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Molecular Dynamics Simulations of Substrate Hydrophilicity and Confinement Effects in Capped Nafion Films

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ABSTRACT

Nafion nanocomposites for energy related applications are being used extensively due to the attractive properties like enhanced water retention, low unwanted crossover of electrolytes and high proton conductivity. We present the results of the molecular-dynamics modelling of Nafion films confined between two walls (substrates) of different polymer-wall interaction strength and of different separation distance to model Nafion nanocomposites. Our goal is to provide insights into the effects of varying hydrophilicity and volume fraction of fillers/nanoparticles on the internal structure and water transport inside the Nafion membrane. The sulfur-sulfur radial distribution function first peak distance and the sulfur-oxygen (water) coordination number in the first hydration shell were negligibly affected by the wall (substrate) hydrophilicity or the film thickness. The Nafion side chains were found to bend towards the substrates with high hydrophilicity which is in qualitative agreement with existing experiments. The amount of bending was observed to reduce with increasing film thickness. However, the side chain length did not
show any noticeable variation with wall (substrate) hydrophilicity or film thickness. The water clusters became smaller and more isolated clusters emerged for highly hydrophilic substrates. In addition, the water cluster sizes showed a decreasing trend with decreasing film thickness in case of very hydrophilic substrates which has also been observed in experiments of supported Nafion films. The in-plane water diffusion was enhanced considerably for very hydrophilic substrates and this mechanism has also been proposed previously in experiments. The in-plane water diffusion was also found to be a strong function of the substrate selectivity towards the hydrophilic phase. Our simulations can help provide more insights to experimentalists for choosing or modifying nanoparticles for Nafion nanocomposites.

**INTRODUCTION**

Hydrogen, as fuel for fuel cells\(^1\), is being increasingly looked as an important alternative source of energy in the transportation sector. There is a lot of research going on in ways to efficiently produce hydrogen by using energy from renewable sources like solar and wind\(^2\). In addition, solar and wind energy will become a larger part of the energy mix in household and industrial usage. Batteries are needed to store energy from renewable sources and use it whenever required. In this respect, the flow batteries are being proposed as one of the solutions for large scale energy storage\(^3\).

Nafion, shown in Figure 1, is a widely used polymer electrolyte membrane (PEM) material in polymer electrolyte membrane fuel cells (PEMFC) and flow batteries\(^4,5\). The polymer membrane allows the diffusion of protons and also prevents the crossover of electrolytes in flow batteries and crossover of methanol in direct methanol fuel cells (DMFC)\(^6\). Nafion nanocomposites are being used to improve proton conductivity\(^7\) and reduce unwanted crossover\(^8\). The PEM is also found in catalyst layers in PEMFCs along with platinum nanoparticles\(^9\). It is evident that there will be
important interfacial interactions of the PEM with the nanoparticles and/or catalyst layers which will affect the device performance\textsuperscript{10}. A better and more comprehensive theoretical understanding of the effects of such interfacial interactions on phase separation and proton transport will be beneficial for designing improved nanocomposites.

A variety of experiments have been conducted on Nafion supported films and Nafion nanocomposites to understand and improve the performance of such materials. It has been suggested that Nafion micelles are cylindrical structures containing water and ions and lined by the sulfonic acid groups\textsuperscript{11}. Micellar orientation of supported Nafion films was parallel to the substrate in case of a hydrophilic substrate and it was oriented away from the more hydrophobic substrate\textsuperscript{12}. As a consequence, it was proposed that the surface-treated nano-patterned substrates

![Nafion chain diagram](image)
could be used to enhance water transport and ionic conductivity in a desired direction within Nafion membrane, since water and ion mobility is taking place mostly along the micelles. Amide thin films on different substrates, like silica and MgO (110), have shown differences in proton conductivity up to an order of magnitude due to differences in interfacial structure\textsuperscript{13}.

The confinement effect is an important factor which influences the membrane structure and water transport. Nafion supported films showed significant reduction in water diffusion at film thickness below 60 nm due to confinement effects\textsuperscript{14}. Nafion films supported on silica showed increased phase separation with increasing film thickness\textsuperscript{15}. GISAXS (Grazing Incidence Small Angle X-Ray Scattering) experiments\textsuperscript{16} of supported Nafion films on silica showed increasing d-spacing in both in-plane and perpendicular directions with increasing film thickness with a faster rate of increase in the latter.

Nafion nanocomposites containing highly hydrophilic nanoparticles, like modified silica, have shown higher proton conductivity as compared to that of bulk Nafion\textsuperscript{7}. Crossover of methanol in direct methanol fuel cells have been reduced by using Nafion nanocomposites\textsuperscript{17}. Vanadium ion crossover has also been reduced by doping Nafion with nanoparticles\textsuperscript{8}. A previous study\textsuperscript{18} has hypothesized the reduction of methanol crossover and increased proton conduction in a Nafion - modified carbon nanotube (CNT) nanocomposite due to the formation of long oriented pathways along the modified CNTs which were selective to water. The side-chain orientation of Nafion chains has been shown to be affected by the hydrophilicity of the substrate\textsuperscript{19}. All of the above mentioned experiments show that the effect of the film thickness/confinement and substrate hydrophilicity/selectivity to water on the internal hydrated nanostructure of Nafion is significant which in turn motivates our molecular dynamics simulation based study.
Nafion nanocomposites show a large variation in nanoparticle sizes (5 nm - 75 nm)\textsuperscript{20,21}. As a first approximation, a flat substrate of lateral dimensions in the range of 4-6 nm should be suitable for atomistic modelling of the Nafion-substrate interactions. The average interparticle distance in a Nafion titania nanocomposite was shown to be 9 nm\textsuperscript{20}. Also, previous supported film experiments have stressed on the importance of a more thorough understanding of Nafion films in thickness less than 10 nm because this is the range of interparticle distance found commonly in catalyst layers\textsuperscript{15}. Therefore, in the present study, the film thicknesses in the range of 6 nm - 11 nm have been chosen to perform the classical molecular dynamics (MD) simulations.

