Proton Transport Mechanism of Perfluorosulfonic Acid Membranes

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Supporting Information

ABSTRACT: An understanding of proton transport within perfluorosulfonic acid (PFSA) membranes is crucial to improve the efficiency of proton exchange membrane fuel cells. Using reactive molecular dynamics simulations, we have examined proton transport in two PFSA materials, Hyflon and the 3M membrane, at three different hydration levels. The interaction between the sulfonate group of the polymer side chains and the hydrated protons was found to have only a small influence on the proton transport dynamics. Instead, proton swapping between sulfonate groups is the primary transport mechanism for the proton transport within the pore. The larger water clusters and more flexible side chain of the 3M membrane allows for an enhancement of this swapping mechanism compared to Hyflon. Membranes that can enhance this mechanism may result in greater proton conductivity.

1. INTRODUCTION

As concern over global energy use and climate change has grown, interest in alternative energy technologies has increased. Hydrogen is proposed as an alternative fuel of the future, and proton exchange membrane (PEM) fuel cells are a proven technology, with potential applications as wide-ranging as cellphones to automobiles.1 The key component of these fuel cells is the polymer membrane between the anode and cathode, which keeps the gaseous fuels separate yet allows protons to pass through and complete the electrical circuit. The standard membrane material for many years has been Nafion, which has a polytetrafluoroethylene (PTFE) backbone for mechanical strength and a sulfonated side chain, which provides hydrophilic regions in the polymer and allows proton transport upon hydration. The separation between the hydrophobic and hydrophilic phases is key to the operation of the membrane, yet details about their arrangement within the membrane are poorly understood because of the amorphous nature of the morphology. Experiments such as small-angle X-ray scattering (SAXS) probe some length scales important within the membrane, while conductivity measurements provide a bulk measurement of charge transport.2 However, to provide a molecular-scale view of the important properties of the system, computational modeling is necessary.

One important factor that affects the conductivity of perfluorosulfonic acid (PFSA) membranes is the length of the side chain. The industry standard Nafion has been surpassed in performance by two shorter side chain polymers, Hyflon and 3M.3,4 Both of these materials show higher crystallinity, and their resultant improved mechanical properties allow membranes containing a higher proportion of charged side chains to be synthesized before the membrane dissolves in water.

The mass of polymer per mole of charged side chains is defined as the equivalent weight (EW), so a higher proportion of charged side chains corresponds to a low EW. This potential for using a lower EW alone is important, but even for a given EW, Hyflon shows slightly higher conductivity than Nafion under the operating conditions of the membrane.3 It is unclear whether this increase is due to the higher crystallinity of Hyflon affecting transport on a large scale or due to the shorter side chain affecting proton mobility within the hydrophilic region. Molecular dynamics (MD) simulations are ideal for investigating the latter case; however, consensus has not yet been reached on the extent of the effect of side chain length. Intuitively, one would imagine that the shorter side chain of Hyflon would result in the hydrated protons located away from the hydrophobic/hydrophilic interface being less attracted by the electrostatic potential of the sulfonate groups, as they will extend less into the hydrophilic pore. The protons would thus be able to move faster in the bulklike water away from the interface. This idea is supported by the nonreactive MD simulations of Karo et al., which have shown protons in Hyflon move further from the interface than Nafion.5 Conversely, however, it has been argued that the side chain of Nafion is bent to such a degree that it extends into the hydrophilic pore almost as little as that of Hyflon, and hence, very little difference between proton motion within a given pore geometry should be observed.6 Simulations studying solutions of the side chain pendants of Hyflon, Nafion, and Aciplex (a membrane of similar length to 3M) agree with this and show that Nafion pendants are bent into interesting
“hydrosphere” complexes of hydroniums and water.\(^7\) They also show the Aciplex pendants are more rigid than Nafion due to the lack of an ether oxygen in the side chain. Our recent reactive MD work comparing the PFSA membrane materials 3M and Nafion shows a more complicated picture, as Nafion is likely to be in either the bent conformation or the straight conformation.\(^8\) This latter study also highlights how flexible these longer side chain membranes can be, thus exploring a wide range of angles relative to the hydrophobic surface.

