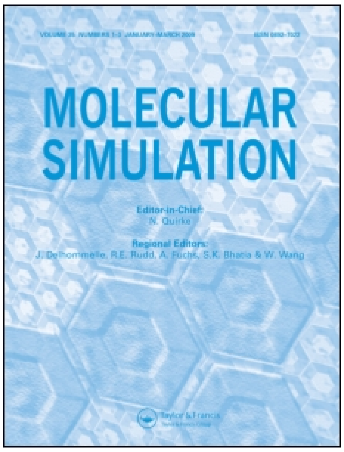

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Behaviour of water molecules in Nafion 117 for polymer electrolyte membrane fuel cell by molecular dynamics simulation

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Proton exchange membranes play a critical role as electrolytes for proton transports in polymer electrolyte membrane fuel cells. A membrane, such as Nafion 117, consists of a polytetrafluoroethylene backbone and side chains that terminate with sulfonate groups ($\mathbf{SO_3^-}$). During operation of fuel cells, membranes become preferentially hydrated by absorbing water needed for effective proton conduction. Water management and movement, therefore, are extremely important for the efficient operation of the fuel cells. In this paper, we set up the molecular models for hydrated Nafion 117 and perform molecular simulations for various temperatures and monomer numbers to analyse the motion of water and hydronium molecules. Diffusion coefficients estimated from the mean-square displacements agree well with the experimental estimation. The distribution and structure of water molecules in Nafion 117 are analysed using radial distribution functions and Voronoi tessellation. The result shows that the distribution of water molecules in the Nafion membrane is quite close to that of hexagonal ices but quite deviated from that of pure water molecules.

Keywords: Nafion 117; PEMFC; self-diffusion coefficients; Voronoi tessellation; water; molecular dynamics simulation

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has received increasing attention as a highly promising power source for vehicles, mobile electronic equipments and other applications. It is expected that the PEMFC will begin to replace conventional power engines within next decades.

During the normal operation of fuel cells, water is generated as a by-product in the cathode, because hydrogen ions transported from the anode meet and react with oxygen molecules in the cathode and this water is supposed to be drained, as shown in Figure 1. The membrane in a fuel cell, however, should contain a sufficient quantity of water to maintain ion conductivity. The water in the fuel cells, especially in the membrane electrode assembly (MEA), is necessary to make effective proton conduction and to maintain the conductivity of the polymer membrane. If the MEA lacks water, the efficiency of the fuel cells decreases, since the transport of sufficient hydrogen ions from the anode to the cathode is not attainable any more. Serious lack of water causes the membrane to dry out and the membrane loses its conducting property in the end. On the other hand, a slightly larger amount of water could interrupt effective transports of hydrogen ions within the MEA and if an excessively large amount of water is retained in the membrane, water channel developed between the anode and the cathode results in a short circuit. The control of the water contents in the MEA, therefore, is one of the most important factors for the efficient operation of fuel cells.

A monomer of Nafion® (produced by DuPont, Wilmington, DE, USA), widely used as a membrane material in a PEMFC, consists of hydrophobic polytetrafluoroethylene (PTFE) backbone with side chains that terminate with the hydrophilic SO_3^- groups and counter-ions M^+ (H^+, Li^+, Na^+, K^+; [1–3]). It has been well known that the Nafion shows excellent proton conductivity only when soaked in water [4–6].

When the Nafion is exposed to water, it swells and undergoes micro-phase segregation. As schematically illustrated in Figure 2, water molecules and positively charged counter-ions are supposed to make aggregates or clusters around negatively charged hydrophilic sulfonate groups [7]. These hydrophilic clusters are embedded in the hydrophobic phase of fluorocarbon backbone [1]. It is thought that the clusters induce the conducting channels in the membrane and then the protons begin to transport through these channels [2,3,8,9]. The proton transport mechanism in water can be regarded as a combination of two coupled motions: the jumping of protons between water molecules, called the Grötthuss mechanism [10], and the diffusion of the entire water complexes through the hydrogen bond network made by water clusters. These clusters seem to exist with the extra protons bound to one (H_3O^+) or two $H_5O_2^+$ water molecules formed by H_2O and