Different varieties of nanoparticles like silica, zirconia, and modified carbon nanotubes\textsuperscript{7,18,22} have been used in Nafion nanocomposites. In addition, Nafion can also exist in catalyst layers between carbon support and platinum nanoparticles\textsuperscript{9,23}. All of these nanoparticles and supports have varying levels of hydrophilicity. The polymer material present between nanoparticles in nanocomposites have been modeled previously using capped films\textsuperscript{24}. Therefore, the model of Nafion capped between substrates of varying hydrophilicity will be effective to provide insights into the importance of the interfacial interactions in Nafion nanocomposites.

Mashio et al.\textsuperscript{25} simulated Nafion supported films on graphite sheet and graphite sheet modified with carboxyl and carboxylate ions using classical molecular dynamics (MD). The number of water molecules, hydronium ions and sulfonic acid groups were observed to increase with the presence of the ionic groups in the graphite sheet. The water clusters reduced in size for the functionalized graphite sheet as compared to the bare graphite sheet. Zhang et al.\textsuperscript{26} simulated Nafion supported films on platinum substrate using classical MD. The film thickness variation showed significant diversity in the water cluster morphology. The water diffusion constants varied non-monotonically with thickness of the Nafion film. Water diffusion in the thickest film (7.3 nm)
was faster than that in a bulk Nafion. Borges et al\textsuperscript{27} performed classical MD simulations of the Nafion (fixed thickness) supported films on walls of varying hydrophilicity. The films showed changes in phase separation patterns due to water flooding the highly hydrophilic walls (substrates). Water diffusion in the films was found to be greater than that in bulk Nafion at the same hydration level without any noticeable trend with varying wall (substrate) hydrophilicity. Borges et al\textsuperscript{28} also found that varying the hydration levels in such supported Nafion films showed distinct changes in the micellar structure within the films. Dissipative particle dynamics (DPD) of Nafion films have shown preferential flooding of water at the quartz substrate\textsuperscript{29} which was also in agreement with experiments\textsuperscript{30}.

Unlike a supported film, the capped Nafion films have interfaces with two substrates. This can induce additional confinement effects. Also, the side chain orientation and the sulfonic acid (protogenic) group preferential accumulation in the presence of a substrate would be different than that in the presence of a free interface. The protogenic group locations and side chain orientations will invariably have an effect on the water clustering within the Nafion capped film. All these reasons make it necessary to study capped Nafion films. Classical molecular dynamics simulations allows capturing the effects of deviations of film mass density from bulk mass density in capped films. In addition, atomistic representation of the Nafion molecule allows us to study the important structural properties like sulfur-sulfur radial distribution functions (RDFs), the side chain orientations and the side chain lengths. The Nafion films were capped by walls of tunable hydrophilicity in our simulations. Such tunable hydrophilicity allows us to study the effects over a wide range of hydrophilicity as opposed to substrates with fixed chemistry. In our simulations, the side chain orientations were found to vary with substrate hydrophilicity and film thickness (confinement effect) while the side chain lengths did not show any such trends. Water cluster sizes
for highly hydrophilic substrates indicated that it was a function of film thickness (confinement effect). In-plane water diffusion for our capped Nafion film simulations was considerably enhanced for hydrophilic substrates which is different from what was observed for supported Nafion film simulations by Borges et al.27 This enhancement of in-plane water diffusion was despite reduced water cluster sizes for highly hydrophilic substrates. In addition, the in-plane water diffusion was found to be a strong function of the selectivity of the substrate to the hydrophilic phase.

MATERIALS AND METHODS

Simulation Details

The structure of the Nafion monomer is shown in Figure 1. The value of \( n \) represents the number of repeat units in a monomer. The value of \( m \) is the degree of polymerization. \( n=7 \) for this study which corresponds to an equivalent weight (EW) of 1100. EW is defined as the weight of the polymer divided by the number of protogenic groups (sulfonic acid groups). EW of 1100 is a very commonly used variety of Nafion and, hence, has been chosen for this study.4,31

The \textit{pcff} (Polymer Consistent Force Field)32 was used for simulating the polymer matrix, water molecules and hydronium ions using LAMMPS33 software. Partial charges for all the atoms were assigned using \textit{COMPASS} (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field34. \textit{COMPASS} charges have been used along with the \textit{pcff} force field in previous simulations35,36,37. The \textit{pcff} force field has been used to accurately model polyelectrolytes like Nafion, SPEEK, sulfonated co-polyimides and other polymers previously38,39,40,41,42. Water molecules38,42,43,44 and hydronium ions38,41,42 have also been
modelled previously using the *pcff* force field. Details about the force field validation are provided in the Supporting Information (Section III).

Nafion was simulated at one hydration level \( \lambda = 15 \) and at two different temperatures of \( T=300 \text{ K} \) and \( T=353 \text{ K} \). The hydration level \( \lambda \) is defined as the number of water molecules per side chain of Nafion. \( \lambda=15 \) was chosen since this is a moderate hydration level considering the fact that hydration levels in Nafion can go as high as \( \lambda=30 \). The sulfonic acid group of Nafion is fully dissociated at \( \lambda=15 \). Therefore, hydronium ions were introduced into the simulation box to account for this dissociation.

Integrated Lennard-Jones potential\(^4^7\),

\[
E = \epsilon \left( \frac{2}{\lambda_{15}} (\sigma/r)^9 - (\sigma/r)^3 \right) , \quad r < r_c
\]  

(1)

has been used to simulate structureless walls at the top and at the bottom of the simulation box\(^2^7\). The cutoff distance \( r_c \) is chosen as 15 Å\(^2^7\). Two different sets of \( \epsilon \) values are used in the simulations. \( \epsilon_{phob} \) represents the interaction energy between the wall and the hydrophobic part of the system which includes all the polymer atoms except the atoms in the sulfonic acid group, water molecules and hydronium ions. \( \epsilon_{phyl} \) represents the interaction energy between the wall and the hydrophilic part of the system which includes all the atoms in the sulfonic acid group, water molecules and hydronium ions.