In the light of these facts, a detailed look at the differences between short- and long-chain PFSA materials is important. Since determining the mechanisms affecting proton transport in PFSA membranes is the goal of this research, using reactive MD to examine this problem is crucial, since no molecular dynamics simulations of Hyflon have included the effects of the Grothuss mechanism.\(^5,9\) The Grothuss mechanism is the process by which hydrated excess protons are able to transport in water much faster than other similar ions, as the excess proton transports through the hydrogen bond network of water by exchanging covalent and hydrogen bonds. Although ab initio MD would capture this process, it would be infeasible to perform simulations of the time and length scale needed to examine proton transport in these PFSA systems. A particular version of reactive MD, the multistate empirical valence bond (MS-EVB) method, was developed to capture the bond breaking and forming in the Grothuss mechanism in an accurate and highly efficient manner.\(^12\) It has previously been used to reveal interesting properties of proton transport in PFSA materials.\(^13,16−19\)

**2. SIMULATION DETAILS**

Three different sets of PFSA systems were simulated, in order to explore the effects of side chain length and equivalent weight (EW). Two different side chain lengths of PFSA were used, corresponding to the 3M membrane and Hyflon. Of these membrane types, Hyflon was simulated with two different EWs. The EWs were chosen as that for Hyflon used in the conductivity measurements of ref 3, 850 g/mol and 1100 g/mol. The EW for 3M was chosen as that used in ref 8, 825 g/mol. The simple cubic simulation boxes were built using the Monte Carlo chain-growing algorithm developed by Knox and Voth\(^20\) for 4 chains of polymers containing 10 monomers each (the chains are shown in Figure 1). Three different hydration levels of 4, 9, and 12 were simulated for each polymer system. Six simulation boxes were created for each simulation setup in order to increase sampling. All simulations were performed using the LAMMPS\(^21\) MD package, with our in-house module used for the MS-EVB calculations.\(^22\) The systems were first relaxed using constant NPT dynamics at 400 K and 1 atm for 6 ns. The systems were then cooled down to 300 K at the same pressure for another 6 ns with constant NPT dynamics. This was followed by 12 ns of simulation in the constant NVT ensemble. Equilibration of the system using the reactive self-consistent iterative MS-EVB\(^23\) (SCI-MS-EVB) potential was then performed for 200 ps in the constant NVT ensemble. Each system was then run for 1 ns each using constant NVE dynamics.

The DREIDING force field\(^24\) was used for the polymer model parameters with some changes outlined below in order to simulate the system as accurately as possible. All charges for the polymers were obtained from a Mulliken population analysis\(^25\) on the optimized structures at the DFT B3LYP 6-31G* level in Gaussian 09\(^26\) and are shown in Figure 1. All bond and angle force constants were taken from ref 27, while the equilibrium bond lengths and angles were taken from our DFT-optimized structures. For all polymers, the dihedral parameters for the CF backbone were taken from ref 27, and the standard Lorentz–Berthelot mixing rules were used for all interactions except for one important interaction between the sulfonate oxygens and the hydronium hydrogens, which we will discuss further below. The 3M simulations previously performed in the group\(^8\) were also
reanalyzed to investigate the effect of this change in the LJ interactions.

For the hydronium and water parameters, the MS-EVB3 model, which was parametrized for use with the SPC/Fw water model, was used. The self-consistent iterative MS-EVB (SCI-MS-EVB) algorithm was applied to perform the simulations of the multiple excess protons in these systems. As our goal is to capture the details of the hydrophilic pores of these systems, we have attempted to match the attraction of the hydronium ion to the sulfonate group as closely as possible to ab initio data. It has been highlighted recently that using simple mixing rules for the LJ interactions between oppositely charged ions can result in inaccurate results. Comparing the radial distribution functions (RDFs) obtained in previous works, from both reactive and nonreactive MD, to ab initio MD studies of PFSA fragments, it is clear that the mixing rules result in overbinding of the hydronium ion to the sulfonate group. Previous work in our group corrected the overbinding of the hydronium ion to the sulfonate group. The parametrization of this interaction using experimental RDFs was a much simpler task, as there were only three elements and three types of molecules, compared to the complex PFSA systems we are examining here. We therefore chose to use the bisulfate ion to parametrize the altered LJ interaction, as there are ab initio MD RDFs to directly compare to our systems and to minimize the complicating factors inherent in PFSA simulations, such as polymer morphology. This approach is superior to simply using LJ mixing rules. We used the charges, bonds, and angle terms from a molecular mechanics force-field developed for sulfuric acid and bisulfate simulations to reproduce the shape of the bisulfate ion correctly, but using the DREIDING LJ parameters, as these are used for the PFSA simulations. We also used the same water and hydronium water models as for the PFSA simulations.

