The Nature of Proton Conduction in a Polymer Electrolyte Membrane, Nafion

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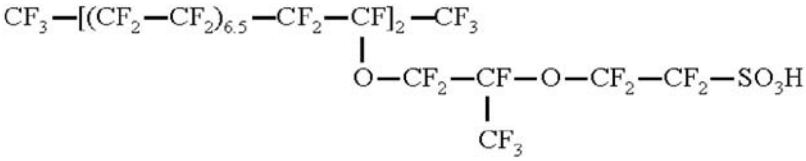
Introduction

Proton transport in the aqueous environment has attracted much attention for more than a century. It is well known that protons are transported by the Grötthuss mechanism (proposed two hundred years ago), which is sometimes referred to by terms such as proton jumping and proton hopping. However, the proton transport mechanisms in constrained systems such as biological membranes, electrolyte membranes and minerals are rather vague, despite the fact that proton transport plays an important role in the functionality of such systems. The focus of study in this paper is a polymer electrolyte membrane, which is placed between the anode and cathode in polymer electrolyte fuel cells (PEFCs). Detailed knowledge of the proton transport mechanisms in these membranes is extremely important because the generation of power by fuel cells is limited by proton conduction. The nature of the proton conduction in such a constrained environment is also very interesting from a purely scientific point of view. Nafion is a membrane widely used in PEFCs due to its very good proton conductivity. Several mechanisms of proton transport have previously been proposed in the literature, but have not yet yielded precise descriptions on the atomistic level; various details of these mechanisms are still unclear and controversial. We believe that this lack of consensus regarding the proton conduction mechanisms results mainly from a lack of direct and unambiguous information provided by experimental studies. However, such an investigation may be more suited to highly sophisticated molecular simulations. Therefore, in the present paper, we have applied first-principles molecular dynamics simulations to investigate the nature of the proton conduction in Nafion.

Computational Details



$CF_3-[(CF_2-CF_2)_{6.5}-CF_2-CF]_2-CF_3$ with side chain $O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$

Figure 1. Schematic illustration of modeled Nafion

To obtain reasonable initial configurations for the use of the first-principles MD simulations, we started by carrying out classical MD calculations. Nafion was modeled as a polymer consisting of two monomers, as described in Fig. 1. Because a computation of the entire Nafion structure including cylindrical channels of water clusters with the first-principles MD is not possible, we examined the basic sandwich structure consisting of the water region with hydrophilic side chains and surrounding hydrophobic regions. The MD simulations were carried out in a periodic three-dimensional cell, in which Nafion and water were stacked in the z-direction. Models with two different water contents were examined. The lattice constants of the x- and *y*-axes were fixed in order to represent the surface area of the micelle that was occupied by each sulfonic acid end group. The lattice constant of the *z*-axis was determined in order to represent the composite density of dry Nafion and water at a temperature of 363 K. The molecular numbers and the lattice constants of unit cells in the models are listed in Table 1. In the present study, two humidity levels, water content (λ = number of water molecules/number of sulfonic acid groups) equal to 4.1 and 12.7, were considered and hereafter we call the former the *L-state* (*low water content state*) and the latter the *H-state* (*high water content state*). Fujitsu Materials Explorer 3.0 was used for this simulation, which was performed assuming the *NVT* ensemble at 363 K using the Nosé–Hoover thermostat. The total simulation time was approximately 200 ps with a time step of 0.2 fs. The proton that originated from the sulfonic acid end group was treated as a hydrated ion (H_3O^+). H_2O and H_3O^+ molecules were treated using the extended simple point charge (SPCE) water model. The Dreiding force field was adopted for all of the intramolecular potential forces of Nafion. Universal force field (UFF) parameters were used to model the nonbonded interactions between H_2O (H_3O^+) and Nafion. The point charge present on each atom was determined by the electrostatic potential (ESP) method after molecular orbital calculations. Snapshots of the simulated final configurations of Nafion/water complexes are shown in Fig. 2. The hydrophilic side chains were oriented toward the water region, and thus, the two-phase structure was maintained. Then, using the configurations obtained from the classical MD simulation as an initial configuration, first-principles MD simulations were performed. The electronic structures of the systems were evaluated by means of density functional theory in the Kohn–Sham formalism. We used the generalized gradient approximation in the Perdew–Burke–Ernzerhof (PBE) form, which is expected to give an accurate description of the hydrogen bonds. Separable norm-conserving pseudopotentials were employed, and only the Γ point was used to sample the Brillouin zone. Adaptive finite elements were used in place of ordinary plane waves for the basis set. All production runs in the present paper were performed with an average cutoff energy of 57 Ry, while the resolution was approximately doubled at the positions of fluorine and oxygen atoms by adaptation of the grids. In the molecular dynamics part, the nuclei were treated classically, and their equations of motion were integrated using the velocity–Verlet algorithm with the forces calculated from the electronic structure. The temperature was controlled by the Berendsen thermostat with a target temperature of 353 K. All hydrogen atoms in the system were given the mass of deuterium to allow the use of a large time step of 1.21 fs in the production run. However, the deuterium atoms are denoted by “H” in the following analysis whenever there is no possibility of confusion. During the molecular dynamics simulations, the electronic states were quenched to the Born–Oppenheimer surface at every time step with the