\( \epsilon_{phob} \) has been fixed at 0.25 kcal/mol and five different values of \( \epsilon_{phyl} = 0.25, 0.50, 1.20, 1.50, 2.00 \) kcal/mol have been to simulate the effects of varying hydrophilicity of nanoparticles\(^2^7\). The paper shows results for these set of values unless mentioned otherwise. Additional simulations have been performed in which \( \epsilon_{phyl} \) has been fixed at 2.00 kcal/mol and five different values of
\(\epsilon_{phob} = 0.25, 0.50, 1.20, 1.50, 2.00\) kcal/mol have been used to understand the effect of contrast between the \(\epsilon_{phyl}\) and \(\epsilon_{phob}\) on the water transport within the Nafion capped film.

A nanocomposite has fillers/nanoparticles dispersed inside the matrix (polymer). The matrix material present between any two nanoparticles is the representative volume element (RVE) being modelled in our simulations. This RVE was modelled by confining 17 Nafion chains along with water molecules and hydronium ions between structureless walls of tunable hydrophilicity\(^{27,28}\) as shown in Figure 2 (a). The walls represent the nanoparticle surfaces of variable hydrophilicity. This representation has been used to model nanocomposites previously\(^{24,48}\). Henceforth, \(\epsilon_{phyl} = 0.25, 0.50\) kcal/mol walls will be referred to as low hydrophilicity (LH) walls and \(\epsilon_{phyl} = 1.20, 1.50, 2.00\) kcal/mol walls will be referred to as high hydrophilicity (HH) walls in what follows. In both these cases, \(\epsilon_{phob}\) has been fixed at 0.25 kcal/mol unless mentioned otherwise.

Three different film thickness values of 6.3 nm, 8.7 nm and 11.5 nm were simulated for each of the wall hydrophilicity values. The film thickness was varied in the Z-direction (Figure 2). The thickness variation represented effectively the variation of the filler fraction in a nanocomposite i.e. higher film thickness corresponds to lower filler fraction and vice versa. The simulations were run for a total of 8 ns and the last 3 ns of the production runs was used for analysis. The density, with variation less than 0.05 \%, had stabilized after 2.5 ns from the start of the simulation and the energy was also stable. The average water cluster size showed variations less than 1 \% during the production run. A detailed description of the model construction and simulation protocol has been presented in the Supporting Information (Sections I and II). Note that all the results shown in this paper are for \(T=353\) K. Qualitatively similar results were
obtained for $T=300$ K. The duration of our simulations and implemented system sizes are consistent with previous simulation studies$^{4,49,50,51}$. Each film simulation consumed around 120-170 CPU hours on 32 cores of the Lisa computing cluster in SurfSara (Amsterdam).

**Calculation Methods**

From the production runs, structural and dynamic characteristics like radial distribution functions (RDFs), side chain orientations, cluster distribution of water molecules and/or hydronium ions and diffusion coefficients of water molecules were calculated.

The number density is defined as the number of atoms of a particular type divided by the total number of atoms of the same type in a layer of thickness 0.2 Å at a particular distance from either of the walls in the Z-direction. The total mass density is defined as the total mass present in a 0.2 Å thick layer, at a particular distance (in Z-direction) from either of the walls, by the volume of the layer.
The radial distribution function \( g(r) \) (RDF) is proportional to the probability of finding an atom B at a distance \( r \) from the reference atom A inside a shell of thickness \( dr \). The coordination number (CN) is the average number of atoms of a particular type found at a certain distance from a particular central atom of a certain type. The Sulfur-Sulfur RDF has been analysed to check for any significant changes in the distance between the side chain protogenic groups. The Sulfur-Sulfur and Sulfur-Oxygen (water) CNs have also been analysed.

Figure 2. (a) Hydrated Nafion film between two structureless walls. Z axis is the direction perpendicular to the walls and X and Y axes are parallel to the walls. Z direction has fixed boundaries and the film is periodic in X and Y directions. Blue color represents water molecules and hydronium ions, orange color is used for Nafion molecules. (b) Side chain vector (vector connecting the first carbon in the backbone to the sulfur in the sulfonic acid group) orientation, i.e. the angle between the side chain vector and the Z-axis. The simulation box is divided into 3 equal layers as shown in Figure 2 (a) and the side chain orientation was computed in these 3 layers.
The side chain orientation is defined as the angle between the side chain vector and the Z-axis as shown in Figure 2(b). The side chain vector is defined as the vector from the carbon connecting the side chain to the backbone, towards the sulfur in the sulfonic acid group. The simulation box was divided into three equal layers from top to bottom. The angle between the side chain vector and the +Z-axis was computed for the top two layers and the angle between the side chain vector and the –Z-axis was computed for the bottom layer. Analysis was done using a custom Matlab script.

The cluster distribution of water molecules was computed for the different hydration levels (λ) using the OVITO software\textsuperscript{52}. A cluster is defined as a group of atoms in which each atom is within a particular pre-defined cut-off distance of at least another atom within that group. The oxygen atom in the water molecule was used for computing cluster sizes, i.e. cluster of 10 oxygen atoms is assumed to represent the cluster of 10 water molecules. The cluster distribution plots number of clusters, averaged over a time interval, versus the cluster size. Python scripts were used to access OVITO API and Matlab scripts were used for further post-processing.

Water channel sizes were computed using the Zeo++ software\textsuperscript{53} which uses Voronoi tessellation for its internal calculations. All the atoms associated with the water molecules were removed and remaining atoms positions and types were provided as input to this software for channel size computation. The water channel sizes for the HH walls were estimated from the water number density profiles and this has been explained in water cluster distribution section later.
The translational diffusion coefficients for water molecules were computed by analysing their mean square displacement (MSD) using the Einstein relation in the diffusive regime\textsuperscript{54}. These diffusion coefficients were computed as an average for the entire Nafion film between the walls. The simulation box was divided into five equal layers from top to bottom in the Z direction and the layer-resolved diffusion coefficients were also computed in these layers using a custom Matlab script.

RESULTS AND DISCUSSION

Snapshots and Density Profiles

Figure 3 shows the snapshots at the end of the production runs for five different values of wall hydrophilicity. For low values of wall hydrophilicity (\(\epsilon_{phyl} \approx 0.25, 0.50\) kcal/mol), there is negligible accumulation of water molecules near the walls. However, for the high hydrophilicity walls (\(\epsilon_{phyl} = 1.20, 1.50, 2.00\) kcal/mol), there is a considerable accumulation of water near the walls.

