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Fuel-Cell Membranes

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 (PEMs) in fuel cells, consists of a fluorocarbon backbone and acidic groups that, upon hydration, swell to form percolated channels through which water and ions diffuse. Although 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. By the use of molecular spin probes that are selectively partitioned into heterogeneous regions of the 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 than 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 PEMs.*

A polymer electrolyte membrane (PEM) placed between a cathode and an anode in a fuel cell, which is a device that converts the 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. The success of Nafion as a 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 and 100 °C.[2] Nafion is composed of a poly(tetrafluoroethylene) backbone with side arms decorated with sulfonic acid groups (see Figure S1 in the Supporting Information). Nafion is known, upon hydration, to swell to form percolated channels through which water, protons, and ions diffuse.[3] The hydrophobic domains of Nafion 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 dimensions were found to increase linearly with the water volume fraction,[3] thus indicating locally flat structures of the channels,[5] whereas scattering patterns are consistent with a rodlike shape of the channels in the hydrated Nafion membrane at water volume fractions below 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 about 20 water molecules per sulfonic acid group in Nafion 117, a proton-diffusion constant (D_p) of approximately $2\times10^{-9}\,m^2s^{-1}$ was estimated by proton-conductivity measurements, and a water-diffusion constant (D_w) of approximately $6\times10^{-10}\,m^2s^{-1}$ was found by pulsed field gradient (PFG) nuclear magnetic resonance (NMR) spectroscopic techniques.[9–12]

Our study takes a new approach by considering the direct influence of the surface chemistry of Nafion on the local D_w and D_p values, a factor not considered in previous reported studies. Ultimately, maximization of the local dynamics should directly enhance the macroscopic proton, ion, and water transport through the PEM, which is in turn a key determinant of fuel-cell efficiency. We quantify the local D_w and D_p values 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 ^{1}H nuclei of water at 9.8 GHz.[13] ODNP relies on the induced nuclear spin transitions of the proton-bearing species—in this case, water and protons—by the excitation of nearby electron-spin flips of spin probes, as mediated by a 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. The theory and interpretation of ODNP have already been well established by many researchers[13–17] and are described in detail in the Supporting Information.

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To enable the selective partitioning of spin probes according to their different affinities for specific regions or surfaces of the water channels in Nafion, we strategically employed the nitroxide derivatives 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, stable free radical), 4-hydroxy-TEMPO, 4-carboxy-TEMPO, and 4-amino-TEMPO as spin probes (see Figure S2 for their chemical formulae). All four nitroxide derivatives are soluble in water. 4-Hydroxy- and 4-carboxy-TEMPO are thought to predominantly reside in the water phase, whereas 4-amino-TEMPO has a primary amine group that is positively charged at $\mathrm{pH} < 7$ and should readily bind to the negatively charged sulfonic acid groups. TEMPO, although 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 Supporting Information. 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. These spectra represent typical spin probes with significant rotational freedom. The cw EPR spectrum for TEMPO yielded a much broader line width, whereas a single broad peak was 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 the nitroxide moiety of TEMPO into one broad peak implies 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 Å) 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 EPR spectra of 4-hydroxy-TEMPO taken up by Nafion at different hydration levels. For fully hydrated Nafion, the signal-to-noise ratio was sufficiently high for EPR spectral simulation to quantify the rotational correlation time of the spin label. 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 approximately 1.4 ns, which implies that 4-hydroxy-TEMPO is moving rather freely in its local environment. As Nafion is gradually dehydrated, which is empirically achieved with a set dehydration period at 60 °C (see the legend of Figure 1b for the dehydration duration), a new spectral signature appears that indicates less-mobilized 4-hydroxy-TEMPO. The amplitude of the signal increased as the dehydration duration increased, as marked with an arrow in Figure 1b in the lower-magnetic-field region.[18–21]

The EPR spectrum of TEMPO taken up in fully hydrated Nafion (Figure 1c) could be simulated with a longer average rotational correlation time ($\tau_r \approx 2.2$ ns) than that of 4-hydroxy-TEMPO (see 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 to stronger dipolar broadening between proximal electron spins at a higher local TEMPO concentration. We verified the contribution of motional broadening versus electron–electron spin dipolar broadening by acquiring cw EPR spectra of the same samples at low temperature (see

