

Molecular-Dynamics Studies on the Structures of Polymer Electrolyte Membranes and the Diffusion Mechanism of Protons and Small Molecules

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We performed a series of molecular dynamics (MD) simulations on Nafion[®] membranes which contain various quantities of water and methanol. The simulations gave a variety of nanoscale phase separated structures, such as cluster structures, channel structures, and cluster-channel structures. This is the first work that an atomistic MD simulation reproduced such nanoscale phase separations from random-phased amphiphatic polymer solutions. The calculated cluster-channel structure is consistent with the experimental results of X-ray diffraction [1]. We also investigated the diffusion coefficients of water, methanol and proton in these membranes. Estimated diffusion coefficients of water in the membranes so much depend on the water contents that the largest value is about 10 times as large as the smallest one, and these values are in qualitatively good agreement with the NMR results [2]. For proton, we employed semi-classical MD approach by using empirical valence-bond (EVB) method [3]. EVB-MD approach can reproduce the hopping transfer of proton and estimate a reasonable value of diffusion coefficient of proton. Furthermore, our simulation indicated that water was rarely found in the hydrophobic domains of the Nafion[®] membranes, whereas methanol penetrated into the hydrophilic / hydrophobic interfacial regions. We found that the methanol permeability around sulfonic groups is one-third of that in the water clusters. It means that methanol molecules are trapped by the hydrophilic groups of the membranes and the majority of methanol passes through the water clusters.

1. Introduction

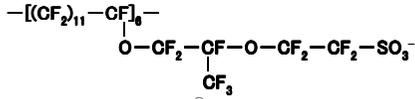
Direct methanol fuel cell (DMFC) is expected as a promising energy source for the next generation. Now, the polymer electrolyte membrane having both high proton conductivity and low methanol crossover is essential for the development of high efficiency DMFC. Nafion[®] is a typical polymer used for DMFC electrolyte membranes. It has been experimentally investigated with respect to its membrane structure and permeability of small molecules and ions. These experimental studies showed that the structures of polymer electrolyte membranes are significantly complicated, and details of the structures at a molecular level are still unclear. Diffusion mechanism of small molecules across the membrane has not yet been enough clarified either, since the information about the

membrane structure is indispensable for the investigation of diffusion mechanism.

In this work, we investigated the Nafion[®] membranes which contain various amounts of water and methanol based upon MD simulations using the force field parameters obtained from ab-initio calculations. In the following sections, nanoscale phase separation is reported, and the diffusion mechanism of small molecules is discussed.

2. Computational details

2. 1. Molecular model for Nafion[®] A molecular model for the Nafion[®] adopted in this work is presented in Fig. 1. Its molecular weight is 4753 and the density of sulfonic acid groups is 1.05 mmol/g.

Fig. 1. The Nafion[®] model used in the simulations.

Initial configurations of the systems were prepared as follows. After generating conformation of each Nafion[®] molecule using rotational isomeric states (RIS) scheme, the Nafion[®] molecules were randomly mixed with water, methanol, and proton at ratios shown in Table 1.

Table 1. Composition of the initial solution.

System	Nafion [®]	H ₂ O	CH ₃ OH	H ⁺
a	2	20	0	10
b	2	40	0	10
c	2	60	0	10
d	2	100	0	10
e	2	140	0	10
f	2	200	0	10
g	2	50	50	10
h	2	100	100	10
i	4	144	144	20

An example of the initial configuration of the whole system is presented in Fig. 2 for the system b. Initial densities of the system were set to be lower than experimental values such that the system could rapidly converge to the equilibrium state. Before starting the MD calculation, in order to the relax initial stress in the system, its configuration was optimized to show a minimum energy.

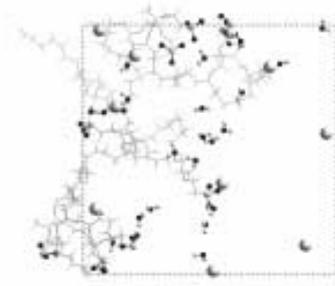


Fig. 2. The initial structure of the system b.

For the system i, flat membrane structure was generated as shown in Fig. 3.

In all cases, the initial structures were obtained using the Cerius² software package of Accelrys Inc.