Two different acid concentrations were examined in ref 34, corresponding to 0.84 and 10.1 M. We constructed these exactly as outlined in that paper and equilibrated for 2 ns using constant NVT dynamics. To begin with we ran two SCI-MS-EVB simulations, one with standard mixing rules and the other with an interaction between the bisulfate oxygen and the hydronium hydrogen derived from earlier aqueous HCl simulations. We show in Figure 2 the results obtained for the two different concentrations studied. The improvement gained between using the standard mixing rules and our more properly parametrized interaction is clearly seen, especially in the first solvation shell peak. In order to explore the sensitivity of these RDFs to various permutations of the ε and σ LJ values, we ran a set of 25 simulations, having 5 values of ε and 5 values of σ. As can be seen in the Supporting Information, the RDFs were most sensitive to the choice of σ. We found that slightly lower values of σ worked better for the low-concentration system, while slightly lower ε worked better for the high-concentration system. However, in order to maintain transferability in the MS-EVB model, and since they worked so well, we opted to keep the same parameters as used for the HCl simulations.

3. RESULTS AND DISCUSSION

Radial Distribution Functions. As the largest difference between the simulations performed in this study and those performed previously in our group is the addition of the parametrized interaction between hydronium and sulfonate, we first examined the effect this has on the RDFs. The simulations performed for this study use a hydration level of 4 Å, slightly lower than the hydration level of 14 used in the previous study on 3M, the latter being labeled “old” 3M in this work. Since we are using reactive molecular dynamics via the SCI-MS-EVB algorithm, the hydrated excess proton charge defect is delocalized over several waters, so it is important to characterize where the center of this delocalized charge resides. We define the center of excess charge (CEC) as a sum over all of the positions of these waters, weighted by their relative probabilities, or

\[ r_{CEC} = \sum_{i=1}^{N} c_i^2 r_i^{COC} \]

where \( r_i^{COC} \) is the position vector of the center of charge of the hydronium ion of the ith MS-EVB state, \( c_i^2 \) is the probability weight for the ith state, and \( N \) is the number of states. The RDFs in Figure 3 between the sulfur of the sulfonate group and the excess proton CEC all show a broad peak between 3 and 6.5 Å, which, as we will see, comprise the first two solvation shells around the sulfonate group. These two solvation shells can be most clearly seen at hydration levels 9, where there is a large peak for the first solvation shell at 3.8–4.2 Å, with a shoulder representing the second solvation shell. The major notable effect from the change in LJ parameters is a clear decrease in intensity for the first solvation shell of 3M and Hyfion, compared to the previous old simulations of 3M using the standard LJ mixing rules outlined in the previous section. This difference is seen most significantly at higher hydration levels. At hydration level 9, the excess proton CEC with the new parameters is equally likely to be on the first or second solvation shell water oxygen, while at hydration level 12 the second solvation shell is somewhat preferred.

To get further insight into the behavior of the excess protons, we chose to define the water with the highest MS-EVB weight as the classical hydronium species. The (new) 3M and Hyfion simulations show generally similar behavior. However, we can see the impact the change in LJ parameters has on the attraction of the excess proton to the sulfonate by the large reduction of the first peak of the 3M RDF for the old parameters relative to the new (Figure 4). The importance of
the solvent-separated hydronium ion compared to the contact hydronium is again seen, especially at the higher hydration levels.

With this qualitative change in the preferred solvation of the excess protons in relation to the sulfonates, one would expect a large change in the transport of the excess protons through the system; however, there is in fact a very small change.

**Self-Diffusion Constants.** In Figure 5 is shown the excess proton self-diffusion constants for the various simulations we have performed, obtained using the mean squared displacements (MSDs) and the Einstein relation, using the procedure outlined in ref 8. As has been seen in all previous experimental work, the diffusion constants are very similar at hydration level 5, below the percolation threshold of PFSA membranes, with higher hydration levels showing increasing proton diffusion.