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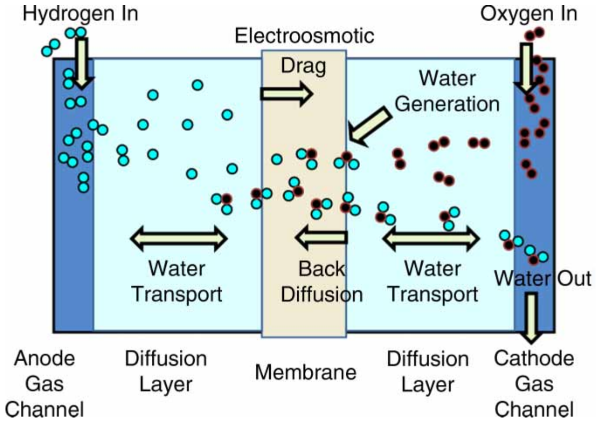

Figure 1. Schematic diagram for water transport process in a typical PEMFC.

H_3O^+ [10–15]. Eikerling et al. [16] showed that the proton transfer in the hydrated Nafion involves the formation of a Zundel ion ($H_5O_2^+$) and the reorganisation of the neighbouring SO_3^- groups. Tanimura and Matsuoka [17] showed that the proton transfer accompanied by a water molecule (H_2O) occurs via the formation of a hydronium ion (H_3O^+). For analysing the behaviour of water molecules in the Nafion membranes, therefore, the H_3O^+ molecules should be considered, implying that the $H_5O_2^+$ molecules made by the important interaction between H_2O and H_3O^+ could be also considered automatically.

To understand the behaviour of water in the Nafion membrane, several models have been developed by many researchers: the cluster-network model by Hsu et al. [18], the local-order model by Dreyfus et al. [19–22], the modified core-shell model by Fujimura et al. [23,24], the sandwich-like model by Haubold et al. [25], the rod-like model from Rubatat et al. [26] and the lamellar model by Litt [27].

These simulation models include the ionic groups aggregating in the Nafion membrane to form clusters for allowing swelling and efficient ionic transports through these clusters [28], although they are different in the geometry and spatial distribution of the ionic clusters, which have not been verified by experiments yet. Since the overall structure of the hydrated membrane is quite complicated, experimental evidences or microscopic experimental observations are quite limited, except for self-diffusion coefficient of water in Nafion.

Takamatsu et al. [29] applied the water sorption method, and Tsushima et al. [30] and Vishnyakov et al. [31] utilised the nuclear magnetic resonance (NMR) spectroscopy to estimate the self-diffusion coefficient of water in Nafion. These experimental diffusion coefficient values range widely between 1×10^{-6} and $1 \times 10^{-8}\,\mathrm{cm^2/s}$, since they are very sensitive to the operational conditions of the membranes, a process used to hydrate the membranes and the duration of the experiment.

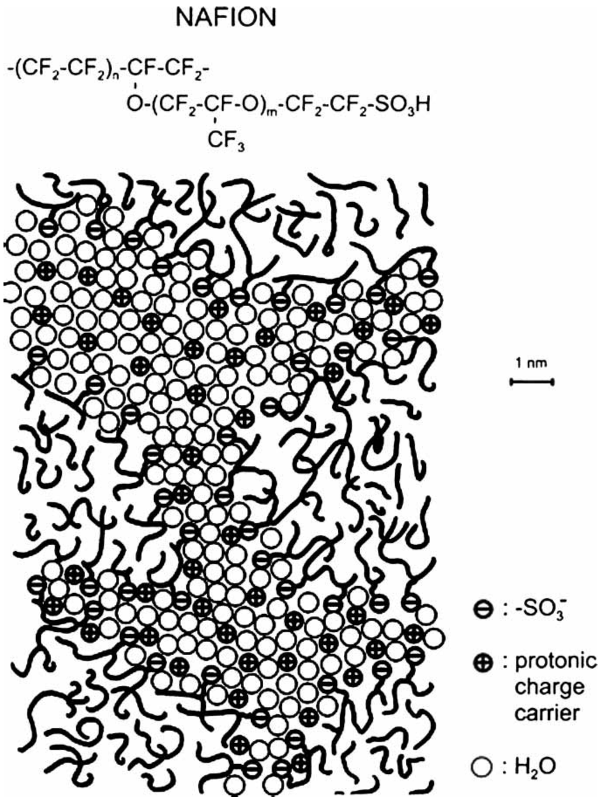

Figure 2. Schematic view for the micro-transport structures in Nafion [7].

