev.* 1955; 99:559.
18. Beier CS, Steinhoff H-J. *Biophys. J.* 2006; 91:2647. [PubMed: 16844740]
19. Freed DM, Horanyi PS, Wiener MC, Cafiso DS. *Biophys. J.* 2010; 99:1604. [PubMed: 20816073]
20. Isas JM, Langen R, Haigler HT, Hubbell WL. *Biochemistry.* 2002; 41:1464. [PubMed: 11814339]
21. Mchaourab HS, Lietzow MA, Hideg K, Hubbell WL. *Biochemistry.* 1996; 35:7692. [PubMed: 8672470]
22. Suguro M, Iwasa S, Kusachi Y, Morioka Y, Nakahara K. *Macromol. Rapid Commun.* 2007; 28:1929.
23. Popp CA, Hyde JS. *J. Magn. Reson.* 1981; 43:249.
24. Ullman EF, Osiecki JH, Boocock DGB, Darcy R. *J. Am. Chem. Soc.* 1972; 94:7049.
25. Xia Y, Li Y, Burts AO, Ottaviani MF, Tirrell DA, Johnson JA, Turro NJ, Grubbs RH. *J. Am. Chem. Soc.* 2011; 133:19953. [PubMed: 22023139]
26. Boyle NG, McBrierty VJ, Douglass DC. *Macromolecules.* 1983; 16:75.
27. Nicotera I, Coppola L, Rossi CO, Youssry M, Ranieri GA. *J. Phys. Chem. B.* 2009; 113:13935. [PubMed: 19791737]
28. Tsushima S, Teranishi K, Hirai S. *Energy.* 2005; 30:235.
29. DeCoursey TE, Cherny VV. *J. Gen. Physiol.* 1997; 109:415. [PubMed: 9101402]
30. Luz ZM, Meiboom S. *J. Am. Chem. Soc.* 1964; 86:4768.
31. Wraight CA. *Biochim. Biophys. Acta.* 2006; 1757:886. [PubMed: 16934216]
32. Wang JH, Robinson CV, Edelman IS. *J. Am. Chem. Soc.* 1953; 75:466.
33. Horita, J.; Cole, DR. *Stable isotope partitioning in aqueous and hydrothermal systems to elevated temperatures.* Amsterdam: Elsevier; 2004.
34. Hardy RC, Cottington RL. *J. Res. Natl. Bur. Stand.* 1949; 42:573.
35. Roberts NK, Northey HL. *J. Chem. Soc. Faraday Trans. I.* 1974; 70:253.

36. Vilčiauskas L, Tuckerman ME, Melchior JP, Bester G, Kreuer K-D. *Solid State Ionics*. 2013; 252:34.
37. Titvinidze G, Wohlfarth A, Kreuer K-D, Schuster M, Meyer WH. *Fuel Cells*. 2014; 14:325.

