Molecular dynamics simulations of substrate hydrophilicity and confinement effects in capped nafion films

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I. Model Construction

The Nafion chains were constructed using Materials Studio\textsuperscript{1}. The molecular structure of Nafion is shown in Figure 1 [main document]. The value of $n$ is taken as 7 for this study, corresponding to an equivalent weight (EW) of 1100. An equivalent weight of 1100 represents common varieties of Nafion like Nafion-117 and Nafion-112. The value of $m$ represents the degree of polymerization and this has been taken as $m=10$. Polyelectrolytes like Nafion\textsuperscript{2}, Aciplex\textsuperscript{3} and PFSI\textsuperscript{4}, which have a PTFE backbone, have been previously modelled using 10 monomers in a single chain.
Three different simulation boxes were constructed corresponding to the three different thickness values (6.3nm, 8.7nm, 11.5 nm) using the Amorphous Cell module of Materials Studio\(^1\). The different simulated thickness values represent varying nanoparticle filler fractions, i.e., the thinner the film, the higher the filler fraction could be. Each simulation box had 17 Nafion chains, 170 hydronium ions and 2380 water molecules. The simulation box was confined in the Z direction and was periodic in the X and Y directions. A fixed boundary was used for the Z direction. The corresponding lateral (X and Y directions) dimensions varied from 6 nm (the thinnest film) to 4.5 nm (the thickest film).

Bulk Nafion simulations were also performed in 3D periodic boxes at the same hydration level \(\lambda=15\) for two different system sizes of 7 and 17 Nafion chains. No finite size effects have been observed on comparing the density, radial distribution functions (RDFs) and water diffusion coefficients.

All the simulation results for bulk and interfacial models shown in the present paper are for a 17 chain Nafion system.

II. Simulation Protocol

Each of the simulation boxes were energy minimized using the conjugate gradient algorithm in LAMMPS\(^5\). Two different temperatures of 300 K and 353 K were chosen for the present simulations (300 K is the room temperature and 353 K is the average operating temperature for PEMFCs).

The equilibration and production runs were also carried out using LAMMPS software\(^5\). For a particular film thickness, the energy of the system was minimized under the influence of the
walls with both $\epsilon_{phob}$ and $\epsilon_{phyl}$ fixed at 0.25 kcal/mol. Then, the simulation box was subjected to a NVT run of 0.2 ns at $T=300 \text{ K}/353 \text{ K}$. After that, the simulation box was subjected to an annealing sequence in which the sample was heated up from 300 K/353 K to 600 K in 50 ps, maintained at 600 K for additional 50 ps and cooled down from 600 K back to 300 K/353 K in another 50 ps. This cycle was repeated for five times. After the annealing cycles were completed, the sample was simulated in the canonical NVT ensemble at $T=300 \text{ K}/353 \text{ K}$ for 0.2 ns. After that, the sample was simulated under NpT conditions for another 7 ns at $p=1 \text{ atm}$ (in the lateral periodic dimensions) and $T=300 \text{ K}/353 \text{ K}$. The density of the sample has been stabilized after about 1.5 ns of NpT simulations. The final configuration after 7 ns of NpT simulations was used as a starting configuration for simulations with five different $\epsilon_{phyl}$ values at a fixed film thickness. Then, each of these different $\epsilon_{phyl}$ value simulation boxes underwent the same simulation protocol as mentioned above (in this paragraph). For a fixed film thickness, different initial configurations were also implemented to increase the statistics and to confirm the accuracy of the simulations.

The Nose-Hoover style thermostat and barostat\textsuperscript{6,7} in LAMMPS\textsuperscript{5} were used for maintaining the temperature and pressure, as imposed during the NVT/NpT simulation. The Verlet integration algorithm\textsuperscript{8} was used for time integration of the equations of motion. The slab PPPM\textsuperscript{9} solver was used for solving electrostatic interactions in the Nafion film simulations while the normal PPPM solver was used for bulk Nafion simulations. The cutoff for non-bonded interactions was set at 10 Å. The time step was 1 fs for all the simulations.

The density of the samples has been stabilized at around 1.5 ns (Fig. S1) from the start of the NpT simulations for both $T=300 \text{ K}/353 \text{ K}$. The last 3 ns of the NpT simulation was used for production and particles trajectories were saved every 500 fs for structural and dynamic property
analysis. The RDFs and average water cluster sizes did not show any significant variation during this time.