By examining the Hyflon results, we can see that the lower EW system shows greater diffusion than the higher EW system. This is the trend observed in both experiment and simulation studies; however, a larger difference between the equivalent weights is observed in experiments, as can be seen in Figure 5.3,11 The 3M membrane shows larger diffusivity than either Hyflon system at hydration level 9, whereas the diffusivity at hydration level 12 is very similar to low EW Hyflon. It is difficult to compare the experimental diffusion of 3M and Hyflon, as there is no published diffusion data for 3M. However, the trend seen here is what one would expect from experiment, since 3M shows greater conductivity than Hyflon, but the expected magnitude of the difference is again not captured.5,4

The above simulation results and their comparison to experiment are important, as they show that there are likely some larger-scale differences, such as morphology or crystallinity, in these polymers that affect the global proton transport, which cannot be captured in these molecular simulations at the tens of nanometers length-scale. However, the information gleaned from reactive MD simulations is still important, first because any shorter length-scale improvements to proton transport should still contribute to overall conductivity gains. Second, dynamical information from these simulations can bridge into mesoscale simulation methods for PFSA5,36 which are able to access the scales necessary to investigate the overall proton conductivity.

The most interesting and important result, however, is that we see essentially no change in the proton diffusion constant of 3M when compared with the previous study8 that had different LJ interactions between the sulfonate and hydronium and a very different solvation structure, as seen in Figures 2−4. Given the previously suggested model5 for proton diffusion within the pores, involving fast protons in bulklike water at the pore center versus slow, trapped protons beside the sulfonates, one would expect an increase in the proton diffusion when the effective attraction between the sulfonate and proton was decreased. Such behavior is not seen in our reactive MD simulations that include the full physics of Grotthuss proton hopping (as opposed to the nonreactive hydronium MD model of ref 5). This surprising result has motivated a search for a different model for proton transport in PFSA pores as outlined below.

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**Figure 3.** RDFs between the center of excess charge (CEC) of the hydrated excess proton and the sulfur of the sulfonate group compared among our four sets of simulations at hydration levels 5, 9, and 12.

**Figure 4.** RDFs between the hydronium oxygen and the sulfur of the sulfonate group compared among our four sets of simulations at hydration levels 5, 9, and 12.

**Figure 5.** Self-diffusion constants for the CEC shown in units of $10^{-7}$ cm$^2$/s, plotted as a function of hydration level. Experimental data were obtained from ref 3 and included in panel a. Panel b shows simulation results alone for ease of comparison.
clearer why the change in LJ parameters that had such a large associated with multiple sulfonates. With this result it becomes least one sulfonate group, and a large majority of time is spent spend at least 95% of the simulation time associated with at group, it is seen that even at high hydration levels the protons f), which includes two solvation shells around a sulfonate (Figure 7).

Examining the data for the higher cutoff radius (Figure 6a–c) and the simulations with the new LJ interactions, one can see from the percentage of time the proton is associated with zero sulfonates that the protons spend 60–70% of their time outside the first solvation shell of any sulfonate group at hydration levels 9 and 12, whereas they only spend 35% of their time unassociated at hydration level 5. Comparing the data for the 3M system with the old and new LJ parameters, we can see that the old, more attractive parameters result in the proton tending to be associated with more sulfonates as well as being outside the first solvation shell of any sulfonate group less often (Figure 7).

Examining the data for the higher cutoff radius (Figure 6d–f), which includes two solvation shells around a sulfonate group, it is seen that even at high hydration levels the protons spend at least 95% of the simulation time associated with at least one sulfonate group, and a large majority of time is spent associated with multiple sulfonates. With this result it becomes clearer why the change in LJ parameters that had such a large effect on the RDFs between sulfonates and protons does not have as large an effect on the diffusion constant of the excess protons. The higher mobility of a proton in the bulk-water-like center of the pore, which suggested that a lower interaction between sulfonate and proton would result in a greater diffusion constant, is in fact largely irrelevant, because the attraction is still strong enough that the proton will spend very little time in the bulk-water-like region. With this information that the excess protons are residing very close to sulfonates at almost all times, we can formulate a new proton diffusion mechanism based on how the proton transfers between individual sulfonate groups. It is important to note at this juncture that our ability to simulate the full Grotthuss hopping physics of excess protons in PFSA hydrophilic pores at nanometer length-scales and nanoseconds time-scales has been crucial for obtaining these insights.

Figure 6. The probability of a hydrated proton being within a given cutoff radius of N sulfonates. Panels a–c correspond to a 4.2 Å cutoff (first solvation shell). Panels d–f correspond to a 6.5 Å cutoff (second solvation shell).

