Atomistic and Coarse-grained Molecular Dynamics Simulation of a Sulfonated Cross-linked Poly (1, 3-cyclohexadiene)-based Proton Exchange Membrane

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Additional figures and tables are included here to support the findings of this work. Tables in this document include the hydration numbers of each type of CG bead calculated from xsPCHD polymer-water pair correlation functions (PCFs) (Table S.1), coordination number of each type of CG bead with hydronium ions evaluated from the polymer-hydronium ion PCFs (Table S.2). The tables correspond to the PCFs shown in Figure 4 in the text.

Figures in this document include the comparison of stretching (Figure S.1), bending (Figure S.2), torsion (Figure S.3) probability distribution functions (PDFs) from atomistic simulation of xsPCHD under unhydrated and hydrated ($\lambda = 10$) conditions. These figures are used to verify the use of the bonded CG potentials from previous work.

Confined Random Walk theory is also briefly introduced in the end.

λ	A	B	C	D
10	5.61	5.28	3.26	2.00
20	5.80	5.73	3.28	2.13

TABLE S.1: Hydration number of each type of CG bead with water evaluated from the PCFs within the distance 5.2 Å at two water contents.

λ	A	B	C	D
10	0.96	1.07	0.74	0.43
20	0.58	0.59	0.48	0.28

TABLE S.2: Coordination number of each type of CG bead with hydronium ions evaluated from the PCFs within the distance 5.4 Å at two water contents.

Figure S.1. Comparison of stretching probability distribution functions (PDFs) from atomistic simulation of xsPCHD under melt (red line) and hydrated (black line) conditions. No significant change is observed.

Figure S. 2. Comparison of bending probability distribution functions (PDFs) from atomistic simulation of xsPCHD under melt (red line) and hydrated (black line) conditions. No significant change is observed.

Figure S.3. Comparison of torsion probability distribution functions (PDFs) from atomistic simulation of xsPCHD under melt (red line) and hydrated (black line) conditions. No significant change is observed.

Confined Random Walk Simulations

Confined random-walk (CRW) simulations have been used to study diffusion in the presence of nanoscale confinement. The CRW simulations are essentially fits to MSDs from MD simulations. In MD simulations, self-diffusivity is calculated via Einstein relation, which relates self-diffusivity to infinite-time mean square displacement (MSD) as a function of observation time

$$D = \lim_{\tau \rightarrow \infty} \frac{\langle \vec{r}_i(t + \tau)^2 - \vec{r}_i(t)^2 \rangle}{2d\tau} \quad (1)$$

where d is the dimensionality of the system, $\vec{r}_i$ is the position of molecular i at time t and τ is the observation time. The angled brackets indicate an ensemble average over both individual particles and time origins, t . In an unconfined three-dimensional random walk (RW) simulation of non-interacting particles repeatedly selects velocities from the Maxwell-Boltzmann distribution and generates diffusivity

$$D = \frac{\langle \Delta r^2 \rangle}{6\Delta\tau} \quad (2)$$

where $\langle \Delta r^2 \rangle$ is the average displacement of a particle during a single step and $\Delta\tau$ is the time step size. The CRW theory introduces two parameters describing confinement: a cage size (r_c) and cage-to-cage hopping probability (p_c). For hydrated PEMs, a cage can be considered equivalent to a water cluster. The CRW simulations fit to MSDs of the short MD simulations by adjusting $\Delta\tau$, r_c and p_c . Importantly, it has been shown previously that the values of r_c and p_c obtained in this way are not meaningless fitting parameters but have the physical values quantitatively associated with their respective properties.

The purpose of including the CRW simulations are two-fold. First, they are computationally inexpensive. Thus, if it is computationally prohibitive to perform atomistic MD simulations out to the Einstein limit where the MSD is linearly proportional to the observation time, then the CRW simulations can be fit to short time (nonlinear) MSD obtained from short atomistic simulations and then used to extend the MSD out to the linear regime. The second purpose is in the generation of values of r_c and p_c , which are useful parameters for physical insight and are required for the percolation theory. More detailed information on the CRW simulations and their validation to test

systems is available in the literature.¹ Application of CRW to Nafion is also available in the literature.²

Supplementary Information References

(1) Calvo-Munoz, E. M.; Selvan, M. E.; Xiong, R. C.; Ojha, M.; Keffer, D. J.; Nicholson, D. M.; Egami, T. *Physical Review E* **2011**, 83.

(2) Esai Selvan, M.; Calvo-Munoz, E.; Keffer, D. J. *J. Chem. Phys. B* **2011**, 115, 3052.