Multiscale Simulation of a Polyelectrolyte Membrane for Fuel Cells

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A multiscale simulation is presented to study the proton-conducting polyelectrolyte membrane Nafion for a fuel cell. Firstly, the mesoscopic structure of the hydrated Nafion membrane was predicted by dissipative particle dynamics simulation. In this method, a molecular structure is represented using a coarse-grained model, and the interaction parameters are estimated by calculating the energy of mixing for each pair of components. A sponge-like structure was spontaneously formed. Secondly, an atomistic structure of the water channel is generated based on the obtained mesoscopic structure by mapping atoms to the concentration profile of each component using a Monte Carlo technique. Then, a molecular dynamics (MD) simulation is performed. The calculated self-diffusion coefficients of water molecule are consistent with the experimental study with respect to both the magnitude and dependence on the water content. The number of water molecules in the first coordination shell around the sulfonic acid group decreases with a reduction in the water content. Thirdly, the electronic state is calculated for a hydronium ion explicitly accounting for the ambient electrostatic energy by the mesoscopic structure. The distribution of the dielectric constant is defined on the basis of the mesoscopic structure and a hydronium ion is then placed in the water region. By iteratively solving Poisson's equation for the electrostatic potential and Schrödinger's equation for the electronic state, the energy of the hydronium ion is obtained. We compared the stability of a hydronium ion in the mesoscopic structure.

1. Introduction

A proton-conducting membrane is a key component of fuel cells. It is supposed for the structure of the hydrated Nafion, a perfluorinated sulfonic acid membrane, that water clusters surrounded by sulfonic acid groups are interconnected [1]. The proton then transfers through these channels. In this system, therefore, the transport property of the proton depends on both the mesoscopic and atomistic structures of the membrane. Furthermore, it is crucial to consider electronic state of a hydronium ion in the membrane for the consideration of the Grotthus-type proton transfer mechanism [2].

Although an atom-based simulation such as the molecular dynamics method has come into wide use for materials design [3,4], it is less realistic when predicting a mesoscopic structure because of the limitation of time- and length-scale involved in the simulation[5]. Therefore, cooperation between the atomistic and mesoscopic simulations is required for an effective materials design of a membrane for a fuel cell system. In this study, we present a hierarchical procedure bridging the gap between the mesoscopic and atomistic simulations in order to study the polyelectrolyte membrane.

2. Method

A multiscale simulation is performed by bridging the different scale calculations from large scale (mesoscopic) to small scale (electronic state). Details are described in the following sections.

2.1. Mesoscopic Simulation The mesoscopic structure of the hydrated Nafion membrane is predicted by a dissipative particle dynamics (DPD) simulation [6,7]. In this method, a molecular structure is represented using a coarse-grained model. The Nafion polymer molecule is modeled by connecting soft spherical particles, which correspond to a group of several atoms, roughly 0.61 nm in diameter. The unit cell, in which the periodic boundary conditions are considered in all directions, has the length of about 28.4 nm and 10-30 vol% water contents. It contains 192,000 DPD particles at the reduced density of ρ =3.

The Flory-Huggins interaction parameters for the DPD simulation are estimated by calculating the energy of mixing for each pair of components. This system is characterized by the nature of the miscibility between water and the hydrophilic end particles of the side chain and immiscibility between the water and Nafion backbone particles.

2.2. Molecular Dynamics Simulation According to the simulated mesoscopic structure obtained by the DPD, a molecular structure is generated by mapping atoms to the position at the corresponding DPD particles. After generating the atom-based molecular models, we perform molecular mechanics (MM) and molecular dynamics (MD) simulations to obtain a stable structure without stress.

The partial charges were estimated using the Gasteiger procedure [8] and the molecule of water was presented by the SPC/E potential [9]. A molecular dynamics run of 200-400 ps was then performed using the NVT ensemble with a Dreiding forcefield [10]. The temperature was 298 K in all the calculations. The van der Waals and coulombic non-bonding interactions were calculated using the Ewald summation method. After the system reach an equilibrium state, the number of water molecules coordinating to the sulfonic acid groups are counted. The diffusion coefficient of the water molecules is determined using the plot of the mean square displacement as a function of time.

2.3. Electronic State Calculation The electronic state is calculated for a hydronium ion accounting for the ambient electrostatic energy by the mesoscopic structure. We define the distribution of the dielectric constant from the mesoscopic structure, and then set a hydronium ion. The electrostatic potential of the mesoscopic region ϕ is determined by solving the following Poisson's equation using the finite differential method (FDM),

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon} - \frac{1}{\varepsilon} \nabla \varepsilon \cdot \nabla \phi . \tag{1}$$

The additional external potential V_ϕ due to the surrounding mesoscopic inhomogeneous structure is obtained through the atomic charges of the hydronium ion and the electrostatic potential ϕ. The electronic state calculation of the hydronium ion is then performed by calculating Schrödinger equation (Eq. 2) based on the density functional theory (Becke & Lee-Young-Parr exchange-correlation potential) using the Gaussian-finite element (FE) mixed basis method [11],

$$H \Psi = E \Psi \quad . \tag{2}$$

where

$$H = -\frac{h^2}{8\pi^2 m} \nabla^2 + V + V_\phi . \tag{3}$$

and the atom-centered charges are obtained. The above operations are iteratively continued until the convergence state is obtained. The energy of the hydronium ion is then estimated.