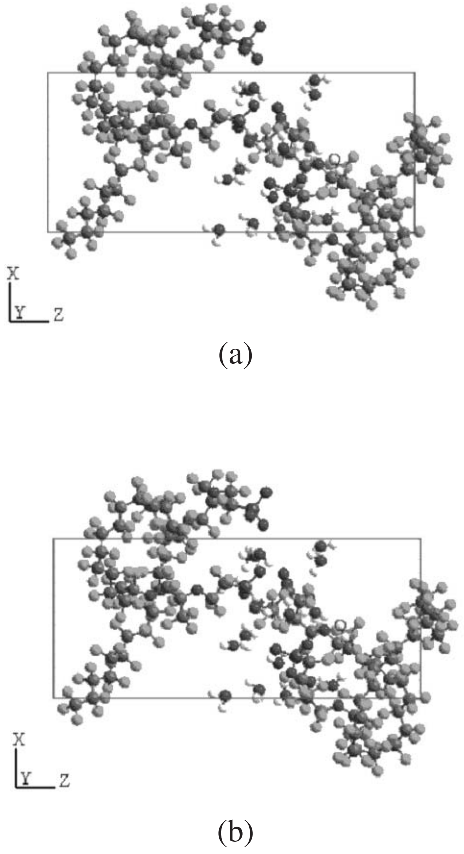


Figure 2. Snapshots of the configurations of (a) *L-state* and (b) *H-state*.

limited-memory variant of the quasi-Newton method. The wave functions were extrapolated from previous time steps. First, equilibration runs up to 10 ps were carried out without an electric field and further simulations without an electric field were carried out up to 20 ps. Then, we performed simulations considering an electric field up to 10 ps. All of the calculations were carried out with our own finite element DFT code *FEMTECK* (Finite Element Method-based Total Energy Calculation Kit). The above method has been successfully applied to liquid molecular systems. The electric field was evaluated using the Berry phase theory, which is most appropriate for treating disordered systems under periodic boundary conditions. We applied an electric field of 0.5 V/nm along the x-direction of the cells to achieve acceptable statistical accuracy at reasonable computational cost, while avoiding noticeable changes in liquid structures. In the present study, because of the limitation of the model, we mainly focus on proton dynamics occurring within a few Å (~8 Å) from $-SO_3^-$. Proton transport from one hydrophilic pocket to another one is beyond the target of the present investigation.