**Association of Protons with Sulfonates.** Before looking at the influence of sulfonate groups on the dynamics, it is useful to see whether the excess protons spend more time associated with or away from sulfonate groups. We can define a radius around the sulfur of the sulfonate group, which, upon entering, the proton is defined as being associated. Two natural choices of radii are suggested by the RDFs of the hydronium oxygen (Figure 4) with the sulfonate sulfur, one for the first solvation shell (4.2 Å), and the other for the second solvation shell (6.5 Å).

On examining the data for the lower cutoff radius (Figure 6a–c) and the simulations with the new LJ interactions, one can see from the percentage of time the proton is associated with zero sulfonates that the protons spend 60–70% of their time outside the first solvation shell of any sulfonate group at hydration levels 9 and 12, whereas they only spend 35% of their time unassociated at hydration level 5. Comparing the data for the 3M system with the old and new LJ parameters, we can see that the old, more attractive parameters result in the proton tending to be associated with more sulfonates as well as being outside the first solvation shell of any sulfonate group less often (Figure 7).

Figure 7. Snapshot of a 3M membrane simulation at hydration level 9. Hydroniums (hydrated excess protons) are shown in green, sulfonate and side chain carbons in yellow, waters in red, and backbone carbons are visualized as a white surface. The center hydronium resides within the first or second solvation shell of three sulfonate groups.

**Residence Times.** One way to examine the extent of the trapping of protons near sulfonates is to look at the residence times. Similar to other work looking at ion residence times,37–39 we determined the time ($t_\text{res}$) when a hydrated excess proton charge defect enters a predetermined cutoff radius around a sulfonate group and then measured the time ($t$) until the proton leaves this cutoff radius. The cutoff was chosen to be 4.5 Å from a sulfur of a sulfonate group, to select the first solvation shell around a sulfonate group, as can be seen in the RDFs. One subtlety that needs to be taken into account is the rapid “rattling” of a proton in and out of the cutoff region, which biases the residence time to very small values without giving any insight into the processes of interest. To compensate for this, a time ($\tau$) is chosen so that any instances where the proton leaves the cutoff region but returns in a time shorter than $\tau$ is counted as if the proton had remained within the cutoff region. We found a value of $\tau$ used in previous work of 2 ps to be sufficient.37–39 The average residence time was determined for each system, and the results are plotted in Figure 8.
The trends in the residence times coincide well with the trends in the diffusion constants for the simulations using the new parameters, with the systems with the highest diffusion constants showing the shortest average residence times. Interestingly, the 3M system with the old LJ interactions shows systematically higher residence times than all of the other systems. This would be expected from simply examining the sulfur–CEC RDF; however, it does not explain why the diffusion constants have remained essentially unchanged.

In addition to looking at how long an excess proton is associated with a sulfonate on average, it is instructive to look at the number of sulfonates the excess protons visits during the 1 ns trajectory. A proton is defined to have visited a sulfonate if it comes within 4.5 Å of the sulfur of the sulfonate, again chosen to select the first solvation shell around a sulfonate group. Figure 9 shows these results, and the trends again map well to the diffusion constants. The systems having faster diffusing protons visit more sulfonates than those having slower diffusing protons. This correlation raises an interesting question of cause and effect. Are the protons simply diffusing faster throughout the whole pore, hence spending less time in the vicinity of a sulfonate and visiting more sulfonates, or are the protons moving more efficiently between sulfonate groups in certain systems, increasing the overall diffusion rate of the excess proton? In essence, it is thus important to determine whether the increase in proton diffusion is occurring away from the sulfonate first solvation shell or if certain systems are more efficient at transferring protons between the sulfonates.

### Diffusion Decomposition

In order to determine which of these two mechanisms of diffusion are increasing most in the anomalous 3M hydration level 9 system, from the SCI-MS-EVB simulations we can decompose the total displacements of the protons into two separate components, similar to the decomposition into hopping and vehicular motions in our previous work. The two proton diffusion components we will choose for this examination are the associated and free components, where a proton is defined as being associated if it is within 4.5 Å of a sulfur of any sulfonate group and free if it is more than 4.5 Å from all sulfonate groups. Thus, we assign a displacement over a 100 fs interval as an associated displacement if the proton is associated at the end of the 100 fs and as a free displacement if the proton is free at the end of the 100 fs. We also try to minimize the effect of rattling by including any times a proton returns to the same sulfonate group within 2 ps (the same τ as defined in the residence calculation) as a contribution to the associated displacement. We can write the CEC displacement vector as

$$\mathbf{r}_{\text{CEC}}(t) - \mathbf{r}_{\text{CEC}}(0) = \Delta \mathbf{r}_{\text{CEC}}(t) = \Delta \mathbf{r}_{\text{assoc}}(t) + \Delta \mathbf{r}_{\text{free}}(t)$$