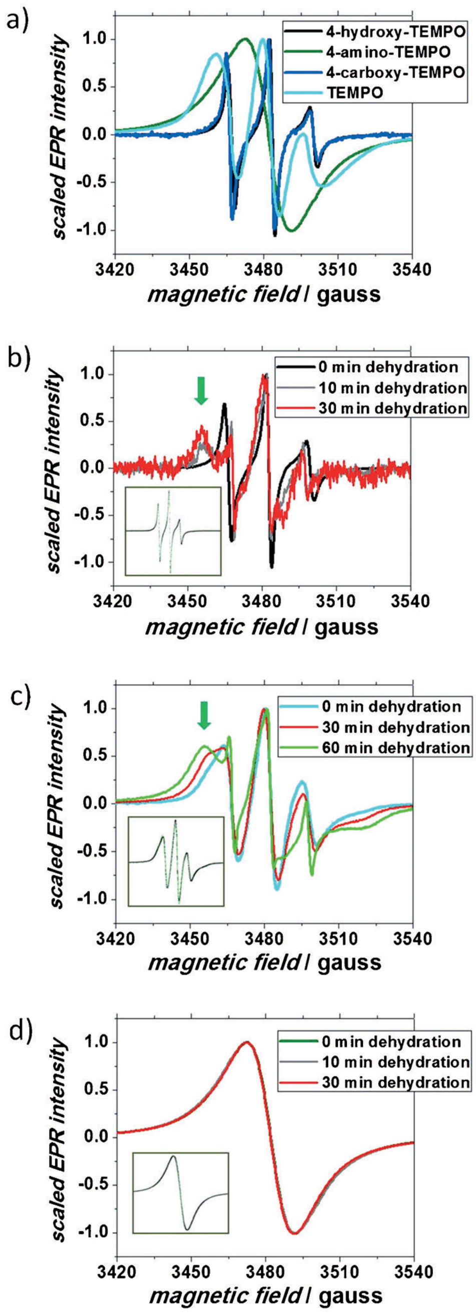

Figure 1. a) EPR spectra of different nitroxide derivatives incorporated into fully hydrated Nafion. b–d) EPR spectra of b) 4-hydroxy-TEMPO, c) TEMPO, and d) 4-amino-TEMPO incorporated into Nafion at different hydration levels. The EPR signals from less mobile spectral components, which appear upon dehydration, are indicated by arrows. The EPR spectra simulated with Easyspin 4.5.1 for fully hydrated Nafion samples are shown as the insets in (b–d).

Figure S3); under these conditions, the contribution from molecular motion is eliminated. The consistently broader spectral features of TEMPO as compared to 4-hydroxy-TEMPO in hydrated Nafion frozen at 8.5 K unambiguously indicated 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 concentrations, shows that there are differential intrinsic driving forces for the absorption of 4-hydroxy-TEMPO versus TEMPO into the water channels. Both 4-hydroxy-TEMPO and 4-carboxy-TEMPO experience repulsion between the (partial) negative charge of their hydroxy or carboxy group and the sulfonic acid group, whereas TEMPO does not. We suggest that TEMPO resides predominantly within the water-channel core on the basis of the only moderately retarded spin-probe motion from the EPR spectrum, but with a much higher local concentration than that of 4-hydroxy-TEMPO. It is also possible that a greater fraction of TEMPO is present at the channel–fluorocarbon interface as 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 G is not altered by the different hydration levels (Figure 1 d). From this result we conclude that 4-amino-TEMPO is adsorbed to the sulfonic acid groups of Nafion, whereas the majority of the sulfonic acid groups exposed to the water channel lie within a proximity of 10 Å 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 that the sulfonic acid groups are closely arranged on a locally flat surface, where the lateral distance between them is unaltered upon dehydration, as the water channels gradually collapse.[5] Such coalescence of the three hyperfine lines of the nitroxide into a single line as a result of strong dipolar coupling has been observed in a poly(vinyl ether) thin film with TEMPO covalently attached to the polymer side chains.[22] Also, nitroxides in some organic solvents with carbon-bonded oxygen atoms, such as tetrahydrofuran or ether, have been found to have a single-line[23–25] EPR spectrum in which the three hyperfine peaks are constantly exchanged.