Using the molecular dynamics simulation method, Vishnyakov et al. [32] obtained the value of $1.3 \times 10^{-9}\,\mathrm{cm^2/s}$ as the self-diffusion coefficient of water in Nafion. Their result was much smaller than the experimental values, because of insufficient equilibrium time and unreasonable torsion energy incorporated into the simulation model.

In this paper, we set up the molecular models for hydrated Nafion 117 and simulate the dynamics of H_2O and H_3O^+ molecules in the Nafion for various temperatures and monomer numbers. The movements of H_2O and H_3O^+ molecules are calculated and the self-diffusion coefficients of H_2O and H_3O^+ in Nafion 117 are estimated, respectively using the mean-square displacements (MSD). In addition, radial distribution function and Voronoi tessellation are applied for analysing the distribution and local structures of the entire water molecules in the membrane.

2. Simulation models

Molecular models of Nafion 117 and simulation snap shots in this study are shown in Figure 3. A Nafion polymer molecule consists of a hydrophobic PTFE: $-(CF_2-CF_2)_n-(CF_2-CF)_m-(CF_2-CF_2)_n-$ and

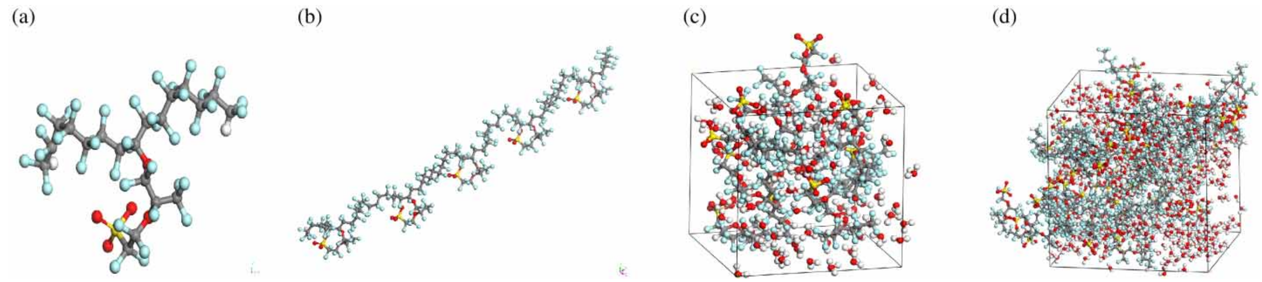

Figure 3. Molecular models for (a) one monomer and (b) five monomers in one Nafion molecule, and simulation snapshots for (c) run no.1: 10 Nafion molecules of one monomer with 50 H_2O and 50 H_3O^+ molecules and (d) run no. 5: 10 Nafion molecules of five monomers with 250 H_2O and 250 H_3O^+, molecules.

$—(CF_2—CF)_m—R$ with a sulfonic acid group: $R = OCF_2$-$—CF(CF_3)—O—CF_2—CF_2—SO_3^-$. The simulation domain sizes vary from 8118.8 $Å^3$ for 10 Nafion molecules of one monomer in a cell to 40,519.4 $Å^3$ for those of five monomers, resulting that the density of the cell is 1.8 g/cm^3. The simulation conditions described in Table 1 are divided into two groups: runs from nos. 1 to 5 for different number of monomers composing one Nafion molecule and runs from nos. 6 to 15 for different simulation temperatures. Each simulation is conducted for 10 Nafion molecules and for hydration degree λ of 10. The hydration degree is defined as the ratio of numbers of H_2O and H_3O^+ to numbers of the sulfonate groups (SO_3^-), $((n_{H_2O} + n_{H_3O^+})/n_{SO_3^-})$, [3].

The software used in the present simulation is Amorphous Cell and Discover molecular modelling system in Materials Studio® with the PCFF force field (Amorphous Cell and Discover, Accelrys. Inc., San Diego, CA, USA; [33–37]). The force field is not polarisable and no charge transport can occur in the simulation. Thus, the proton transport mechanisms cannot be included in the simulation. The partial charges imposed to molecules in the system are described in Figure 4 and these values of intramolecular and intermolecular interaction parameters have been widely applied elsewhere [38,39].