(2)

$$\langle |\Delta \mathbf{r}_{\text{CEC}}(t)|^2 \rangle = \langle |\Delta \mathbf{r}_{\text{assoc}}(t)|^2 \rangle + \langle |\Delta \mathbf{r}_{\text{free}}(t)|^2 \rangle$$

(3)

where $\Delta \mathbf{r}_{\text{assoc}}(t)$ and $\Delta \mathbf{r}_{\text{free}}(t)$ are the “associated” and “free” components of the excess proton CEC displacement, and $\langle |\Delta \mathbf{r}_{\text{CEC}}(t)|^2 \rangle$, $\langle |\Delta \mathbf{r}_{\text{assoc}}(t)|^2 \rangle$, and $\langle |\Delta \mathbf{r}_{\text{free}}(t)|^2 \rangle$ are the MSDs of the total, associated, and free displacements, respectively.

Upon inspection of the decomposed MSDs (reproduced in the Supporting Information), it became clear that the two forms of excess proton motion are highly anticorrelated, i.e., the last term in eq 3 is negative, which has been seen in other decompositions of the CEC MSD. This is not particularly surprising when the method of decomposition is examined. If we consider the sulfur of a sulfonate group as the origin of a frame of reference, we can easily visualize the vectors of the displacements when the proton crosses the cutoff radius. A proton leaving the cutoff region in some direction $\mathbf{n}$ will return to the cutoff region with a direction of approximately $-\mathbf{n}$. We can also see from the way that we decompose the trajectory that leaving the cutoff region will be assigned to the free component, whereas entering the cutoff region will be assigned to the associated component. Thus, when an excess proton exits and re-enters the cutoff region (or vice versa), the free and associated MSDs will generally become anticorrelated. However, we can easily get a measure of this anticorrelation by rearranging eq 3 above as

$$\langle \Delta \mathbf{r}_{\text{assoc}}(t) | \Delta \mathbf{r}_{\text{free}}(t) \rangle = \frac{1}{2} \left[ \langle |\Delta \mathbf{r}_{\text{CEC}}(t)|^2 \rangle - \langle |\Delta \mathbf{r}_{\text{assoc}}(t)|^2 \rangle - \langle |\Delta \mathbf{r}_{\text{free}}(t)|^2 \rangle \right]$$

(4)

We can add this anticorrelation to each component of the MSD

$$\langle |\Delta \mathbf{r}_{\text{CEC}}(t)|^2 \rangle = \left[ \langle |\Delta \mathbf{r}_{\text{assoc}}(t)|^2 \rangle + \langle |\Delta \mathbf{r}_{\text{free}}(t)|^2 \rangle \right]$$

$$+ \left[ \langle |\Delta \mathbf{r}_{\text{free}}(t)|^2 \rangle + \langle |\Delta \mathbf{r}_{\text{free}}(t)|^2 \rangle \right]$$

$$= \text{shiftedMSD}_{\text{assoc}} + \text{shiftedMSD}_{\text{free}}$$

(5)

to get more reasonable looking graphs, shown in Figure 10. The error bars are relatively significant because of the large values of the MSDs before the removal of anticorrelation;

Figure 9. Probability distribution of $N_n$, the numbers of sulfonate groups visited by protons in each system over the 1 ns trajectories at hydration levels 5, 9, and 12.
The free components of hydration levels 9 and 12, respectively.

total MSD. Panels a and c correspond to the associated components of RDFs between the sulfurs of the sulfonate group compared among our four sets of simulations at hydration levels 5, 9, and 12.

however, we are still able to gain useful insight into the dynamic behavior of the diffusing protons in these two regions.