Figure 4 shows the water number density profiles for different wall hydrophilicity values for the 6.3 nm film. The water number density profile for the \(\epsilon_{phyl} = 0.25\) kcal/mol wall was very uniform throughout the thickness of the film. The water number density shows small peaks near the walls for a slightly higher hydrophilicity wall (\(\epsilon_{phyl} = 0.50\) kcal/mol). Previous simulations of Nafion supported on primarily hydrophobic graphite have shown emergence of small peaks in the water density profiles when the graphite was modified by hydrophilic carboxylate ions\textsuperscript{25}. The water number density near the walls is much higher for HH walls as compared to the LH walls due to a considerable accumulation of water close to the walls, as seen in Figure 3. Also, the
water number density near the centre of the film is higher for the LH walls as compared to the HH walls.

Figure 5 shows the water, carbon and sulfur number density profiles for the lowest and highest hydrophilicity wall for the 6.3 nm film. The carbon number density shows small peaks near the walls in the LH case. These peaks disappear for the HH wall and a smooth profile appears which reaches a stable value at a distance further away from the walls as compared to the LH case. This suggests carbon atoms are moving away from the walls in the highest hydrophilicity case due to water accumulation near the walls. The sulfur number density is similar to the water number density profile i.e. number density near the walls is considerably higher for the HH wall as compared to the LH wall. This indicates that both sulfur and water show preferential accumulation at the HH wall. Similar trends in the carbon, sulfur and water density profiles are also observed for other film thicknesses as well.

Figure 6 shows the total mass density profiles, normalized by the bulk density, for different film thickness values for the lowest and highest hydrophilicity walls. The X-axis in Figure 6 is the relative distance ($t/T$), defined as the distance ($t$) from a wall divided by the film thickness ($T$). The bulk domain is defined as the space where the normalized mass density is equal to 1. For both the low and high hydrophilicity cases, a broadening of the bulk domains can be observed with increasing film thickness. However, there is an important difference between these two cases. The LH wall shows an almost uniform density profile throughout the film thickness whereas the HH wall shows high density values near the walls. These high density values are due to the preferential accumulation of the hydrophilic components, like water and sulfur, near the walls.
Figure 3. Snapshots for (a) $\epsilon_{phyl} = 0.25 \text{ kcal/mol}$ (b) $\epsilon_{phyl} = 0.50 \text{ kcal/mol}$ (c) $\epsilon_{phyl} = 1.20 \text{ kcal/mol}$ (d) $\epsilon_{phyl} = 1.50 \text{ kcal/mol}$ (e) $\epsilon_{phyl} = 2.00 \text{ kcal/mol}$ where blue color shows the water molecules and hydronium ions, and orange color shows the Nafion atoms.

Figure 4. Water (oxygen) number density profiles for the 6.3 nm film at different wall hydrophilicity ($\epsilon_{phyl}$) values.
Figure 5. Water (oxygen), carbon and sulfur number density profiles for the 6.3 nm film for (a) LH film, \( \epsilon_{\text{phyl}} = 0.25 \text{ kcal/mol} \) and (b) HH film, \( \epsilon_{\text{phyl}} = 2.00 \text{ kcal/mol} \).

Figure 6. Total film mass density, normalized by the bulk density = 1.79 g/cc, profiles for different film thickness values for (a) LH film, \( \epsilon_{\text{phyl}} = 0.25 \text{ kcal/mol} \) and (b) HH film, \( \epsilon_{\text{phyl}} = 2.00 \text{ kcal/mol} \).
Radial Distribution Functions (RDF) and Coordination Numbers (CN)

The distance between protogenic sulfonic acid groups is an important characteristic to probe the internal structure of the membrane. Previous simulation studies have shown that the sulfur-sulfur distance (inter-protogenic group distance) less than 6.5 Å increased water binding to sulfonic acid groups and also affected the ease of the proton dissociation. Hence, the sulfur-sulfur RDF at small atomic separations (< 8 Å) and sulfur-sulfur CN have been analyzed in this study to check for any significant changes. The water structure around the sulfur atom is also important for proton dissociation. The sulfur-oxygen (water) CN has also been analyzed to check for any significant changes in the first hydration shell (~4.7 Å, Figure S1).

Figure 7. (a) Sulfur-Sulfur radial distribution functions (RDF) (b) S-S coordination numbers (CN) for the 6.3 nm film and the different wall hydrophilicity values ($\epsilon_{phyl}$). RDF and CN for bulk Nafion has also been shown.
Figure 7 (a) shows the S-S RDF values for different levels of the wall hydrophilicity for the 6.3 nm film. The RDF plots for $\varepsilon_{phyl} = 0.25, 0.50, 1.20$ kcal/mol have their first maximum at almost the same distance as the bulk Nafion first peak distance of 4.3 Å. RDF plots for $\varepsilon_{phyl} = 1.50, 2.00$ kcal/mol have the first peak at a slightly higher distance of 4.5 Å. The Nafion chains tend to move away from the HH walls, due to the preferential accumulation of water, and are packed into a more confined space towards the centre of the film. This could increase the repulsion between the negatively charged sulfonic acid groups which can explain the slightly higher distance of the first peak for $\varepsilon_{phyl} = 1.50, 2.00$ kcal/mol walls. This effect can also be seen for the $\varepsilon_{phyl} = 2.00$ kcal/mol wall for higher film thicknesses as well (Figure S2). In conclusion, the negligible increase in the position of the first peak implies that hydrophilicity of the substrate has no considerable effect on the S-S distance.

However, the values of the S-S RDFs for the HH walls ($\varepsilon_{phyl} = 1.20, 1.50, 2.00$ kcal/mol) were visibly higher than those for the LH walls ( $\varepsilon_{phyl} = 0.25, 0.50$ kcal/mol) up to a distance of 8 Å (Figure 7(a)). A similar trend is also observed for thicker films also (Figure S2). The accumulation of the Nafion chains near the centre of the film would increase the probability of finding a sulfur atom within the close proximity of another sulfur atom. This would explain the rise in the RDF values for the HH walls.

Figure 7(b) shows the S-S coordination numbers (CN) for the 6.3 nm film for different wall hydrophilicity levels. The HH walls show a slightly higher CN as compared to the LH walls for all distances. This pattern is seen for higher film thicknesses as well (Figure S3). This slightly higher CNs for HH walls combined with no noticeable change in S-S RDF for close range
distances (< 8 Å) implies that there should not be any detrimental effect on S-S close range ordering in the HH wall films.