In simulations, the movements of molecules can be estimated by the MSD, $\sigma_i^2(t)$), which is a measure of the average distance a molecule travels and defined as [40]:

$$\left\langle \sigma_i^2(t) \right\rangle = \left\langle (r_i(t) - r_i(0))^2 \right\rangle, \tag{1}$$

where $r_i(t) - r_i(0)$ is the distance travelled by molecule i over time interval t. The slope of the MSD is related to the self-diffusion constant, D, given by Ref. [40]:

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{\mathrm{d}t} \sum_{i=1}^{N} \left\langle (r_i(t) - r_i(0))^2 \right\rangle, \tag{2}$$

where N is the number of diffusing molecules and the summation on the right-hand side is for the MSD of all diffusing particles. In addition, diffusion mechanisms of molecules can be understood by the relation between MSD and time, given as

$$\langle \sigma^2(t) \rangle \sim Dt^{\alpha}. \tag{3}$$

The exponents α, which is a slope of log–log plots of MSD have different values depending on the types of the transport mechanisms: $\alpha = 0.5$ for single-file motion, $0.5 < \alpha < 1$ for sub-diffusion (known as inhibited diffusion), $\alpha = 1$ for the Fickian diffusion (normal-mode diffusion),

Table 1. Simulation conditions for Nafion with water molecules.

	Number of molecules in simulation domain				
	Nafion				
Run nos.	Number of Nafions	Number of monomers in one Nafion molecule	H_2O	H_3O^+	Temperature (K)
1	10	1	50	50	353
2	10	2	100	100	
3	10	3	150	150	
4	10	4	200	200	
5	10	5	250	250	
6	10	3	150	150	283
7					293
~					~
15					373

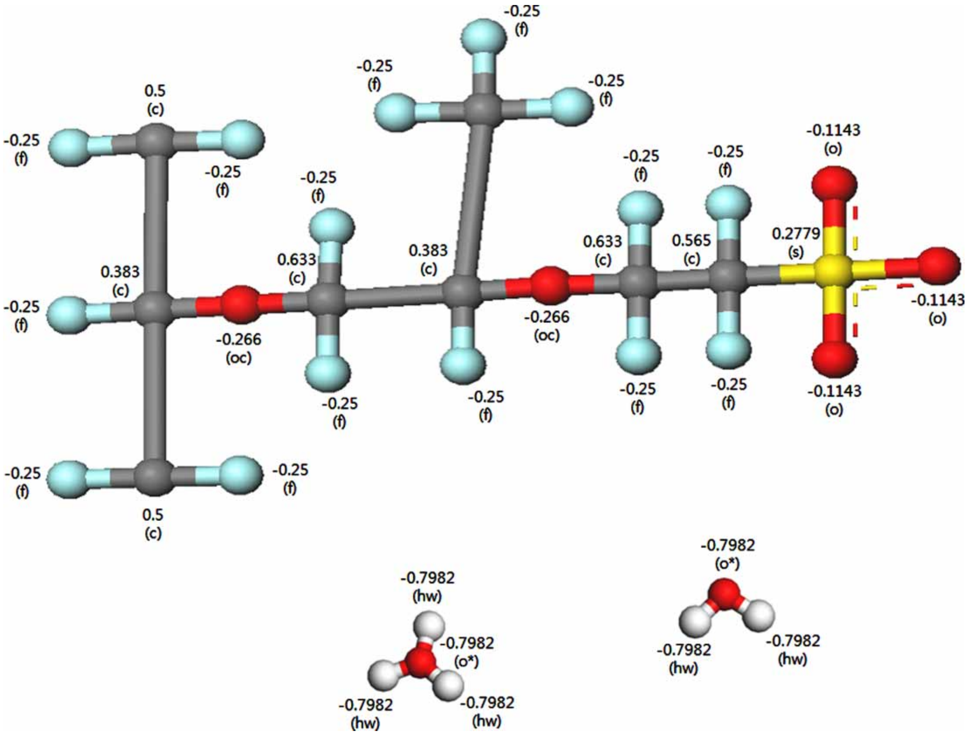

Figure 4. Schematic view with partial charges of Nafion unit molecule, hydronium ion and water molecule.