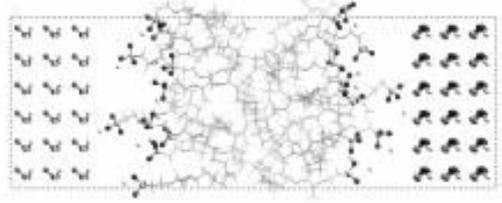


Fig. 3. The initial flat membrane structure for the system i.

2.2. Classical Force-Field functions Intra- and Intermolecular potential function for the molecule is of the form

$$\begin{aligned} V^{classic} = & \sum_{l=1}^{N_{bond}} \frac{1}{2} K_l^{bond} (R_l - R_l^0)^2 \\ & + \sum_{l=1}^{N_{angle}} \frac{1}{2} K_l^{angle} (\theta_l - \theta_l^0)^2 \\ & + \sum_{k=1}^{M_{torsion}} \sum_{l=1}^{N_{torsion}} \frac{1}{2} K_{k,l}^{torsion} \{1 - \cos(n_{k,l} \phi_l - \phi_{k,l}^0)\} \\ & + \sum_{l=1}^{N_{inversion}} \frac{1}{2} K_l^{inversion} (1 - \cos |\omega_l - \omega_l^0|) \\ & + \sum_{i=1}^{N_{non-1}} \sum_{j>i}^{N_{non}} D_0 \left\{ \left(\frac{r_{ij}^0}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right\} \\ & + \sum_{i=1}^{N_{non-1}} \sum_{j>i}^{N_{non}} \frac{q_i q_j}{r_{ij}} \end{aligned} \quad (1)$$

For Nafion[®] molecule, the DREIDING parameter set [4] was applied to the force constants of bonds and angles (K^{bond} , K^{angle}), dihedral angle parameters ($K^{torsion}$, n , ϕ^0) of side chain, and inversion parameters ($K^{inversion}$, ω^0). The AMBER [5] was applied to the vdW parameters (D_0 , R^0) for ether oxygen in the Nafion[®] molecule, and force constants of bonds and angles of methanol. For CF₂ and SO₃⁻ groups of Nafion[®], vdW parameters were taken from the references [6] and [7], respectively. Potential parameters reported in the reference [8] were adopted for the intermolecular interaction, equilibrium bond distance, and equilibrium bond angle parameters of methanol. Water was treated using a flexible TIP3P potential [9].

The other parameters are determined by ab-initio MO calculations. Equilibrium bond distances and bond angles for Nafion[®] molecule were calculated

at B3LYP/6-31G(d,p) level. The atomic charges were also calculated based upon the same level of calculations by CHELPG electrostatic potential fitting method. Dihedral angle parameters ($K^{torsion}$, n , θ) of the principal chain were fitted to the potential curve obtained from the MO calculations at HF/6-31G(d,p) level of calculation. All of the MO calculations were performed by using Gaussian98 program package [10].

2.3. Semi-classical treatment of proton: the EVB approach In this work, we modified the Tuckerman's empirical valence-bond (EVB) method [3] to estimate the diffusion properties of proton in electrolyte membranes. In the EVB approach, equations of motion of atoms on the potential surface, that is obtained from ab-initio molecular orbital or density functional calculations, are solved including multi-body effects.

Semi-classical potential function is defined as

$$V^{quantum} = \langle \Psi | H | \Psi \rangle = \sum_{i=1}^n a_i^2 V_{ii} + 2 \sum_{i=1}^{n-1} \sum_{j>i}^n a_i a_j V_{ij}, \quad (2)$$

where coefficient a_i is the i -th element of the eigenvector of H , and V_{ij} is the ij element of the H matrix.