Table 1 Summary of simulation conditions

	Condition	
	L-state	*H-state*
Molecule numbers in a unit cell		
N_{Nafion}	2	2
$N_{\mathrm{H_2O}}$	13	47
$N_{\mathrm{H_3O^+}}$	4	4
Water content λ		
$\left(N_{\mathrm{H_2O}} + N_{\mathrm{H_3O^+}}\right) / N_{\mathrm{SO_3^-}}$	4.25	12.75
Size of unit cell		
x/Å	12.3042	12.3042
y/Å	12.3042	12.3042
z/Å	28.1239	35.1549

Results

At first, we investigate the size and the connectivity of water clusters. The results of cluster analysis shown in Fig. 3 indicate, the hydrogen bond network in the *L-state* is not continuous, forming small water clusters. In contrast, the network is connected to a large extent in the *H-state*, as in bulk water. This feature is in agreement with the result of a classical MD study which employed much larger model systems than ours.

According to the analysis of the trajectories, in agreement with experimental observations, the diffusion coefficient of protons in the *L-state* is calculated to be much smaller than that in the *H-state.* To investigate the origin of the slow proton diffusion in the *L-state* in more detail, we analyzed the hopping probability of the protons. We obtained hopping probabilities of 5.6% for the *H-state* and 4.5% for the

L-state. During 100 simulation time-steps, this implies that proton hopping occurs on average 5.6 times in the *H-state* and 4.7 times in the *L-state*. The difference between the hopping probabilities in the two states is small, a result that is at odds with the general concept of the vehicular mechanism. Thus, the question arises as to why the proton diffusion in the *L-state* is much slower. An answer can be found by examining the nature of the proton hopping in the *L-state*. As described above, the hydrogen bond network of water in the *L-state* is broken to some extent. Therefore, Grötthuss-like structural diffusion is permitted only within the water clusters. Thus, the water molecules in the *L-state* behave analogously to those in supercritical conditions. The disconnected hydrogen bond network of water in the *L-state* causes proton transfer to occur in a *non-constructive* manner; a proton is transferred temporarily from a water molecule to its neighboring molecule by hopping, but then returns to its original location (Details see Fig. 4). In contrast, as seen in Fig. 4, we can also define proton transfer that contributes constructive to proton conduction. Many proton transfers within small water clusters in the *L-state* can be described as non-constructive, and these processes do not contribute significantly to the actual diffusion of protons. The accurate microscopic description of proton motion revealed from the simulations is accordingly completely different to that of the vehicular mechanism, which assumes protons transport as bonded to a “*vehicle*” water. The extraordinarily high mobility of protons in an aqueous environment has been explained by the concept that proton hopping facilitates proton conduction significantly. However, our computations reveal, in contrast to the generally accepted concept, that the occurrence of proton hopping alone does not guarantee good proton mobility. What is equally important is the structure of water hydrogen bond network, which limits paths that protons can travel around. Poor and good conductivities of protons inside Nafion, therefore, can be reasonably explained by the ratio of the constructive and non-constructive proton transfer events. An increase of the occurrence of the former relative to the latter increases the mobility of protons.

