Supporting Information

Theoretical Analyses on Water Cluster Structures in Polymer Electrolyte Membrane by Using Dissipative Particle Dynamics Simulations with Fragment Molecular Orbital Based Effective Parameters

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Functional forms of the potentials used in DPD

In Eq. (7) of the main text, the dissipative force $\mathbf{F}_{ij}^{D}$ is a hydrodynamic drag and is given by[1]

$$\mathbf{F}_{ij}^{D} = \begin{cases} -\gamma\omega^{D}(r_{ij})(\mathbf{n}_{ij}\cdot\mathbf{v}_{ij})\mathbf{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}, \qquad \text{(S1)}$$

where γ is a friction parameter related to the viscosity of the given system. $\omega^{D}(r_{ij})$ is the weighting function and the velocity difference is defined as $\mathbf{v}_{ij} = \mathbf{v}_j - \mathbf{v}_i$.

The random force $\mathbf{F}_{ij}^{R}$ corresponds to thermal noise and is governed by the parameter σ and another weighting function $\omega^{R}(r_{ij})$ as follows:[1]

$$\mathbf{F}_{ij}^{R} = \begin{cases} \sigma\omega^{R}(r_{ij})\zeta_{ij}\Delta t^{-1/2}\mathbf{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}. \qquad \text{(S2)}$$

The randomness is incorporated through the element ζ_{ij}, which is a randomly fluctuating variable with Gaussian statistics,

$$\langle\zeta_{ij}(t)\rangle = 0, \qquad \text{(S3)}$$

$$\langle\zeta_{ij}(t)\zeta_{kl}(t')\rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t') . \qquad \text{(S4)}$$

They are assumed to be uncorrelated for different particle pairs and time. There is a relation between two weighting functions and two parameters,

$$\omega^{D}(r_{ij}) = [\omega^{R}(r_{ij})]^2 \qquad \text{(S5)}$$

$$\sigma^2 = 2\gamma kT . \qquad \text{(S6)}$$

In our simulation, the weighting function was chosen as follows:[1]

$$\omega^{D}(r_{ij}) = [\omega^{R}(r_{ij})]^2 = \begin{cases} (r_c - r_{ij})^2 & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}. \qquad \text{(S7)}$$

The variable $\Delta t^{-1/2}$ in Eq. (S2) is used to ensure the consistent diffusion of particles independent of the step size of the integrations.[1,2]

The spring force $\mathbf{F}_{ij}^{S}$ for a polymer is considered as harmonic springs for the equilibrium bond distance $\boldsymbol{r}_s$ if i is connected to j,[1]

$$\mathbf{F}_{ij}^{S} = -C(\boldsymbol{r}_s - \boldsymbol{r}_{ij})\mathbf{n}_{ij}. \quad \text{(S8)}$$

The parameter set appeared in the above-mentioned equations is given in Table S1. Additionally, the actual a_{ij} parameters in $\mathbf{F}_{ij}^{C}$ are compiled in Table S2.

References

1 R. D. Groot and P. B. Warren, Dissipative Particle Dynamics: Bridging the Gap between Atomistic and Mesoscopic Simulation, *J. Chem. Phys.*, 1997, **107**, 4423.

2 R. D. Groot and T. J. Madden, Dynamic simulation of diblock copolymer microphase separation, *J. Chem. Phys.*, 1998, **108**, 8713–8724.

Table S1. The values of the parameters used in DPD potentials.

Parameter	Value
σ	3
γ	4.5
r_s	0.86
C	4.0

Table S2. The a_{ij} parameters used in this work.

Pair	Nafion	SPEEK
A-B	24.44	22.55
A-C	49.54	41.14
B-C	49.05	36.54
A-W	107.91	116.80
B-W	116.05	88.69
C-W	11.60	12.65
A-A	25.0	25.0
B-B	25.0	25.0
C-C	25.0	25.0
W-W	25.0	25.0

Figure S1. Plots of time-dependent water connectivity for SPEEK (circle) and Nafion (a) (diamond) in the case of 30 vol% water content.