Figure 8 shows the Sulfur- Oxygen (water) (S-Ow) CNs for the 6.3 nm film for different wall hydrophilicity levels. The S-Ow CNs are slightly lower for HH walls as compared to the LH walls and this pattern is seen for higher film thicknesses as well (Figure S4). This is due to the fact that a considerable amount of water accumulates near the HH walls which reduces the average number of water molecules near the sulfur atoms. However, the CNs for both the LH and HH walls are quite similar up to 4.7 Å (first coordination shell of S-Ow, Figure S1) which implies that high wall hydrophilicity does not have a detrimental effect on close range water solvation structure around the sulfur atoms in the sulfonic acid group.

Figure 8. S-Ow coordination numbers (CN) for the 6.3 nm film and the different wall hydrophilicity values (εphyl). CN for bulk Nafion has also been shown.
Side Chain Orientation

The catalyst layer in fuel cells can have Nafion present in between platinum nanoparticles\(^9\). Also, Nafion can have an interface with carbon in the catalyst layer and in the electrodes in a fuel cells\(^9\). The side chain orientation with respect to the nanoparticles will have an impact on the compatibility of such nanocomposites\(^9\). Therefore, the effects of varying substrate hydrophilicity and filler fraction on the side chain orientation have been investigated.

Figure 9 shows the layer resolved orientation of side chains for the 6.3 nm film for different values of wall hydrophilicity in three equal film layers. As can be seen, the angle between the side chain and the Z-axis does not show noticeable variation across the layers for the LH walls.

![Figure 9. Side chain orientation with respect to the Z-axis in three layers for the 6.3 nm film for different wall hydrophilicity ($\epsilon_{\text{phyt}}$) values.](image-url)
However, the angle value reduces considerably in the top and bottom layers for the HH walls. Similar pattern was also observed for higher film thickness values as well (Figure S5).

The simulations for each of the different hydrophilicity values started from the same initial configuration. Therefore, the decrease in the angle in the top and bottom layers for the HH walls is purely due to the effect of the walls. This same effect was also seen for a different set of initial configuration values which further confirms our hypothesis. It can be concluded that the HH walls tend to bend the side chains towards them which agrees qualitatively with experimental observations\textsuperscript{19}.

Figure 10 shows the side chain orientation for the lowest and highest hydrophilicity wall. The angles for the lowest hydrophilicity wall in all three layers shows negligible variation with varying film thickness. A similar trend is observed for the other LH wall ($\epsilon_{phyl} = 0.50$ kcal/mol) also (Figure S5 (a)). In contrast, the value of the angles in the top and bottom layer increase

Figure 10. Side chain orientation with respect to Z-axis in three layers for different film thickness values for (a) $\epsilon_{phyl} = 0.25$ kcal/mol LH wall and (b) $\epsilon_{phyl} = 2.00$ kcal/mol HH wall.
progressively with increasing film thickness for the highest hydrophilicity wall. A similar trend is observed for another HH wall ($\epsilon_{phyl} = 1.50$ kcal/mol) as well (Figure S5 (c)). For the remaining HH wall ($\epsilon_{phyl} = 1.20$ kcal/mol), the amount of side chain bending towards the walls was subdued for film thickness of 8.7 nm and 11.5 nm (Figure S5 (b)). This implies that the effect of side chains bending towards the walls for the HH walls reduces with the increasing film thickness, at least in the film thickness range investigated. In conclusion, the wall hydrophilicity and/or varying filler fraction of a nanoparticle can be used to alter the side chain orientation with respect to the nanoparticle surface.

**Side Chain Length**

The differences in the side chain lengths have been shown to affect the diffusion of water within the PEMs\(^5\). Therefore, the side chain lengths have been analysed for different wall hydrophilicity and the film thicknesses, and the same has been shown in Figure 11. The bulk

![Side Chain Length Graph](image)

**Figure 11. Nafion side chain lengths for different wall hydrophilicity ($\epsilon_{phyl}$) values and different film thicknesses**
Nafion side chain length was on average about 7.3 Å. The capped Nafion film side chain lengths did not show any considerable deviation from the bulk value. There was no noticeable trend for the side chain lengths with wall hydrophilicity and/or film thickness. Therefore, it can be concluded that changes in water diffusion amount (if any) should not be due to the changes in side chain lengths in capped Nafion films.

**Water Cluster Distribution**

Water clusters present in the hydrated Nafion nanostructure form percolated channels at sufficiently high hydration levels\(^5\). These percolated channels allow the transport of protons across the membrane which allows the fuel cells and flow batteries to function. However, these percolated water channels can also allow unwanted crossover of methanol and vanadium ions. Nafion nanocomposites have been shown to reduce the crossover of methanol\(^1\) and vanadium ions\(^8\). Therefore, it is important to understand the effect of nanoparticle hydrophilicity and filler fraction on the water cluster distribution.

All the water cluster analysis shown here are for a cut-off distance of 3.7 Å (see the Calculation methods section earlier) averaged over 3 ns of the simulated physical time. This cut-off distance was chosen since it is close to the first coordination shell (Figure S6) of water and, hence, this distance will encompass a majority of the water molecules. A single large cluster is observed for this cut-off distance of 3.7 Å for bulk Nafion (Figure 12). No such large cluster is observed for a cut-off distance of 3 Å for bulk Nafion, since this distance is close to the first peak of oxygen (water)-oxygen (water) RDF (Figure S6) and, hence, encompasses few water molecules.

Figure 12 shows the water cluster distribution at different wall hydrophilicity values for the 6.3 nm film. The cluster distributions for the LH walls \(\epsilon_{phyt} = 0.25, 0.50 \text{ kcal/mol}\) are very close
to the bulk cluster distribution. The largest cluster sizes (cluster size close to 2400) for the HH walls ($\varepsilon_{phyl} = 1.20, 1.50, 2.00$ kcal/mol) are smaller in size as compared to the LH walls. Also, there is an emergence of clusters in the size range of 900 to 1500 for the HH walls. This shows that the cluster sizes decrease considerably for increasing hydrophilicity of the walls for a fixed film thickness. Similar effects are also seen at higher film thickness values as well (Figure S7).