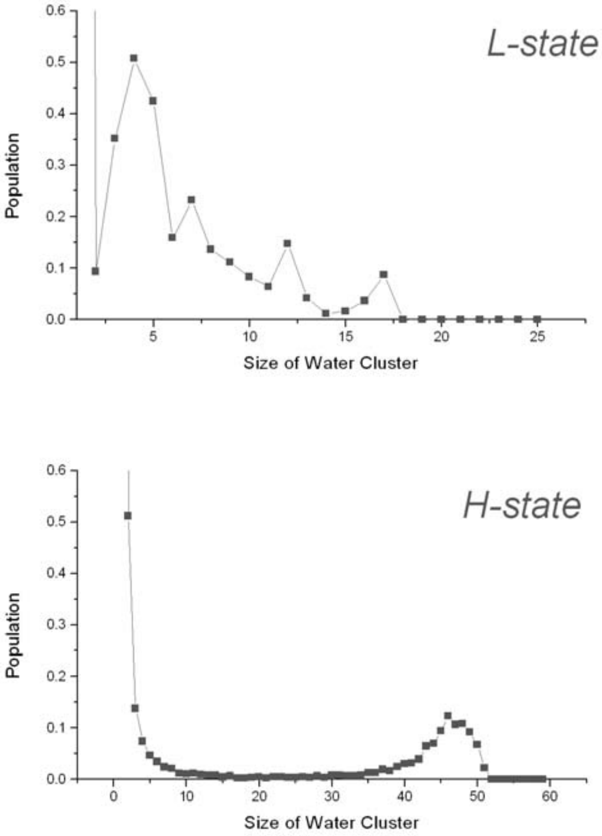


Figure 3. Results of the cluster analysis. A hydrogen bond was said to be present if the O···H bond length was less than 2.0 Angstrom. In this analysis, we identified clusters of water molecules connected by a hydrogen bond network in all snapshots. The number of water molecules in each cluster was then extracted and the average population of each size of cluster was calculated. Populations of clusters with a variety of sizes were found in the *L-state*. Conversely, the population of clusters composed of 10 - 40 water molecules in the unit cell was nearly zero in the *H-state*, which indicates that water molecules in the H-state have very similar character to those in bulk water.

More details of our results such as proton dynamics occurring next to sulfonic group will be presented at the meeting. Here we summarize main conclusions derived from our findings. we have used first-principles MD simulations to investigate the nature of proton conduction in Nafion. The hydrogen bond network of water is completely different in the *L-state* and *H-state*, being discontinuous in the former and continuous in the latter. Analysis of the trajectories for each state shows that the proton hopping probability has little dependence on water content. For the *L-state*, our simulations show that the diffusion coefficients of the protons and water are very similar, which is in accord with previously reported experimental observations. However, the results of our simulations demonstrate that the previously proposed explanation for the slow diffusion in terms of a simple vehicular-like mechanism does not correctly describe the motion of protons on an atomistic level. Indeed, proton hopping between adjacent water molecules occurs in both the *L-state* and *H-state*, but due to the disconnected nature of the water hydrogen bond network in the *L-state*, this type of proton hopping does not contribute constructively to the proton conduction.

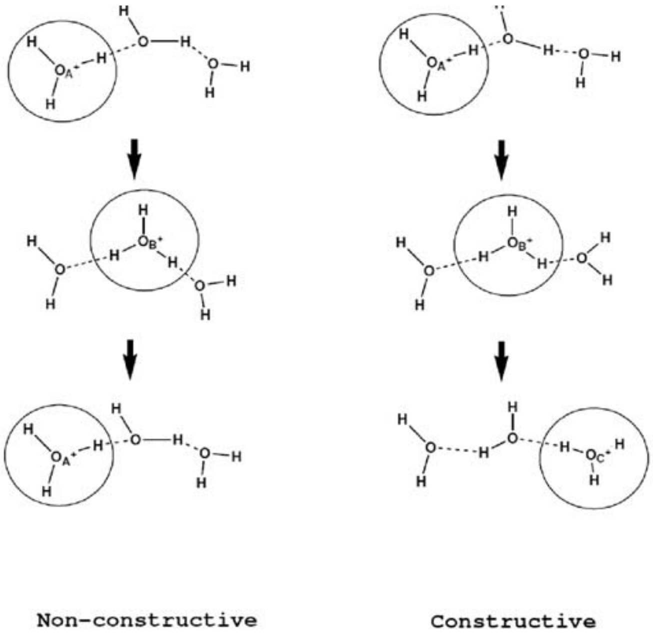


Figure 4. The constructive proton transfer is the transfer of a proton that moves further away from its original location. The non-constructive proton transfer is the transfer of a proton that comes to the position of the oxygen site of the original water in the end. Contribution to proton conduction is larger in the former and smaller in the latter.

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