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Molecular dynamics studies on the structures of polymer electrolyte membranes and diffusion mechanism of protons and small molecules

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ABSTRACT

We performed a series of molecular dynamics (MD) simulations on Nafion® membranes containing various quantities of H_2O and CH_3OH. The simulations afforded diverse nanoscale phase-separated structures, such as clusters, channels, and cluster–channels. The calculated cluster–channel structure qualitatively agrees with the experimental results of X-ray diffraction studies. We also investigated the diffusion mechanisms for H_2O, protons, CH_3OH, H_2, and O_2 in these membranes. To reproduce the hopping transfer of protons, we employed a semi-classical MD approach using the empirical valence bond method. The estimated diffusion coefficients of H_2O and proton in the membranes significantly depended on the H_2O content, and these values showed qualitatively good agreement with the experimental results. The diffusion coefficient of proton in H_2O-rich membranes was much larger than that of H_2O, and the proton mainly formed $H_5O_2^+$ complex. Furthermore, the simulation results indicate that the majority of CH_3OH permeates through the H_2O clusters, and the majority of H_2 and O_2 permeates through the hydrophobic region of the membrane.

1. Introduction

Soft materials, such as polymers, gels, surface-active agents, and liquid crystals, have attracted much attention because they show many types of morphology, e.g., cluster, cylinder, and layer structures, depending on the components or manufacturing processes. These unique structures are formed by diverse intermolecular interactions, e.g., van der Waals, coulomb, and hydrogen bonding interactions. For molecular design of soft materials, systematic investigations are desired to determine the relationship between the self-organization processes and intermolecular interactions.

Soft materials are used in many industrial applications because of their various functions arising from diverse structures. One of the most significant applications of soft materials is in polymer electrolyte fuel cells (PEFCs), and they are regarded as promising next-generation energy sources. Polymer electrolyte membranes with both high proton conductivity and low fuel (CH_3OH or H_2) crossover are essential for developing efficient PEFCs.

Dupont's Nafion® is a typical polymer used for PEFC electrolyte membranes. The membrane structure of Nafion® and its permeability of small molecules and ions have been experimentally investigated [1]. Gierke proposed a cluster–channel model based on X-ray diffraction (XRD) study [2]. In the model, the Nafion® membrane was assumed to form an unusual structure, in which several H_2O clusters formed inside the membrane were connected by narrow H_2O channels. The elevated uptake of H_2O/CH_3OH mixture by Nafion® membranes was observed by Nandan et al. [3]. During swelling of the membrane for use in direct methanol fuel cells, the mechanical properties worsen and the crossover rate (CH_3OH flux) increases. Additionally, the structures of the Nafion® membranes containing various quantities of H_2O or H_2O/alcohol mixture were analyzed by XRD [4,5], neutron scattering [6], atomic force microscopy [7], and vibrational spectroscopy [8,9]. The results showed that the structures of the polymer electrolyte membranes are very complex, and the details of the structures at a molecular level are still unclear. The diffusion mechanism of small molecules across the membrane has not yet been well elucidated. The information on the membrane structure is essential for investigating diffusion mechanism.

On the other hand, recent progress in both computer hardware and simulation methodology has made it possible to obtain reliable and useful information on the structure and dynamics of this membrane at a molecular level using molecular simulation techniques, such as molecular dynamics (MD), molecular orbital (MO) and Monte Carlo (MC) calculations [10–16]. Proton conduction mechanism and fuel crossover phenomena may be described in

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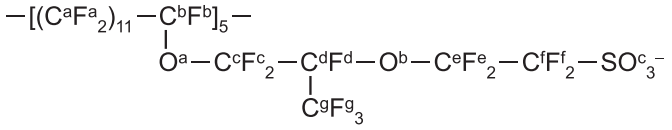

Fig. 1. Nafion® model used in the simulations.

Table 1
Composition of Nafion® solution.

System	Nafion®	H_2O	CH_3OH	H_2	O_2	H_2O_2	H^+
a	2	20	0	0	0	0	10
b	2	40	0	0	0	0	10
c	2	60	0	0	0	0	10
d	2	100	0	0	0	0	10
e	2	140	0	0	0	0	10
f	2	200	0	0	0	0	10
g	2	50	50	0	0	0	10
h	2	100	100	0	0	0	10
i	4	144	144	0	0	0	20
j	4	288	0	20	20	20	20

terms of diffusion paths if the structure of a membrane is known. Molecular simulations may also improve the design of polymer electrolyte membranes; a trial-and-error method is used at present.