The immediately surprising thing to note in these graphs is the large MSD of the sulfonate-associated protons. The protons within the first solvation shell of the sulfonate group contribute a non-negligible amount to the overall diffusion, arguing against the more simplistic argument that the fast moving protons within the center of the PFSA pore are the most important for increasing overall diffusion rates. It has been assumed previously that the excess proton must hop between sulfonate groups via intermediate water molecules and that the proton leaving the electrostatic attraction of the sulfonate is the rate-limiting step.10 The systems with the most notable increase in the diffusion of associated protons are the two 3M systems at hydration level 9. Since these two systems are the ones that have shown particularly high diffusion, we can investigate a mechanism for the increase in diffusion by involving the proton moving between sulfonate-associated locations within the pore.

Sulfonate–Sulfonate Interactions. The large diffusivity of the excess protons that are within the first solvation shell of the sulfonate group indicates that the protons are not merely trapped in this electrostatic potential well but are free to move throughout the system. One mechanism for this to occur would be if two sulfonates were to meet, a proton could easily pass between them as their respective potential wells overlap. We have already shown in Figure 6 that there is a high probability of protons being in the second solvation shell of more than one sulfonate group and a non-negligible probability of protons being in the first solvation shell of more than one sulfonate, so this diffusion mechanism is clearly plausible. We can also examine the sulfur–sulfur RDFs shown in Figure 11, and using our knowledge of the solvation shells of the sulfonate groups obtained from Figures 3 and 4, we can get a sense of how well these shells overlap. Given that the first solvation shell is within 4.2 Å of the sulfonate and the second solvation shell extends 2.3 Å past that to 6.5 Å, we can associate the first peak in the S–S RDF to the range where there is one or two solvation shells between the sulfurs, since the peak extends roughly in the expected 4.2–8.4 Å range.

We can associate the second RDF peak in Figure 11 to the range where there are two or three solvation shells, again since the peak extends roughly in the expected 8.4–10.7 Å range. Therefore, there is good overlap between both first solvation shells of adjacent sulfonate groups, which, by looking at the sulfur–CEC RDFs in Figure 3, means that the excess proton would see a flat free energy surface over which to move between adjacent sulfonate groups, regardless of the interaction between the sulfonate and excess proton.

Side Chain Conformations. Figure 12 shows the conformations of the side chains averaged over the simulations. We have defined two vectors, one from the carbon at the joint of the backbone (which we call “C1”) to the sulfur, which is shown as the red arrow in Figure 12a, and the other, shown as the green arrow in Figure 12a, which is a vector whose direction points from C1 to the ether oxygen. We use the quantity $d$, which is the length of the red arrow, as a measure of the extension of the side chain into the hydrophilic pore. We define $\theta$ to be the (unsigned) angle between the green and the red arrows, and it describes how “bent” the side chain is.

Figure 12b–d shows the probability distributions of these quantities for hydration level 9 (essentially identical results were obtained for the other hydration levels). In all three membrane systems we can see two clearly separated areas of stability, each separated by a $d$ value of about 1 Å, corresponding to different amounts of extension of the side chain. The change in EW has a negligible influence on the conformations of the side chains explored. The major noticeable difference between Hyflon and 3M is the amount of extension of the side chain. 3M extends 2.5 Å further than Hyflon, which is not surprising given 3M’s greater side chain length. Also noticeable is the greater flexibility of the 3M side chain. The more bent conformation of the 3M side chain explores a larger range of angles than the bent conformation of Hyflon, while the more extended conformation of 3M explores only a slightly smaller range of angles than Hyflon. The longer extension and greater angular movement means that the 3M side chain can more easily move around within the hydrophilic pore, promoting the passing of protons back and forth between sulfonate groups and thereby yielding a higher proton diffusion constant than Hyflon.

The behavior described above is not sufficient to completely explain all of the increase in diffusion, since, for example, we can see that at hydration level 5 there is a large degree of structuring of the sulfurs yet there is no large increase in

Figure 10. Plots of the shifted associated and free components of the total MSD. Panels a and c correspond to the associated components of hydration levels 9 and 12, respectively. Panels b and d correspond to the free components of hydration levels 9 and 12, respectively.

Figure 11. RDFs between the sulfurs of the sulfonate group compared among our four sets of simulations at hydration levels 5, 9, and 12.
diffusion. To explain this we will examine larger length-scale properties of the system in the next section.