![Figure 12. Water cluster distribution for the 6.3 nm film at different wall hydrophilicity values and also for bulk Nafion. The cluster distribution shown is for the cluster sizes from 100 to 2380.](image)

The insets in Figure 12 show a continuous percolating cluster for the LH wall films spanning the whole box in all 3 dimensions and isolated clusters for the HH wall films near the centre of the box (film). The HH wall films also form two percolating roughly cuboidal water channels.
along the walls which is reflected in the two peaks in the cluster distribution at around 800 and 1400. The thickness of these channels in the z-direction for the 6.3 nm film is around 9-10 Å as estimated from the water number density plots (Figure 4) i.e. difference between the distance where the number density reaches its minimum after the 3rd peak from any wall (box edge) and the distance where the number density first acquires a non-zero value. The only water channel in the lowest hydrophilicity wall 6.3 nm film had a maximum channel diameter of 13.6 Å and a minimum diameter of 6.5 Å. The corresponding quantities for the single channel in bulk Nafion were 11.5 Å and 5.3 Å respectively. It is clear that water, which has an average van der Waals diameter of 2.8 Å, can diffuse through both the LH and HH wall films. However, the HH wall film provides uniformly wide and straight water channels along the walls whereas the LH wall film water channel has bottlenecks (minimum diameter) and is more tortuous (extends through

![Diagram](image_url)

Figure 13. Cluster count, normalized by the bulk cluster count, vs different wall hydrophilicity ($\epsilon_{phyl}$) values for different film thickness values
the box in all 3 dimensions). As a result, water is observed to diffuse noticeably faster in the in-plane direction for the HH wall films as compared to the LH wall films which has been discussed later in the water transport section.

Figure 13 shows the water cluster count normalized by the bulk water cluster count for different wall hydrophilicity and film thickness values. All the normalized cluster counts are larger than 1 which implies larger number of water clusters for all the wall hydrophilicity values and the film thickness, as compared to bulk Nafion water cluster count. This indicates a more dispersed water cluster network in the Nafion films as compared to the bulk Nafion.

The water cluster count increases for the HH walls as compared to the LH walls for all three different film thickness values (Figure 13). This effect is universal and is weakly dependent on the film thickness. The higher cluster count indicates a more dispersed water cluster network for the HH wall films as compared to the LH wall films which can also be seen in the inset for the HH wall films in Figure 12. The existing experiments have shown that unwanted crossover reduces due to the highly hydrophilic nanoparticles like silica, clay etc. added to Nafion. In fact, the existence of long-range oriented pathways along the modified carbon nanotubes was the proposed mechanism for the observed enhanced proton transport and reduced methanol crossover in a Nafion – modified CNT nanocomposite. Our simulations also show the preferential accumulation of water along the HH walls and a concomitant increase in the water cluster count due to the emergence of a more dispersed water phase and isolated water clusters. It is likely that less polar molecules like methanol will move away from the highly hydrophilic nanoparticles similar to carbon moving away from the HH walls as seen in Figure 5 (b). This will increase the chances of such molecules being trapped in the isolated clusters which are found at larger distances from the HH walls as seen in the inset for HH wall films in Figure 12.
Figure 14 shows the average water cluster size for different wall hydrophilicity and film thickness values. The average cluster sizes are almost constant for increasing film thickness values for the LH walls. However, there is a distinct pattern for the HH walls which shows that the average water cluster sizes show an increasing trend with increasing film thickness. The water channels along the HH walls become more connected through the centre of the film (box) with increasing film thickness. This is evidenced by the increasing average number of clusters in the 2200-2330 size range and a concomitant decrease in the 800-1400 size range with increasing film thickness (Figure 12, Figure S7). This behaviour for the HH walls indicates higher phase

![Graph showing average cluster size vs film thickness](image)

Figure 14. Average cluster size vs different film thickness values for different wall hydrophilicity ($\epsilon_{\text{phyl}}$) values. Average cluster size for bulk Nafion is also shown. The dash-dot line shows the trend for low hydrophilicity walls and the dash line shows the trend for high hydrophilicity walls. These lines are not numerical fits.
separation for increasing film thickness. Previous TEM (Transmission Electron Microscopy) images\textsuperscript{15} and GISAXS experiments\textsuperscript{16} also show similar trends vs film thickness for Nafion films supported on hydrophilic silica substrates.

**Water Transport**

Water diffusion through the Nafion nanostructure plays an important role in the working of fuel cells and flow batteries. In these devices, the protons attach themselves to water molecules and are transported from anodic to cathodic side or vice versa via the so-called vehicular transport mechanism. There is also an alternative method of proton transport in which the proton hops across hydrogen bonds in the water phase. Nanoparticles are added to Nafion to enhance water retention and proton conductivity\textsuperscript{7,57}. Therefore, it is important to study the effect on water transport due to the nanoparticle hydrophilicity and filler fraction.

Water diffusion constants ($D_x$, $D_y$ and $D_z$) have been computed in the X, Y and Z directions using the Einstein relation for diffusive motion. Diffusion constants have been calculated from the time period where water transport is in a diffusive regime (Figure S8). Water diffusion in the films’ XY-plane is studied using the in-plane diffusivity ($D$),

$$D = (D_x + D_y)$$  \hspace{1cm} (2),

and was compared to the analogous (two-third of total water diffusion coefficient) values for Nafion bulk ($D_{bulk}$),

$$D_{bulk} = \left(\frac{2}{3}\right) \ast (D_{bulk-x} + D_{bulk-y} + D_{bulk-z})$$  \hspace{1cm} (3)
Henceforth, the diffusion in the XY plane will be referred to as in-plane water transport. The total water diffusion coefficient ($1.5 \times D_{\text{bulk}}$) in bulk Nafion for $\lambda = 15$ at $T = 353$ K was found to be $1.93 \times 10^{-5}$ cm$^2$/s from our simulations\(^1\).

![Figure 15](image)

Figure 15. Film averaged (a) in-plane water diffusion constants ($D$) normalized by the corresponding two-dimensional water diffusion ($D_{\text{bulk}}$) constant at $\lambda = 15$ for bulk Nafion. (b) Water diffusion anisotropy ratio values vs wall hydrophilicity ($\epsilon_{\text{phyl}}$) for different film thicknesses.