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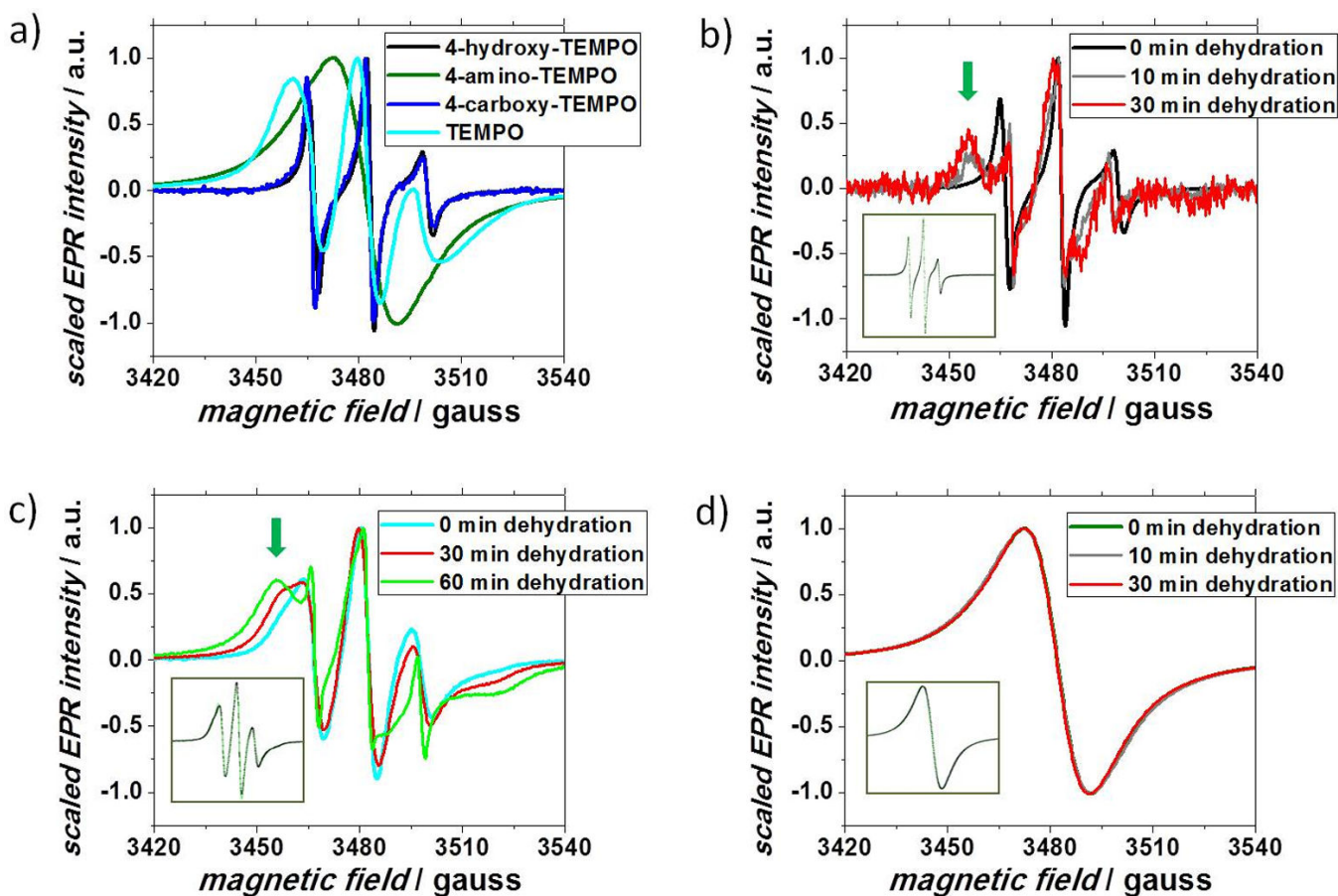


Figure 1.

a) EPR spectra of different nitroxide derivatives incorporated into fully hydrated Nafion as indicated in the legend. EPR spectra of b) 4-hydroxy-TEMPO, c) TEMPO, and d) 4-amino-TEMPO incorporated into Nafion at different hydration levels. The EPR signals from less mobile spectral components, appearing upon dehydration, are indicated by arrows. The EPR spectra for fully hydrated Nafion samples and simulated fit with Easyspin-4.5.1 are shown as the insets in b) – d).