Having identified that different nitroxide derivatives probe different local environments in Nafion, we addressed the next question of whether the local water diffusivity varies spatially with the location of the nitroxide. This behavior can be assessed by ODNP measurements. In fully hydrated Nafion, the majority of the NMR signal at the ^{1}H Larmor frequency of about 14.8 MHz at 0.35 T comes from the ^{1}H signal of water molecules. Constant irradiation with an external microwave source at the electron-spin Larmor frequency of about 9.8 GHz at an external field of 0.35 T induces the enhancement of the ^{1}H NMR signal amplitude through hyperpolarization and shortens the ^{1}H spin–lattice relaxation time. The enhancement of the ^{1}H NMR signal and change in the ^{1}H relaxation time are driven by the dipolar interaction between proximal electron and ^{1}H spins. This dipolar interaction induces an electron–^{1}H transition upon irradiation at about 9.8 GHz when the relative motion of ^{1}H-bearing water with respect 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 the Supporting Information, we computed a coupling constant, ξ, from the ^{1}H NMR signal enhancement and change in relaxation rates that describes the extent of electron–^{1}H dipolar relaxation. The constant ξ is a unitless 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–^{1}H coupling depends on the relative dynamics of the ^{1}H-bearing molecules, in this case water and protons, it contains information about the distance between the electron and nuclear spins and their diffusion constants, whereas the closest electron–^{1}H distance is unaltered in fully hydrated systems. The quantitative relationship 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 the ^{1}H spin. Given the electron Larmor frequency of 9.8 GHz at 0.35 T, ODNP probes the diffusion process on a timescale of approximately 100 ps and across a 10 Å length scale[13,15] and thus provides dynamics information at different time and length scales to those of PFG NMR spectroscopy.

The measured ξ values for the nitroxide derivatives residing at different locations in the hydrated Nafion are listed in Table 1. The values obtained with 4-hydroxy-TEMPO and TEMPO are similar, at $\xi \approx 2\times10^{-3}$, and are very small relative to the value of $\xi \approx 57\times10^{-3}$ obtained for 4-amino-TEMPO. This significant difference is highly interesting, as 4-amino-TEMPO was identified to bind to sulfonic acid groups, whereas 4-hydroxy-TEMPO/TEMPO freely survey the water-filled channels. Importantly, the concentrations of TEMPO and 4-amino-TEMPO in the Nafion membranes are comparable. The translational correlation time, τ, computed by employing a force-free hard-sphere diffusion model[15] is 280 ps (see equations (3) and (4) in the Supporting Information) for water moving near 4-amino-TEMPO, and is thus considerably smaller than the 2.2 μs found for water near 4-hydroxy-TEMPO or TEMPO. For reference, both values are still significantly smaller than the longitudinal and transverse relaxation times for ^{1}H signal of

Table 1: Measured coupling constant (ξ) for various nitroxide derivatives in Nafion membranes swollen in H_2O or D_2O.

Nitroxide derivative imbibed in Nafion	ξ for Nafion swollen in H_2O ($\times10^{-3}$)	ξ for Nafion swollen in D_2O ($\times10^{-3}$)[a]
4-hydroxy-TEMPO	1.9 ± 0.2	> 7
TEMPO	1.8 ± 0.2	> 2
4-amino-TEMPO	57 ± 0.2	> 270

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

water in swollen Nafion, which range from a few to hundreds of milliseconds.[26,27] This result confirms that the modulation in the ξ value is not influenced by the intrinsic nuclear-spin relaxation, but by the dynamics of water.