Figure 15 (a) shows the in-plane water diffusion, normalized by the bulk water diffusion constant for different wall hydrophilicity values and for the different film thicknesses. The in-plane water diffusion is noticeably higher for the HH walls ($\epsilon_{\text{phyl}} = 1.20, 1.50, 2.00$) as compared to the LH walls ($\epsilon_{\text{phyl}} = 0.25, 0.50$), for all three different film thicknesses. The existing experiments have shown micellar orientation in Nafion supported films along hydrophilic

\(^1\) Please refer to the Supplementary Information Section III for more information
substrates and away from hydrophobic substrates\textsuperscript{12}. It was further proposed that treated nano-patterned substrates can be used to enhance the directional transport of water within the Nafion membrane, since the water transport is mostly along the micelles\textsuperscript{12}. A similar enhancement of water transport for the HH walls (substrates) is also observed in our simulations.

It is important to keep in mind that the water cluster sizes showed a significant size reduction for the HH walls. The bulk classical MD simulations of PEMs like Nafion\textsuperscript{49}, SPEEK\textsuperscript{51}, PFIA\textsuperscript{58} have shown the water diffusion to increase with increasing water cluster sizes. However, the capped Nafion films show a decrease in water diffusion despite larger water cluster sizes for the LH walls. This is due to the formation of water channels parallel to the HH walls with a uniform width as compared to the long tortuous water channel with bottlenecks in the LH wall film.

Previous simulations done for a supported Nafion film did not show any noticeable distinction between water diffusion constants for less and more hydrophilic substrates\textsuperscript{27}. But the capped Nafion films, simulated in this paper, show a clear difference in water diffusion rates between the low and high hydrophilicity walls. The possible reason for this behaviour has been explained later by analysing the layer resolved in–plane diffusion. There was no monotonicity observed in the film averaged diffusion coefficients with respect to the film thickness in the thickness range investigated. This non-monotonicity observation agrees well with the previous experimental conductivity\textsuperscript{15} and simulated water diffusion rates\textsuperscript{26} in the film thickness range investigated.

Anisotropy in water diffusion is defined as the in-plane water diffusion constant ($D$) divided by twice the Z- direction diffusion constant ($D_z$). Figure 15 (b) shows the anisotropy in water diffusion for different hydrophilicity walls and different film thickness. Anisotropy for the HH walls is higher than that for the LH walls. This effect is due to the high in-plane diffusion near
the walls in the HH walls. Anisotropy in water diffusion, for the HH walls, decreases considerably on increasing film thickness from 6.3 nm to 8.7 nm. This can be explained possibly by the strong confinement in Z-direction in the thinnest films.

In-plane water transport was resolved in 5 equal layers in the Z-direction. Figure 16 shows the layer resolved in-plane water diffusion constant, normalized by the bulk two-dimensional water diffusion constant, for the 6.3 nm film. The water diffusion constants are slightly smaller than bulk values for the LH walls. For the HH walls, the diffusion constant near the centre of the film is close to that for the bulk, but the diffusion increases considerably on moving closer to the walls. Similar trends are also observed for higher film thicknesses as well (Figure S9). It is the presence of such highly mobile water layers near both the walls in a capped Nafion film that can explain the noticeably high film averaged in-plane water diffusion constant for the HH walls. Previously simulated supported Nafion films were shown to have considerably less in-plane water diffusion near the free interface as compared to that near the highly hydrophilic substrates. In contrast, we observe occurrence of highly mobile layers at both the walls (substrates) for the HH cases across all the film thicknesses. This fact can explain the considerably higher film averaged in-plane diffusion for the capped Nafion films confined by HH walls as compared to LH walls unlike the previously simulated supported Nafion films.

Figure 17 shows the layer resolved in-plane water transport for the lowest and highest hydrophilicity wall for different film thickness. For the lowest hydrophilicity wall, the in-plane water diffusion constants start to deviate more from the bulk diffusion constant with increasing film thickness. Water is confined towards the centre of the film in the LH wall films. Increasing film thickness allows water more space to move inside the film away from the walls. This could be the reason for the slightly higher deviation from bulk diffusion values for the higher film...
thickness films. For the highest hydrophilicity wall, water diffusion is not affected noticeably by film thickness. Water is mostly concentrated near the walls for these cases, and so increasing film thickness plays a negligible role in in-plane water diffusion in the thickness range investigated.

![Diagram](image)

Figure 16. Layer resolved in-plane water diffusion constants \( (D) \) normalized by the two-dimensional water diffusion constant \( (D_{\text{bulk}}) \) at \( \lambda=15 \) for bulk Nafion. Results are shown for the 6.3 nm film for varying wall hydrophilicity \( (\epsilon_{\text{phy}l}) \).

Enhanced in-plane transport of water has been observed for the HH walls. It is important to ascertain whether this high in-plane transport is due to just the high hydrophilicity of the walls or due to the contrast between the \( \epsilon_{\text{phy}l} \) and \( \epsilon_{\text{phob}} \) for the films. Simulations were run by fixing \( \epsilon_{\text{phy}l} = 2.00 \text{ kcal/mol} \) and varying \( \epsilon_{\text{phob}} = 0.25, 0.50, 1.20, 1.50, 2.00 \text{ kcal/mol} \) to
understand the effect of this contrast on the in-plane water transport. Figure 18 shows the in-plane water diffusion constants, normalized by the corresponding bulk values, for different $\epsilon_{phob}$ values for the 6.3 nm film. In-plane water diffusion constants decreased with increasing $\epsilon_{phob}$ values. This implies that the water diffusion is a function of the contrast between the $\epsilon_{phyl}$ and $\epsilon_{phob}$ values. Higher contrast results in more in-plane water diffusion. The insets also show a preferential accumulation of water at low $\epsilon_{phob}$ values or high contrast between the $\epsilon_{phyl}$ and $\epsilon_{phob}$ values. Nanoparticles can be made more selective towards water by modifying their surface.