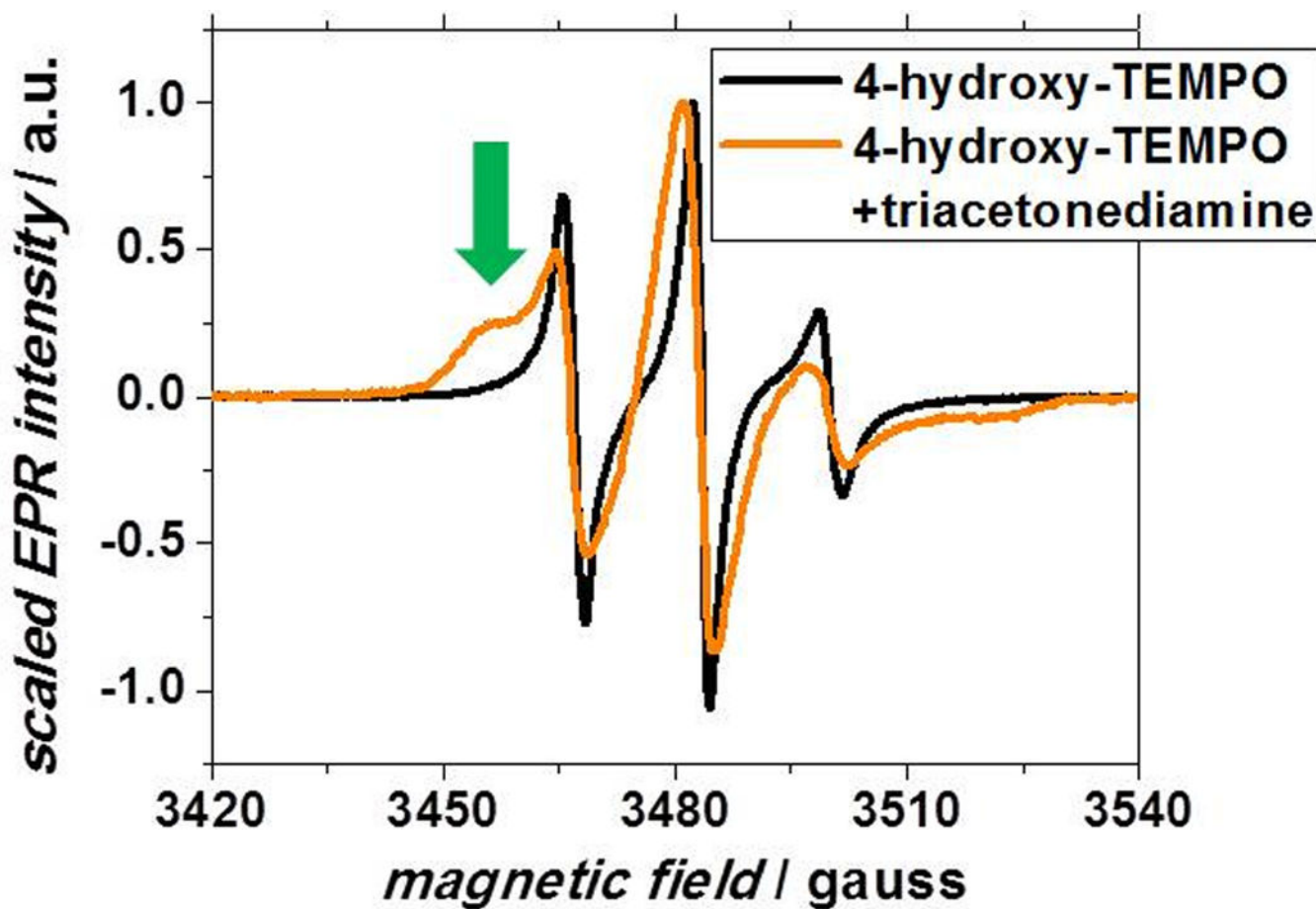


Figure 2. EPR spectra of 4-hydroxy-TEMPO in Nafion with and without pre-imbibing Nafion with 4-amino-2,2,6,6-tetramethylpiperidine triacetonediamine). The intensity of the less mobile component (indicated by an arrow) increases in the presence of triacetonediamine.