III. Force Field Validation

Bulk Nafion was simulated at $T=300$ K and 353 K and at $p = 1$ atm to ascertain the validity of the force field. The density at $\lambda = 15$ at $T=300$ K was 1.83 g/cc and at $T=353$ K was 1.79 g/cc. These density values were within 5% of previously observed experimental Nafion density at $T=300$ K$^{10,11}$ and simulated Nafion density at $T=363$ K$^{12}$. The radial distribution functions (RDFs) for sulfur-oxygen (water) and sulfur-oxygen (hydronium) for bulk Nafion are shown in Figure S1. The peak distances for these RDFs also agree well with previous simulations$^{13,14}$. The first peak of sulfur-sulfur (S-S) radial distribution function, as seen in Figure S2, was at 4.4 Å which is within the range of the first peak distances observed in previous simulation studies$^{2,14}$. The oxygen (water) - oxygen (water) first peak, as seen in Figure S3, was at 2.9 Å which is also quite similar to the previous simulation studies$^{2,15}$.

The diffusion coefficient of water in Nafion at $\lambda = 15$ for $T=300$ K was $0.98*10^{-5}$ cm$^2$/s and at $T=353$ K was $1.93*10^{-5}$ cm$^2$/s. These values were within the range of the previous simulation data$^{14,12}$ and the experimental$^{16}$ water diffusion coefficient values at $\lambda = 15$. The diffusion coefficient for hydronium was $0.25*10^{-5}$ cm$^2$/s ($T=300$ K) and $0.48*10^{-5}$ cm$^2$/s ($T=353$ K) which agreed well with the previous simulation$^{14}$ and experimental values$^{17,18,19}$.

The density of bulk hydrated Nafion has been decreased with increasing hydration levels and with increasing temperature. The water and hydronium diffusion coefficient values have been increased with increasing hydration levels and with increasing temperature. This is consistent with the previous simulations and experiments.
The sulfur-sulfur radial distribution function (RDF) (Figure S2), sulfur-sulfur coordination number (CN) (Figure S3), sulfur-oxygen (water) CN (Figure S4), oxygen (water) - oxygen (water) RDF (Figure S5), layer resolved side chain orientations (Figure S6), water cluster distributions (Figure S7), film averaged in-plane water mean square displacement (Figure S8) and layer resolved in-plane water diffusion coefficients (Figure S9) have been shown below.

IV. Sulfur-Sulfur Radial Distribution Functions

Figure S2. Sulfur-Sulfur radial distribution functions (RDF) for different wall hydrophilicity values for (a) 8.7nm film (b) 11.5 nm film. The RDF values for bulk Nafion are also shown.
V. **Sulfur-Sulfur Coordination Number**

Figure S3. Sulfur-Sulfur coordination numbers (CN) for different wall hydrophilicity values for (a) 8.7nm film (b) 11.5 nm film. The CN values for bulk Nafion are also shown

VI. **Sulfur-Oxygen (Water) Coordination Number**

Figure S4. Sulfur-Oxygen (water) coordination numbers (CN) for different wall hydrophilicity values for (a) 8.7nm film (b) 11.5 nm film. The CN values for bulk Nafion are also shown
VII. Side Chain Orientation

Figure S5. Side chain orientation with respect to Z-axis for different film thickness values for (a) $\epsilon_{\text{phyl}} = 0.50$ kcal/mol wall (b) $\epsilon_{\text{phyl}} = 1.20$ kcal/mol wall (c) $\epsilon_{\text{phyl}} = 1.50$ kcal/mol wall. Relative distance ($t/T$) is defined as the distance from a wall ($t$) divided by the film thickness ($T$).
Figure S6. Radial distribution functions (RDF) for Ow-Ow for different wall hydrophilicity values for (a) 6.3 nm film (b) 8.7 nm film (c) 11.5 nm film. RDF for bulk Nafion has also been shown.
Figure S7. Water cluster distributions for cluster sizes from 100 to 2380 for different wall hydrophilicity for (a) 8.7 nm film (b) 11.5 nm film. Bulk Nafion water cluster distribution is also shown.
X. Mean Square Displacement

Figure S8. Mean square displacement (MSD) vs time plots for water in the planar direction (X and Y direction combined) for different wall hydrophilicity values (in kcal/mol) for (a) 6.3 nm film (b) 8.7 nm film (c) 11.5 nm film. Bulk Nafion MSD is also shown. The dotted line denotes a slope of unity.
XI.  Layer Resolved Diffusion Coefficients

Figure S9. Layer resolved in-plane water diffusion constants (D) normalized by two dimensional water diffusion constant (D$_{\text{bulk}}$) at $\lambda=15$ for bulk Nafion. Results are shown for (a) 8.7 nm and (b) 11.5 nm film for varying wall hydrophilicity. Relative distance (t/T) is defined as the distance (t) from a wall divided by the film thickness (T).
REFERENCES