Figure 17. Layer resolved in-plane water diffusion constants ($D$) normalized by the two-dimensional water diffusion constant ($D_{bulk}$) at $\lambda=15$ for bulk Nafion. Results are shown for varying film thicknesses for (a) $\epsilon_{phyl} = 0.25$ kcal/mol wall and (b) $\epsilon_{phyl} = 2.00$ kcal/mol wall.
CONCLUSIONS

Capped Nafion films were simulated at a moderate hydration level ($\lambda=15$) at $T=353$ K to model the interactions present in a representative volume element consisting of the matrix (hydrated polymer) confined between any two nanoparticles in a Nafion nanocomposite. The Nafion films were capped by walls of different hydrophilicity to study the effect of nanoparticle hydrophilicity.
on the Nafion nanostructure. The film thickness was varied to study the effect of nanoparticle filler fraction on the Nafion nanostructure and water transport.

The simulated sulfur-sulfur radial distribution functions indicated that there was negligible effect on the close range sulfur-sulfur distance due to the wall hydrophilicity and the film thickness. Although, the RDFs and the CNs suggested that sulfur atoms were more likely to be near each other in a distance less than 8 Å for the higher hydrophilicity walls. The number of water molecules around the sulfonic acid group in the first solvation shell (up to a distance of 4.7 Å) also showed negligible differences with varying wall hydrophilicity. Therefore, nanoparticle hydrophilicity and filler fraction should not have a detrimental effect on the sulfur-sulfur close range distance or the close range hydration structure around the sulfonic acid group.

The Nafion side chain lengths did not show any noticeable trend with wall hydrophilicity and/or film thickness. However, the side chains were found to bend towards the high hydrophilicity (HH) walls. Also, the amount of bending reduced with increased film thickness for the HH walls. Experiments have also shown increased bending of the side chains towards highly hydrophilic substrates\textsuperscript{19}. In effect, nanoparticle hydrophilicity and filler fraction could be used to control side chain orientation with respect to the nanoparticles.

Reduced crossover of methanol has been observed in experiments for Nafion doped with hydrophilic nanoparticles\textsuperscript{17,18}. The emergence of isolated water clusters as indicated by the higher cluster count for the highly hydrophilic substrates could explain such experimental observations. On average, the water cluster sizes increased with increasing film thickness for the high hydrophilicity walls which indicates stronger phase separation with increasing thickness.
Qualitatively similar experimental observations have been seen for supported Nafion films on a silica substrate\textsuperscript{15,16}.

The water in-plane transport was enhanced considerably by the high hydrophilicity (HH) walls, in spite of lower water cluster sizes for the HH wall films. This effect was observed for all the different film thicknesses. Layer resolved in-plane transport indicated a very highly mobile water layer near both the walls for the HH wall films. The LH wall ($\varepsilon_{phyl} = 0.25 \text{kcal/mol}$) 6.3nm film had a single water channel with a maximum and minimum diameter of 13.6 Å and 6.5 Å respectively. The water channels in the HH wall films were roughly cuboidal blocks along the walls with a width of 9-10 Å. The water channels in the HH wall films had no bottlenecks (minimum diameter) and were visibly less tortuous than the water channel in the LH wall film. These observations explain the enhanced in-plane film averaged transport for the HH wall films.

Previous experiments have also proposed directional enhancement of water transport by altering the hydrophilicity of substrates\textsuperscript{12}. The water diffusion anisotropy ratio, ratio of in-plane water diffusion to the water diffusion in the perpendicular direction, was noticeably higher for HH wall films as compared to the LH wall films. Water diffusion anisotropy ratio appeared to reduce with increasing film thickness.

The in-plane water transport was also examined for different values of the contrast between $\varepsilon_{phyl}$ and $\varepsilon_{phob}$ values. In-plane diffusion of water was enhanced for the larger contrast between $\varepsilon_{phyl}$ and $\varepsilon_{phob}$. In effect, the enhanced in-plane transport of water was found to be a function of the contrast between $\varepsilon_{phyl}$ and $\varepsilon_{phob}$ values. This fact can be of use in designing nanoparticles by increasing selectivity to the hydrophilic phase.
To summarize, our simulations showed that high selectivity of walls (nanoparticles surfaces) towards the water phase results in water channels forming along the walls and isolated water clusters emerging at distances further away from the walls. Less polar molecules like methanol are likely to move away from the selectively hydrophilic surfaces (walls) and get trapped in these isolated clusters. Our simulations show that average water cluster sizes for hydrated Nafion films confined by highly hydrophilic surfaces (HH walls) increase with increasing film thickness. This is due to the increasing connectivity between the water channels, which form along the highly hydrophilic surfaces, through the centre of the film. Therefore, it can be suggested that increasing the filler fraction (reducing film thickness) will lead to lesser connectivity of these water channels, which form along the hydrophilic surfaces, at larger distances from these surfaces which in turn can lead to lower crossover of low polarity molecules like methanol. Our simulations also showed that the side chains of Nafion can be made to orient towards highly hydrophilic surfaces (HH walls) and the amount of orientation can be increased by reducing the film thickness (increasing filler percentage of nanoparticles). Our simulations show that water is preferentially accumulated near the highly hydrophilic surfaces (HH walls). In addition, the close range solvation structure near the sulfonic acid group was minimally affected with varying wall hydrophilicity. Therefore, the orientation of side chains towards the water rich environment near these surfaces (hydrophilic nanoparticle surfaces) can be advantageous in a high temperature environment. Our simulations also showed directional enhancement of water transport for highly hydrophilic surfaces (HH wall films) due to highly mobile water layers along these surfaces.

In the present study, we did not explicitly model curvature effects of the surface (wall) on the transport of water. Nevertheless, these effects can be important. Experiments have shown that 1-D and 2-D nanoparticles like modified CNT and graphene oxide result in higher proton
conductivity\textsuperscript{18,59,60} due to long range transport along these nanoparticles and the ordering of these nanoparticles themselves. Larger scale simulations incorporating explicit fillers into the simulation box will provide more insights into these effects.

ASSOCIATED CONTENT

Supporting Information

Model construction, simulation protocol, force field validation, S-S RDF and CN, S-Ow CN, Ow-Ow RDF, side chain orientation, water cluster distribution, mean square displacement and layer resolved diffusion coefficient.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest

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