Electronic Supplementary Information

for

Enhanced oxygen transport in ionomer films on platinum electrodes via a local electric field

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Note S1. Details of CPM

A constant potential method (CPM) is applied to control the electrostatic potential between two electrodes.[1] In this method, the charges of the electrode atoms are described as a Gaussian function, which are allowed to fluctuate during simulations to maintain the constant potential difference between two electrodes. The Gaussian function parameter for Pt electrodes is set to 19.79 nm^{-1}. The electrolyte atoms have a fixed charge. The CPM is conducted with the *conp* module implemented in LAMMPS.[2] In this module, 3D-periodic Ewald summation with shape corrections is applied to describe the slab geometry of system.[3] The model system contains two parallel Pt slabs with high potential and low potential, respectively, and the ionomer films as shown in Fig. S1. The given potential differences between high-potential electrode and low-potential electrode are 4 and 6 V.

Note S2. Details of simulation

The ionomer film is compressed in the Z direction by moving the potential wall until the ionomer density is equal to the density of the bulk PFSA membrane. Then, the following processes are performed: a) 1 ns NVT simulation at 1000 K using the L-J potential parameters (ε) reduced by two orders of magnitude; b) 1 ns NVT simulation to return the L-J potential parameters (ε) to the initial values and the temperature to 353 K to relax the system and eliminate the initial bias. Then, the potential wall is lifted to ~80 Å from the Pt electrode, followed by another 3 ns NVT simulation to make the configuration reach equilibrium. 1800 O_2 molecules are inserted into the gas region above equilibrium ionomer films. During MD simulations, those O_2 molecules are deleted from the simulation system when reaching the Pt electrode surface. Meanwhile, new O_2 molecules are continuously inserted in the simulation box to maintain a constant O_2 number. A NVT MD simulation for 10 ns is performed to ensure a steady-state permeation process and another NVT MD simulation for 15 ns is performed to collect data for analysis.

Note S3. Comparisons of CPM and FCM

CPM and fixed charge method (FCM) are compared in this subsection. To evaluate the given electric field, the electric potentials (ϕ_{layer}) between the Pt-ionomer interface and ionomer-gas interface are computed. As shown in Fig. S2a, the electric potentials, ϕ_{layer}, for the cases with uniform charge densities of 0.22, 0.45 and 0.67 e nm^{-2} and applied external potentials of 4, 6 and 8 V are in the range of -1.0 and 0 V, which are consistent with the real working potentials of cathode catalyst layers. Moreover, the density distributions of water molecules in the thickness direction based on the two methods are computed and shown in Fig. S2b. The simulated density distributions are the same based on the two methods, and the water density near the Pt electrode both increases in comparison with the case without an electric filed. Therefore, the differences in ionomer films structures based on the two methods are negligible. The Pt electrode is represented by a uniformly charged slab in the next simulations to save computational cost.

Note S4. Calculation of the diffusivity (D)

A NVT MD simulation for 10 ns based on equilibrium ionomer film configurations

(Fig. 1b) is performed at 353 K and 1.0 atm. The atom trajectory collected every 0.5 ps is used to calculate the diffusivity (D):

$$D=\frac{1}{6N}\lim_{\Delta t\to\infty}\frac{1}{\Delta t}\left[\sum_{\mathrm{i}=1}^{N}\left(\vec{r}_{\mathrm{i}}(t+\Delta t)-\vec{r}_{\mathrm{i}}(t)\right)^{2}\right] \tag{1}$$

where N is the total number of diffusion atoms, $\vec{r}_{\mathrm{i}}$ is the center position vector of the diffusion atom i, and t is the simulation time. Diffusivity is equal to the linear regime slope of mean squared displacement (MSD) curve as shown in Fig. S4 and Table S1.

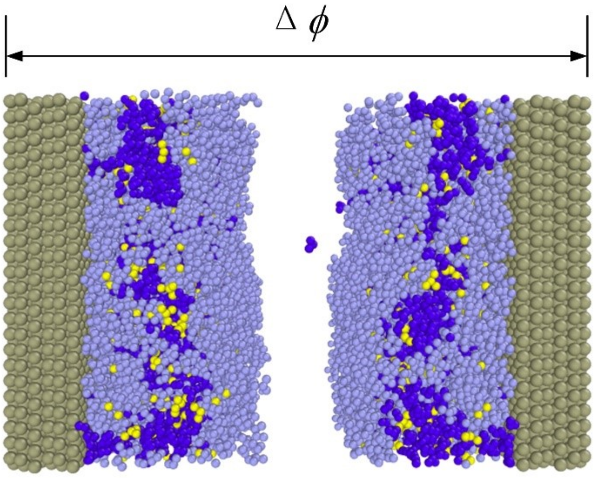

Figure S1. Schematic of simulation system using CPM in MD simulations.