3. Results and Discussion

In the mesoscopic simulation, a sponge-like structure was spontaneously formed as shown in Fig. 1; water particles and hydrophilic particles of the polymer side chains formed aggregates and were embedded in the hydrophobic phase of the polymer backbone. In this figure, the Nafion polymer skeletons are illustrated by flexible rods and water particles are denoted by spheres. The cluster size and its dependence on the water content were in agreement with previous reports [1]. The mesoscopic structure of the channel region can be utilized for the following atomistic simulation.
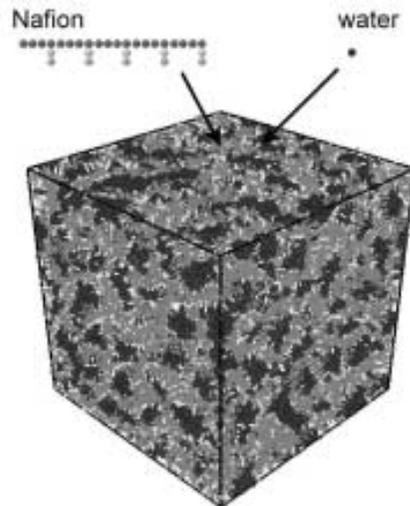

Fig. 1. Mesoscopic structure of the hydrated Nafion membrane calculated by DPD simulation (water content $H_2O/SO_3H = 6.0$).

Several atomistic structures of a water channel are obtained for different water contents as shown in Fig. 2. Each cell consists of 12 Nafion dimers, 24 protons, and water molecules of (a)284, (b)144, and (c)64. The densities of the system were (a)1.67, (b)1.84, and (c)1.97 g/cm^3. The sizes of the system were (a)2.31×2.31×6.16, (b)2.31×2.31×5.16, and (a)2.31×2.31×4.58 nm. A molecular dynamics simulation was then performed to analyze the structure and the dynamics of the water around the sulfonic acid group which is located on the end of the side chain of Nafion.

Coordination structures were observed for each water contents. Figure 3 shows an example for the case (a) λ=11.8. Coordinating water molecules around the sulfonic acid group are indicated by spheres. The radial distribution function for pairs formed by the atoms of sulfur (S) in the sulfonic acid group and the oxygen (O) in water was calculated as shown in Fig. 4. As a result, the sulfonic acid group was coordinated to the water molecule within 0.5 nm. The number of water molecules in the first coordination shell around the sulfonic acid group was about 8, which is the same magnitude as the experimental study [12].

Figure 5 shows the dependence between the coordination number and the water content. The coordination number increases with the increasing water content until λ=6. The number of water is almost unaffected by the water content over λ=6. This is due to the space limitation of hydration to the sulfonic acid group in the first coordination shell. It is also recognized that water molecules scarcely coordinate to the oxygen atoms in the middle of the side chain. This implies that only the end of the side chain including the sulfonic acid group comes in contact with the water region.

The calculated self-diffusion coefficients of water molecules are shown in Fig. 6. The simulated diffusion coefficients were found to vary from 1-7×10^{-6} cm^2/s, which are consistent with the experimental study [13] with respect to both the magnitude and dependence on the water content.

The electronic state is then calculated for a hydronium ion explicitly accounting for the ambient electrostatic energy by the mesoscopic structure. As shown in Fig. 7, the distribution of the dielectric constant is defined on the basis of the mesoscopic structure and a hydronium ion is then placed in the water region. In this figure, the distance from the sulfonic acid group is 0.14 nm at position A, and 1.5 nm at position B. By iteratively solving the Poisson's equation for the electrostatic
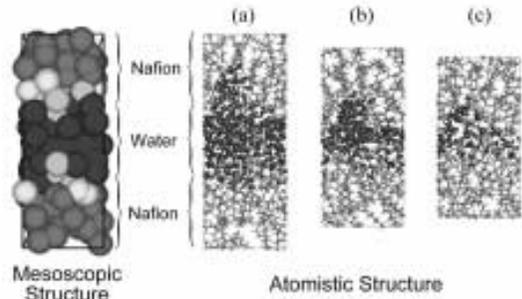

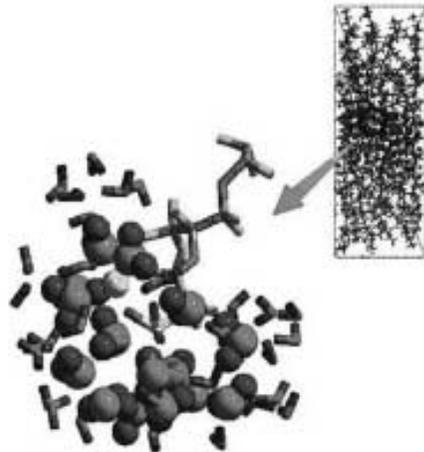Fig. 2. Atomistic structures based on the mesoscopic structure; water content λ = H$_2$O/SO$_3$H, (a) 11.8, (b) 6.00, and (c) 2.67.