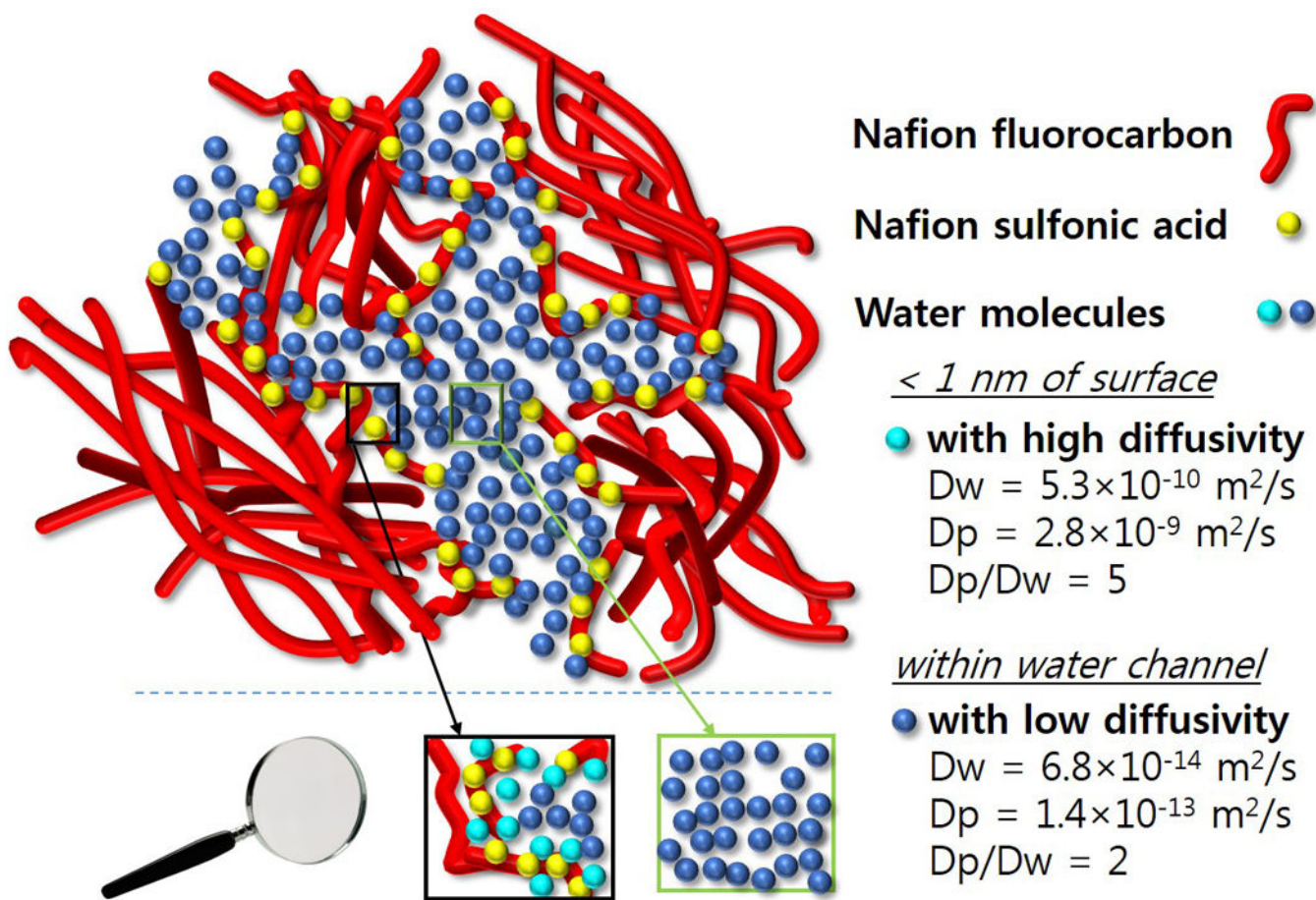


Figure 3.

Pictorial summary of distinctly heterogeneous water and proton diffusivity. D_p and D_w represent the diffusion constants of proton and water, respectively, as measured by ^1H ODNP relaxometry. The D_p and D_w values are found to dramatically vary across the heterogeneous Nafion membrane structure encompassing the water channels, sulfonic acid groups and fluorocarbon-based polymer phase, with significantly higher D_p and D_w values found near the fluorocarbon interface of the water channels.

Table 1Measured coupling constant (ξ) for various nitroxide derivatives in Nafion membranes swollen in H₂O or D₂O

Nitroxide derivatives imbibed in Nafion	ξ for Nafion swollen in H ₂ O ($\times 10^{-3}$)	ξ for Nafion swollen in D ₂ O ^[a] ($\times 10^{-3}$)
4-hydroxy-TEMPO	1.9 \pm 0.2	> 7
TEMPO	1.8 \pm 0.2	> 2
4-amino-TEMPO	57 \pm 0.2	> 270

[a] The coupling constants were estimated as described in the caption for Figure S5 in SI.

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