Water Clustering. In addition to the examination of local proton motion, it is important to characterize how protons are able to move through the system as a whole. The connectivity of the hydrophilic pores in PFSA membranes is important to allow protons to migrate from one side of the membrane to the other and thus not become trapped in isolated pores. We can quantify the connectivity of the hydrophilic pores by determining the sizes of all the water clusters in the MD simulation. We first define a cutoff radius of 3.5 Å around a water or hydronium in order to capture all waters or hydroniums within its first solvation shell. We then search the same radius around each of these waters to find the waters in their first solvation shells and continue until we have found all the clusters in the system. Shown in Figure 13 are the cumulative probability distributions for the sizes of the clusters in each system. Many small clusters exist at hydration level 5, typical of a nonpercolating system, whereas almost all waters are in one large cluster at hydration level 12, which will allow for more facile proton transport throughout the whole system.

At all three hydration levels there is a clear trend of greater connectivity as one goes from high EW Hyflon to low EW Hyflon to 3M. Larger cluster sizes correspond to higher diffusivity of the proton for hydration levels 9 and 12. Larger clusters make little difference at hydration level 5, highlighting the need for a 3D network for the proton to move through, seen in the comparison of lamellar and cylinder morphologies to the relatively confined cluster network model in previous work. The larger cluster sizes of 3M compared to Hyflon can lead to an increase in diffusion not only due to the larger range of movement for the proton through these larger clusters but also due to an increase in the sulfonate-mediated proton "passing" mechanism described earlier. The increase in the sulfonate passing mechanism is caused by the decrease in hydrophobic/hydrophilic surface area of these large clusters. It was seen in ref 11 that larger cluster sizes contributed to lower interfacial surface area, which makes sense given that, all other things being equal, the combination of two clusters will have lower surface area than the individual clusters. This lower surface area means that the side chains that reside on the interface will be forced closer together, promoting solvation shell overlap and proton passing.
4. CONCLUSIONS

This study has demonstrated that changes in the EW and chain length of PFSA polymers result in changes in local proton diffusion; however, these changes do not fully explain the changes in observed experimental conductivity. The local proton diffusion results do capture the trend of increased diffusion in 3M compared to Hyflon, and also capture the trend of increased diffusion upon reduction of Hyflon EW. However, the magnitudes of these changes are not as large as seen experimentally. This suggests there is a larger-scale difference in the morphologies of these two membranes that also influences the proton conduction, such as the crystallinity of the membrane.41

An important insight that has come from this study is that there was essentially no effect on the rate of diffusion of the proton upon reducing the attraction of a hydrated proton to the sulfonate group. Since the protons were very heavily attracted to the sulfonate groups in our previous study, one would have expected the more loosely ion-paired protons in this study to move faster in the membrane. As this is not the case, it became clear that “detachment” from the sulfonate group is not the primary bottleneck for proton diffusion within the hydrophilic pore. We instead find that the hydrated proton is essentially always within two solvation shells of a sulfonate group and that the solvation shells of neighboring sulfonate groups overlap substantially, rendering the depth of the potential well surrounding the individual sulfonates less important. The excess proton does not have to climb out of the potential well to move from a sulfonate group; it can more easily transfer to an adjacent, overlapping potential well, if and when there is an adjacent sulfonate group nearby. In the case of the 3M membrane, this transferring of the hydrated protons between sulfonates is even more efficient, as the flexibility of the longer 3M side chain allows for better contact between neighboring side chains, increasing the net proton diffusion.

Overall, the present results suggest that any way of improving the exchange of protons between side chains of ionomer systems such as these PFSA membranes can help increase the diffusivity of protons within the hydrophilic pores. In this study, we find that the greater flexibility of the 3M side chain compared to that of Hyflon, as well as its better-connected hydrophilic pores, contributes to its increase in proton diffusivity. Again, we point out that these results do not take into account the large-scale membrane morphological differences, and hence, we expect these to have an influence on the overall conductivity as well. Previous work in our group10 has already shown that sulfonate—sulfonate spacing is strongly affected by the morphology and geometry of the hydrophilic pore and that this has an effect on proton transport, which further highlights the need for investigation into the effect of morphology on proton transport. Future research in our group will focus on connecting the molecular-level reactive MD simulations to mesoscopic scale modeling in order to provide a more complete multiscale picture of proton transport in PFSA membranes.

ASSOCIATED CONTENT

Supporting Information
Equilibrium bond lengths and angles used in this study, obtained from ab initio calculations, and a figure showing the anticorrelation of decomposed associated and free MSDs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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REFERENCES