From $\tau = 280$ ps, the D_w value for water molecules near sulfonic acid was computed to be $5.3 \times 10^{-10}\,\mathrm{m^2 s^{-1}}$ (see equation (5) in the Supporting Information), which is comparable to $D_w \approx 6 \times 10^{-10}\,\mathrm{m^2 s^{-1}}$ found by PFG NMR spectroscopy for swollen Nafion with approximately 20 water molecules per sulfonic acid group.[9] In contrast, from $\tau = 2.2\,\mu s$, the D_w value for water molecules in the central region of the water channel was computed to be $6.8 \times 10^{-14}\,\mathrm{m^2 s^{-1}}$, that is, it is smaller by four orders of magnitude. Thus, whereas nearby water is virtually immobile in terms of translational motion, 4-hydroxy-TEMPO freely rotates with $\tau_r \approx 1.4$ ns, as deduced by EPR lineshape analysis. In contrast, 4-amino-TEMPO adsorbed to a sulfonic acid group surveys local water, which diffuses much faster, possibly as a result of its vicinity to the 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 groups and the oxygen atom of the polymer side chains. Therefore, water molecules adjacent to such a surface experience a smaller energy barrier to diffusion, thus yielding faster surface-water diffusivity. It is likely that the translational water diffusion is further enhanced by the ability of 4-amino-TEMPO to strongly bind to, and thus neutralize, the negative charges of the sulfonic acid groups, which are otherwise responsible for surface–water attraction. Thus, 4-amino-TEMPO on the one hand alters the properties of the surface probed, while on the other hand offering the opportunity to probe intrinsic effects of the fluorocarbon on water diffusivity. Although it is known that water molecules near sulfonic acid groups and in the middle of water channels exchange on a time scale of less than 1 ms,[28] given the time scale of about 100 ps and the length scale of 10 Å for the 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—molecules that were in the channel core milliseconds earlier—now diffuse according to the environment that the surface water experiences. Thus, with 4-amino-TEMPO probes, ODNP measures the dynamics of water near sulfonic acid groups, and with 4-hydroxy-TEMPO, ODNP measures the dynamics of water in the middle of the water channels.

To further elucidate the roles of the sulfonic acid groups and the hydrophobic fluorocarbon on water mobility, we chose an experimental design that exploits a nonparamagnetic structural analogue of 4-amino-TEMPO, 4-amino-2,2,6,6-tetramethylpiperidine (triacetonediamine; see Figure S2), which similarly occupies the sulfonic acid groups. Pretreated Nafion was sequentially put into a 33 mM solution of triacetonediamine and a 33 mM solution of 4-hydroxy-TEMPO. In this way, 4-hydroxy-TEMPO was imbibed into the water channel after triacetonediamine had a chance to bind to sulfonic acid groups. When compared with the sample without triacetonediamine, the population of the less-mobile component (indicated by an arrow) increased significantly (Figure 2), thus yielding similar spectral features to those observed with TEMPO in partially dehydrated Nafion (see Figure 1 c).

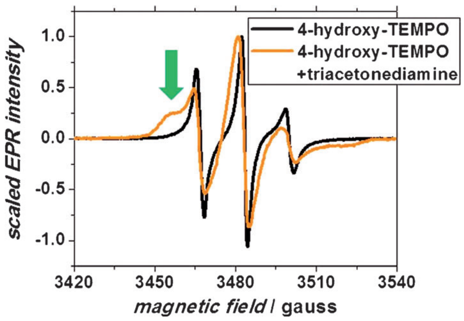

Figure 2. EPR spectra of 4-hydroxy-TEMPO in Nafion with and without the pretreatment of Nafion with 4-amino-2,2,6,6-tetramethylpiperidine (triacetonediamine). The intensity of the less mobile component (indicated by an arrow) increases in the presence of triacetonediamine.

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

Table 1 summarizes the measured ξ values for Nafion swollen in D_2O, whereby the ξ values were estimated from ODNP-enhancement values measured at the highest microwave power. The ODNP enhancement could not be accurately extrapolated to the maximum value owing to inherent limits in signal sensitivity given the very low concentrations of ^{1}H-bearing species (see the caption of Figure S5 for details). Thus, these reported ξ values systematically represent lower bounds. Even so, dramatically larger values were found for 4-