In this study, we investigated Nafion® membranes containing various quantities of H_2O and CH_3OH by MD simulations using the force field parameters obtained from *ab initio* quantum–mechanical (QM) calculations. In the following sections, nanoscale phase separation and the diffusion coefficients of small molecules and proton are reported. In addition, the diffusion paths of H_2O, CH_3OH, H_2, and O_2 are examined in atomic resolution by quantitative properties such as the position dependent diffusion coefficients and the density profiles of the atoms. This information is useful in the molecular design of polymer electrolyte membranes with a low amount of fuel crossover.

2. Computational procedure

2.1. Molecular models and MD calculations

A molecular model for the Nafion® membrane used in this study is shown in Fig. 1, whose molecular weight is 4754 g/mol and the density of sulfonic acid groups is 1.05 mmol/g. In previous studies [17–21], the MD calculations were performed with polymer models of similar size to ours, and the simulated data for thermodynamic properties, dynamics of polymer chain, and gas permeability exhibited agreement with experimental results. In this study, we started our MD calculations from randomly mixed Nafion® molecules in H_2O to obtain a realistic membrane structure. The polymer membrane formed from this type of random initial configurations is completely free from any assumption for the structure.

The Nafion® random solution systems were prepared by the following scheme. After generating the torsion angles of each Nafion® chain randomly, the Nafion® chains, H_2O, CH_3OH, H_2, O_2, H_2O_2, and H^+ were randomly placed into the cubic unit cell with the appropriate number of molecules as shown in Table 1. An example of the initial structure is shown in Fig. 2 for system b. The initial density of the system was set to be lower than the experimental values to ensure rapid convergence to the (local) equilibrium state. Prior to the MD calculations, energy optimization at a constant volume was performed to relax the initial stress in the system.

For systems i and j, flat membrane structures were generated using the number of molecules shown in Table 1. The initial structure of system i is shown in Fig. 3. Energy optimization was also performed for systems i and j. For all cases, the molecular

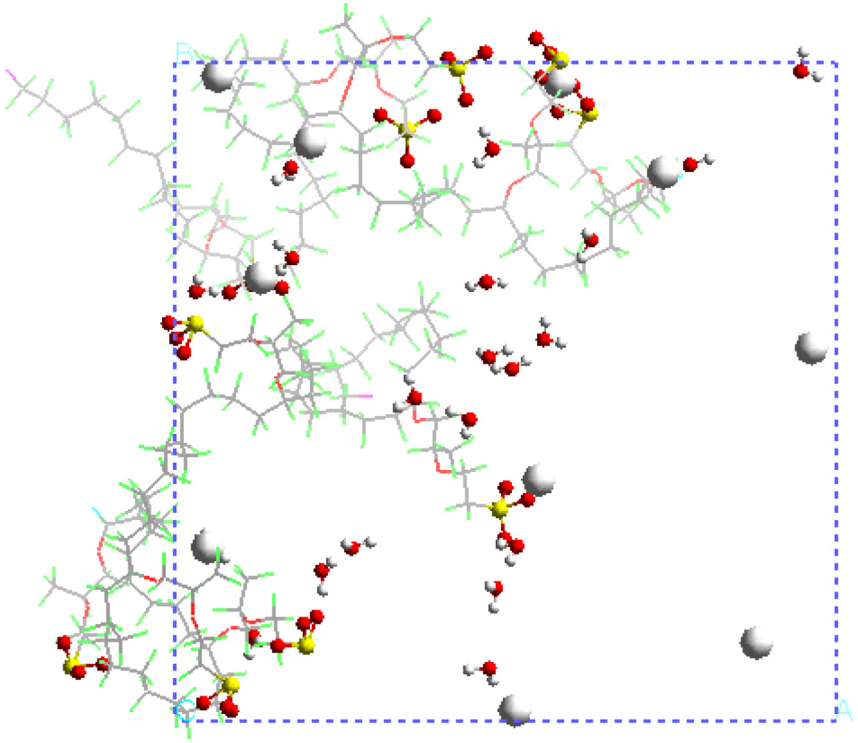

Fig. 2. Initial structure of system b.