The element V_{ii} is defined as

$$\begin{aligned} V_{ii} = & \sum_{l=1}^3 K_b^+ (1 - \exp[-a(r_l - r_0^+)])^2 \\ & + \frac{1}{2} \sum_{k=1}^{N_{H_2O}} \sum_{l=1}^{N_k} K_b(r_l - r_0)^2 \\ & + \frac{1}{2} \sum_{l=1}^3 K_\theta^+ (\theta_l - \theta_0^+)^2 \\ & + \frac{1}{2} \sum_{k=1}^{N_{H_2O}} \sum_{l=1}^{N_\theta} K_\theta (\theta_l - \theta_0)^2 \\ & + \sum_{j=1}^{N_{H_2O}} D_0^+ \left[\left(\frac{r_{ij}}{R_0^+} \right)^{12} - 2 \left(\frac{r_{ij}}{R_0^+} \right)^6 \right] \\ & + \sum_{i=1}^{N_{H_2O}-1} \sum_{j>i}^{N_{H_2O}} D_0 \left[\left(\frac{r_{ij}}{R_0} \right)^{12} - 2 \left(\frac{r_{ij}}{R_0} \right)^6 \right] \\ & + \sum_{i=1}^4 \sum_{l=1}^{N_{H_2O}} \sum_{j=1}^3 \frac{q_i^+ q_j}{r_{ij}} \\ & + \sum_{k=1}^{N_{H_2O}-1} \sum_{i=1}^3 \sum_{l>k}^{N_{H_2O}} \sum_{j=1}^3 \frac{q_i q_j}{r_{ij}} \end{aligned} \quad (3)$$

and V_{ij} is defined as

$$V_{ij} = V_{ij}^0 \exp[-b(r_{ij} - r_{eq})^2] + V_{end}. \quad (4)$$

We determined the potential parameters in eqs. (2)-(4) based on the Tuckerman and coworkers' ab-

initio MO calculation about $H_5O_2^+$ supermolecule [3]. Our EVB-MD approach adopted the semi-classical scheme for only one proton in the system, whereas the others are treated as classical particle. Ennari and coworkers' parameter [11] is applied for classical proton. Point charges of $H_5O_2^+$ are estimated in accordance with Wei and Salahub [12], in order to evaluate the interaction between semi-classical and classical layers.

2.4. MD conditions MD simulations were performed in NPT ensemble at $T=25$ and $P=0.1$ MPa using the Nosé-Hoover thermostat [13] and the Parrinello-Rahman algorithm [14], respectively. Equations of motion were solved by the RESPA algorithm [13, 15, 16] with multiple time steps shown in Table 7. The Ewald summation [17] was applied to estimate long-range electrostatic interactions using real space cut-off radius of $r_c=10$, gaussian distribution width of $\sigma=0.21$, and reciprocal vectors were taken up to $|\mathbf{n}|^2 \leq 30$. The Lennard-Jones (LJ) interaction was evaluated with a cut-off radius of 10 . Book keeping technique was also applied. All MD calculations were performed using our original MD code on SGI Octane, IBM RS/6000 44P workstations, and Intel Pentium4 based Linux-PCs.

3. Results and Discussion

3.1. Nanoscale phase separated structures of Nafion® Snapshots of the systems a, b, and f obtained from MD trajectories are shown in Figs. 4, 5, and 6 respectively. In the case of the system with a small content of water (system a), water clusters are generated in Nafion® membrane. Diameter of the cluster is about 10 . As the quantity of water increases (system b), water channels are formed, whose diameter is about 10 . Furthermore, when the system includes rich water (system f), the structure is constructed by both water clusters and channels connected with each other. The diameter of the present clusters is about 20 , and that of the channels is about 10 . In the water cluster, sulfonic acid groups of the polymer side chain protrude from the polymer. The present cluster-channel structure (system f) in Fig. 6 is consistent with the experimental results, the nanoscale phase-separated structure of Nafion® proposed by Gierke based on the small-angle X-ray scattering analysis [1]. It is interesting to find that our snapshot is quite similar to the structural model proposed by Gierke.

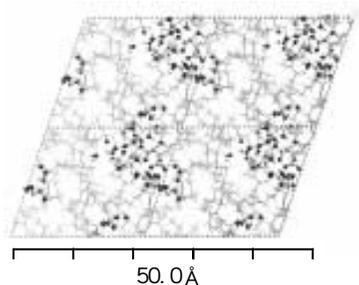


Fig. 4. Snapshot of system a.