FIg. 3. Coordination structure of water molecules around the sulfonic acid group in the atomistic structure for the water content H$_2$O/SO$_3$H =11.8 (right). Coordinating water molecules are indicated by spheres.
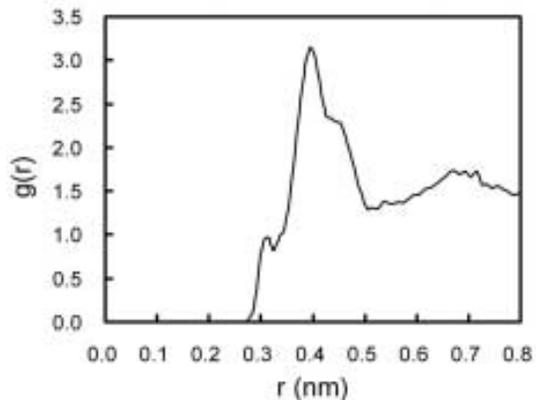

Fig. 4. Atomistic structures based on the mesoscopic structure; water content λ = H$_2$O/SO$_3$H, (a) 11.8, (b) 6.00, and (c) 2.67.

potential and Schrödinger's equation for the electronic state, the energy of the hydronium ion is obtained. We compared the stability of a hydronium ion in the mesoscopic structure and found that a hydronium ion at position B is 48.1 kcal/mol more stabilized compared with position A due to the dielectric polarization effect of the mesoscopic structure.

4. Conclusions

We have proposed a cooperative procedure to bridge the gap between atomistic and mesoscopic simulations and successfully demonstrated this method for the polyelectrolyte membrane for fuel cells. The mesoscopic structure of the hydrated Nafion membrane was cleared, and the diffusion coefficient of water molecules and the number of water molecules in the first coordination shell around the sulfonic acid group could be predicted. We found that a hydronium ion is more stabilized in the middle of a water cluster because of the dielectric polarization effect of the mesoscopic structure.

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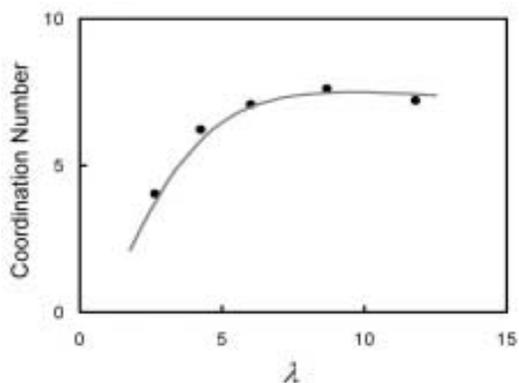[13] T.A.Zawodzinski, Jr., *et al.*, *J. Phys. Chem.*, **95**, 6040 (1991).

Fig. 5. Coordination numbers as a function of the water contents λ.
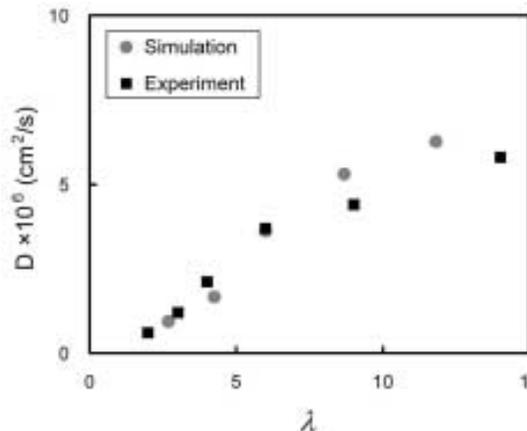

Fig. 6. Self-diffusion coefficients of water molecules obtained by molecular dynamics simulation for various water contents λ compared with the experimental study [13].
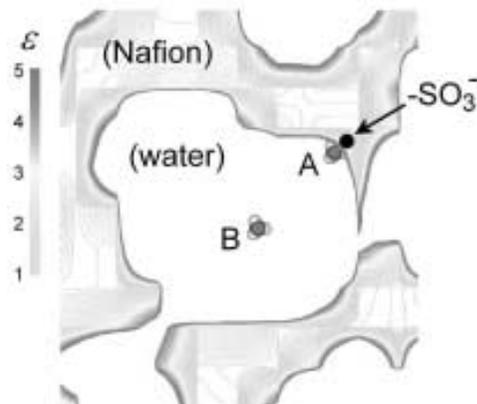

Fig. 7. Hydronium ions in the water cluster of the hydrated Nafion membrane for the water content $H_2O/SO_3H = 11.8$. The distribution of the dielectric constant in the Nafion region is indicated by the contours.