amino-TEMPO and 4-hydroxy-TEMPO in Nafion hydrated with D_2O than in Nafion hydrated with H_2O. The nominally indistinguishable ξ value found for TEMPO in D_2O and H_2O is probably due to the most severe sensitivity limitation found for ODNP measurements with TEMPO in D_2O. The actual ξ value in D_2O will be larger if extrapolated to higher microwave powers; however, such extrapolation is not possible owing to the limitation of the low ^1H signal-to-noise ratios of samples whose ^1H populations are largely exchanged with ^2D, thus requiring an 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 as compared to that in H_2O probably arises from a small fraction of 4-hydroxy-TEMPO probing the protons bound to sulfonic acid groups. The D_p value estimated for protons near sulfonic acid groups from the value of $\xi \approx 270\times10^{-3}$ measured with 4-amino-TEMPO is approximately $2.8\times10^{-9}\,m^2s^{-1}$, which is a value comparable to that of $D_p \approx 2\times10^{-9}\,m^2s^{-1}$ estimated from conductivity measurements at a hydration level of approximately 20 water molecules per sulfonic acid group.[9] Although the absolute proton mobility is smaller than in bulk water, the diffusivity ratio of proton and water measured with 4-amino-TEMPO in Nafion was $D_p/D_w \approx 5$, which, not surprisingly, is comparable to the known value of $D_p/D_w \approx 7$ in bulk water with $D_p \approx 1.7\times10^{-8}\,m^2s^{-1}$[29–31] and $D_w \approx 2.4\times10^{-9}\,m^2s^{-1}$.[31,32] In contrast, D_p/D_w is only about 2 for the central region of the water channels, as measured with 4-hydroxy-TEMPO.

Protons and deuterons can exchange fast. Therefore, if H^+ is replaced with D^+ and incorporated into HDO or H_2O, the measured ξ value should remain equal to that in H_2O or decrease slightly, as the mobility of HDO is nearly the same as that of H_2O,[33] whereas abundant D_2O and D^+ diffuse 1.2–1.5 times slower than H_2O and H^+ in the bulk.[29,34,35] Thus, the observation of an increased ξ value for 4-amino-TEMPO and 4-hydroxy-TEMPO in D_2O demonstrates that a significant fraction of the protons remain bound to the sulfonic acid groups and are not readily exchanged by deuterons, and that these bound proton species diffuse more than 5 times faster than water. Readily exchanging and rapidly diffusing protons with residence times of about 100 ps or longer can also yield the observed result if there is a strong isotope effect of a much stronger hydrogen-bonding affinity for the charged sulfonic acid site than that of the deuteron; however, the discussion of such possibilities is outside the scope of the current literature. The existence of tightly bound, yet highly mobile protons offers experimental support to the Grotthuss-type mechanism for cooperative proton transport in Nafion membranes.[36] However, it is unclear whether this mechanism operates exclusively, 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 near the sulfonic acid groups, the fluorocarbon surface, and the water-channel core (Figure 3). Our findings suggest that the local water diffusivity, and hence water transport, can be significantly enhanced by the accessible fluorocarbon surface area. Crucially, this study reveals why the specific surface chemistry of Nafion membranes should be a key design element, besides the channel structure, for optimizing water and proton transport. Furthermore, experimental access to local and surface water diffusivity with site, domain, and phase selectivity will be important for the study of a large array of heterogeneous materials, for which adsorption and transport to and out of active sites are critical to their function, whereby heterogeneous catalysts and fuel-cell PEMs are prominent materials of upmost significance.

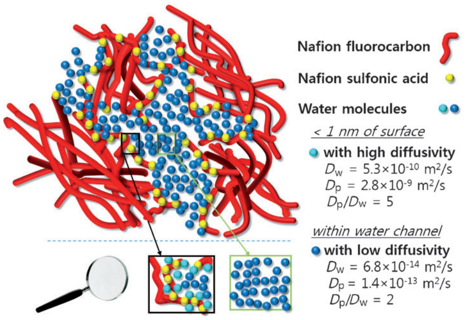

Figure 3. Schematic summary of the distinctly heterogeneous water and proton diffusivity. D_p and D_w are the diffusion constants of proton and water, respectively, as measured by ^1H ODNP relaxometry. The D_p and D_w values were found to vary dramatically across the heterogeneous Nafion membrane structure encompassing water channels, sulfonic acid groups, and a fluorocarbon-based polymer phase, with significantly higher D_p and D_w values found near the fluorocarbon interface of the water channels.

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