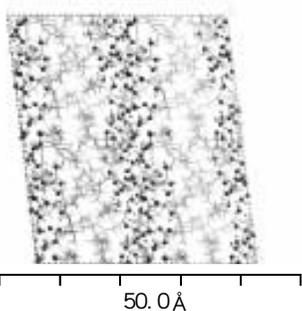


Fig. 5. Snapshot of system b.

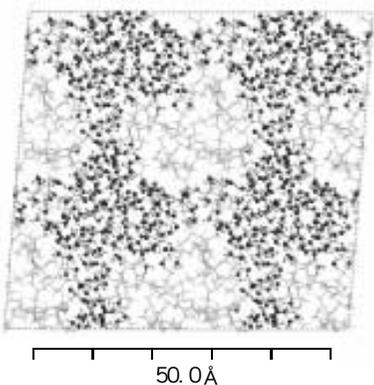


Fig. 6. Snapshot of system f.

3.1. Diffusion coefficients of water, methanol, and proton Diffusion coefficients of water, methanol, and proton in Nafion[®] (systems a-h) evaluated from the slope of the mean square displacement, from $t=2$ ps to 10 ps, are presented in Fig. 7 (a) as a function of water content. As water content in the membrane increases, the diffusion coefficient of water increases. Within this range of water content,

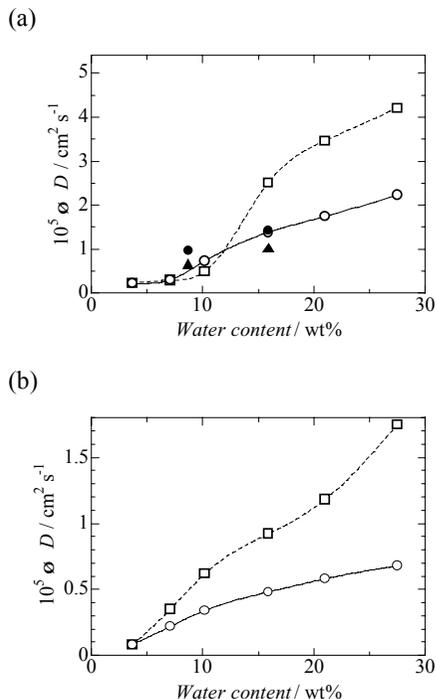


Fig. 7. Diffusion coefficient of water, methanol, and proton in the Nafion[®] membrane as a function of water content. (a) Calculated values, (b) experimental values [2], ○: water in Nafion[®] membrane which contains no methanol, ●: water in Nafion[®] membrane which contains methanol, ▲: methanol in Nafion[®] membrane which contains methanol, □: proton in Nafion[®] membrane which contains no methanol.

the largest value is about 10 times as large as the smallest one. We also found that the diffusion coefficient of proton was larger than that of water. This result implies that the protons in these systems are transferred by hopping.

The calculated diffusion coefficients are compared with experimental values from NMR and proton conductivity measurements [2] in Fig. 7 (b). The calculated diffusion coefficients of water and proton are larger than the experimental ones. The difference between the calculation and experiment may be caused by the smaller molecular weight of Nafion[®] model adopted in the present study. However, our calculation gives satisfactorily good results in respect to membrane permeability of water and proton. In fact, water content dependence of the calculated diffusion coefficients of water and

proton are in qualitatively good agreement with the experiment. Further, the calculation predicted a smaller diffusion coefficient for methanol than water, because methanol molecule is much larger than water molecule. The present result is consistent with the experimental study by Gottesfeld [18].

3.2. Methanol crossover Number density profile of atoms normal to the membrane are given in Fig. 8 for the systems i. The profiles clearly show that water molecules or protons are rarely found inside the membrane but many of protons are located around the sulfonic group. In contrast, a certain number of methanol molecules pass through the sulfonic group and penetrate into the hydrophilic / hydrophobic interface region. This indicates that methanol has stronger affinity for Nafion® principal chain than water.

Diffusion coefficients normal to the membrane D_x and parallel to it may also be defined D_{yz} as follows

$$D_x(x) = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle |x(t) - x(0)|^2 \rangle_x, \quad (5)$$

$$D_{yz}(x) = \frac{1}{2} \left[\lim_{t \rightarrow \infty} \frac{1}{2t} \langle |y(t) - y(0)|^2 \rangle_x + \lim_{t \rightarrow \infty} \frac{1}{2t} \langle |z(t) - z(0)|^2 \rangle_x \right], \quad (6)$$

where the average were taken over the molecules which were found in the region $x - \Delta x \leq x_i \leq x + \Delta x$ at $t=0$. Value of the diffusion coefficients were calculated from the slope of the mean square displacement from $t=2$ ps to 10 ps.