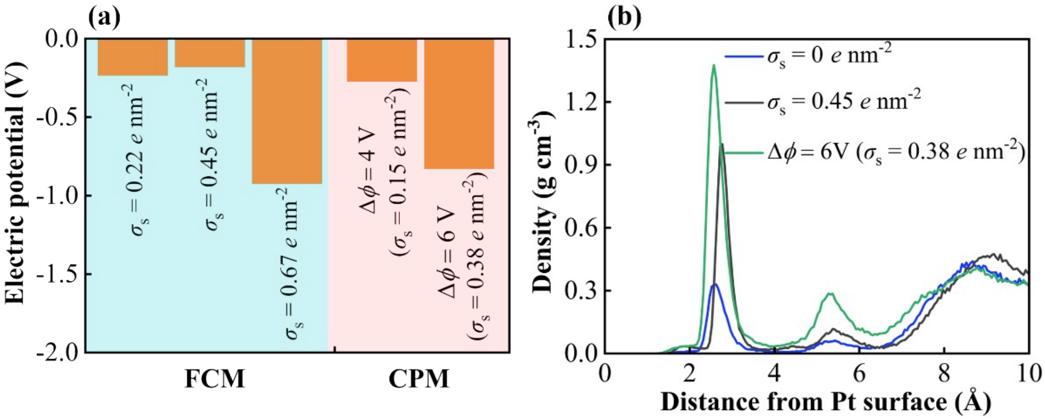

Figure S2. (a) Electric potential differences between the Pt-ionomer interface and ionomer-gas interface at different Pt surface charge densities (FCM) and different applied external potentials (CPM); (b) density distributions of water molecules in the thickness direction for the cases without electrical field and with a Pt surface charge density of 0.45 *e* nm^{-2} (FCM) and an applied external potential of 6 V (CPM).

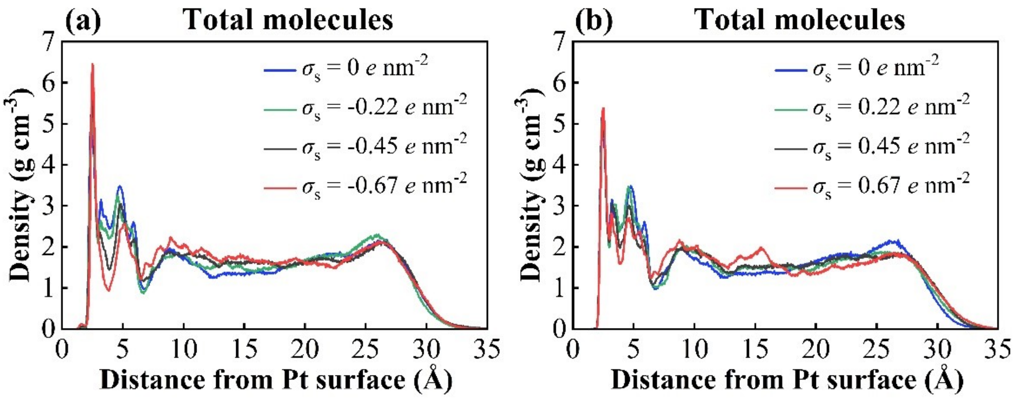

Figure S3. Density distributions in the thickness direction of all molecules for Pt surface charge densities of ±0.22, ±0.45, ±0.67 and 0 *e* nm^{-2}.

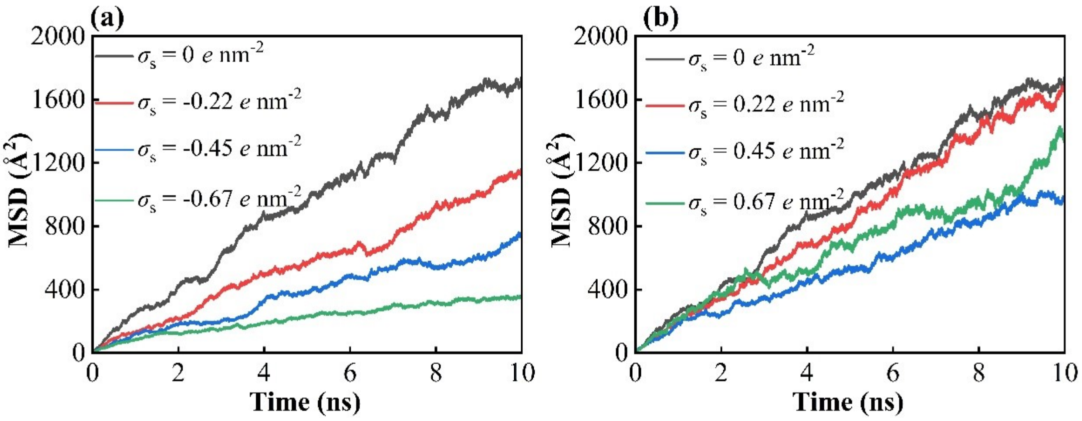

Figure S4. The mean square displacement (MSD) of hydronium ions for Pt surface charge densities of ±0.22, ±0.45, ±0.67 and 0 *e* nm^{-2}.