Methanol permeability coefficient P was also evaluated from the density profile ρ and the diffusion coefficient D_{yz}

$$P(x) = \frac{K \times \rho(x) \times D_{yz}(x)}{d}, \quad (7)$$

where the partition coefficient was assumed to be $K=0.4$ [18], and the membrane thickness $d=210 \mu\text{m}$ was adopted. Furthermore, we calculated the methanol crossover by

$$J(x) = P(x) \times \Delta c \quad (8)$$

where the concentration gradient was assumed to be $c=9.38 \times 10^{-4} \text{ mol cm}^{-3}$ (3 wt% methanol). The calculated methanol crossover is given in Fig. 9. The methanol crossover around sulfonic groups ($x=8, 32$) was estimated to be one-third of that the water clusters ($x=0, 40$). It means that

methanol molecules are trapped by the hydrophilic group of the membrane and the majority of methanol passes through the water clusters.

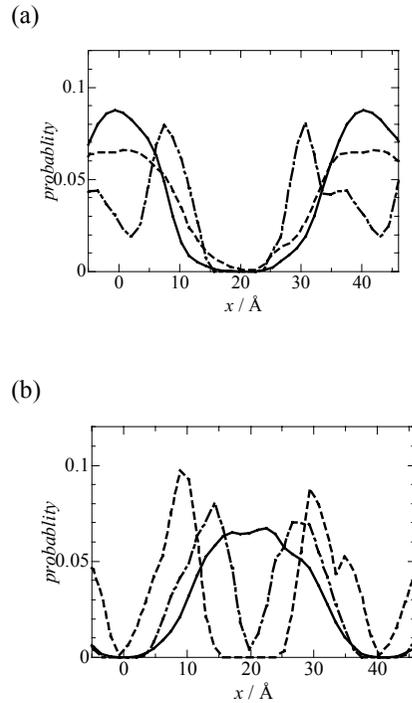


Fig. 8. Number density profile of atoms normal to the membrane for the system j. (a) Solid line: oxygen of water, dashed line: oxygen of methanol, dashed dotted line: proton, (b) solid line: fluorine of Nafion® principal chain, dashed line: sulfur of sulfonic acid group, dashed dotted line: ether oxygen of Nafion® side chain.

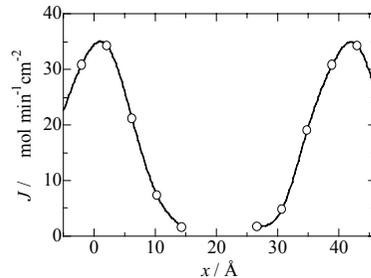


Fig. 9. Methanol crossover normal to the membrane for the system i.

4. Conclusions

We performed a series of MD simulations for Nafion[®] membrane which contains various amount of water and methanol using the force field parameters modified for Nafion[®] by ab-initio MO calculations.

The calculations gave a variety of nanoscale phase separated structures such as cluster structures, channel structures, and cluster-channel structures, depending on the contents of water and methanol. The calculated cluster-channel structure is consistent with the experimental results of X-ray diffraction. Our calculations indicated that water and proton were rarely found in the hydrophobic domain of the Nafion[®] membrane, whereas methanol penetrated into the hydrophilic / hydrophobic interfacial regions.

We also investigated the diffusion coefficients of water, methanol, and proton in the membrane. For the purpose of calculating diffusion coefficient of proton, we employed semi-classical MD approach by using empirical valence-bond (EVB) method. Although the calculation predicted larger diffusion coefficients than the experiment, their water content dependence is in qualitatively good agreement with the experimental result. Furthermore, we found that the methanol crossover around sulfonic group is as small as one-third of that in the water cluster. It means that methanol molecules are trapped by the hydrophilic group of the membrane and the majority of methanol passes through the water clusters.

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