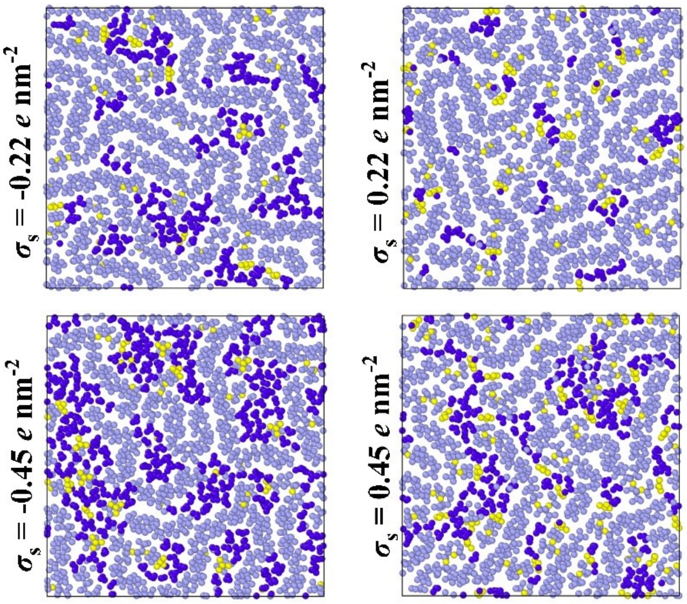

Figure S5. Snapshots of the X-Y plane at a distance of 7.3 Å from Pt electrode for surface charge densities of ±0.22 and ±0.45 e nm^{-2}. The light blue, yellow and dark blue beads represent the fluorocarbon groups of PFSA, sulfur/oxygen atoms.

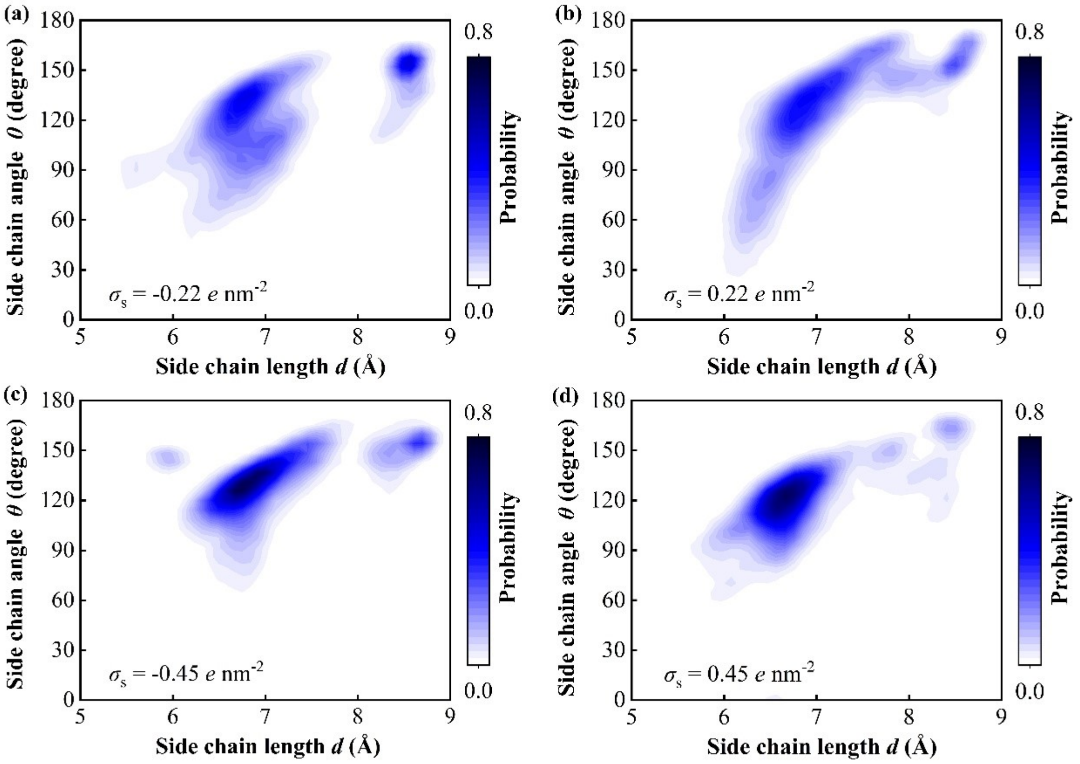

Figure S6. Probability distributions of *d* and *θ* of side chains for surface charge densities of ±0.22 and ±0.45 *e* nm^{-2}.

Table S1. Diffusion coefficients of hydronium ions for surface charge densities of ±0.22, ±0.45, ±0.67 and 0 *e* $\mathrm{nm^{-2}}$.

Charge density	Diffusion coefficient ($\mathrm{nm^2\ ns^{-1}}$)			
	0 *e* $\mathrm{nm^{-2}}$	0.22 *e* $\mathrm{nm^{-2}}$	0.45 *e* $\mathrm{nm^{-2}}$	0.67 *e* $\mathrm{nm^{-2}}$
Negative	17.85	11.04	7.06	3.83
Positive	17.85	17.29	9.97	11.37

References

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3 I.-C. Yeh and M. L. Berkowitz, J. Chem. Phys., 1999, **111,** 3155-3162.