$1 > \alpha > 2$ for super-diffusion (known as accelerated diffusion), and finally $\alpha \geq 2$ for ballistic motion [41–45].

In this study, the distributions and structures of water molecules in Nafion are also estimated using radial distribution functions (RDF) and Voronoi tessellation technique, respectively. The pair-wise correlation function such as RDF is a measure of the probability of finding the presence of a molecule from the reference one in the specific region. This function can explain how molecules are distributed in the system or whether molecules form clusters, channels, or other structures in the systems, defined as [46]:

$$\rho g(r) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta(r - r_i) \right\rangle, \tag{4}$$

where ρ is the number density.

Voronoi tessellation analysis [47–49] provides a natural definition of ‘solvation neighbours’ of a centre water molecule. Two Voronoi polyhedra are defined to be neighbours if they share a common face in the Voronoi construction. The Voronoi tessellation analysis results in the total surface area, A and total volume, V, of a certain polyhedon, and thus its asphericity parameter, η, can be estimated as:

$$\eta = \frac{A^3}{36\pi V^2}. \tag{5}$$

By definition, η is equal to one for a sphere and equal to 1.33, 1.35, or 1.91 for body-centred cubic, face-centred cubic and simple cubic structures, respectively [50–54]. It can be assumed that the structural phase for ice is hexagonal, when η reaches 2.25 and beyond [50–52]. The value of η quantifies the deviation of the polyhedron from a perfect sphere, and thus a larger η indicates a structure far from a perfect sphere.

3. Results and discussion

Initially, the simulations were minimised using two methods: steepest descents and conjugate gradients methods, until the maximum derivative reached the value of 1×10^{-7} kcal/(mol Å), [55]. The summation methods were the atom based method for the minimisation and the cell multiple method with 5 Å update width during simulation [56]. The system temperature was controlled by the Anderson method [57]. For every simulation in this study, the equilibrium time and dynamic time for calculating the properties were 100 ps under the NVT ensemble condition. Especially, the total energy of the whole system was used for a standard criterion of system equilibration. If the fluctuation of total energy was less than 1% during 1 ps (1000 steps) and temporal averages of total energy did not change much less than 1%, we assumed the system had been equilibrated. Simulations with longer times were carried out for equilibration and production processes, but no significant difference was observed.

After the minimisation and equilibration processes, simulation during first 100 ps resulted in the average values of MSD of water and hydronium molecules with respect to time, as shown in Figure 5. Here, each simulation was performed for 10 Nafion molecules with sufficient number of water molecules in the simulation domain as described in Table 1. In other words, run no. 1 denotes the simulation run corresponding to 10 Nafion molecules of one monomer and 100 water molecules (50 H_2O and H_3O^+) in the domain. Even though the number densities in the simulations of run nos. 1–5 are equal to each other, the MSD decreases significantly.

Figure 6 compares the self-diffusion coefficients of H_2O and H_3O^+ molecules and their average values, estimated from the MSD of H_2O and H_3O^+ based on Equation (2). The diffusion coefficients of H_2O are slightly larger than those of H_3O^+, since the molecular weight of H_3O^+ is larger than that of H_2O and H_3O^+ molecules interact with the Nafion molecules. The H_3O^+ molecules have an entirely positive charge and the H_2O molecules are neutral. Positively charged H_3O^+ molecules, therefore, can interact with negatively charged sulfonate groups in Nafion more effectively with the result that the movements of H_3O^+ molecules could be impeded slightly. This explains one proton transport mechanism in Nafion membrane, hopping of a proton between water molecules and sulfonate groups. As expected from the MSD in Figure 5, the diffusion coefficient decreases as the monomer number in one Nafion molecules increases. However, it is not clear why the self-diffusion coefficient of the case for three monomers is larger than that for two monomers. Although we simulated several times, similar behaviours were observed. This might be due to fact that the structural distribution of Nafion monomers in the simulation cell affects the water transport, which has not been investigated in this study. Furthermore, the exponents for Equation (3) are 0.80 and 0.81 for the cases of two and three monomers, respectively. This implies that the water transport for the case of three monomers is inhibited slightly less than for the case of two monomers.

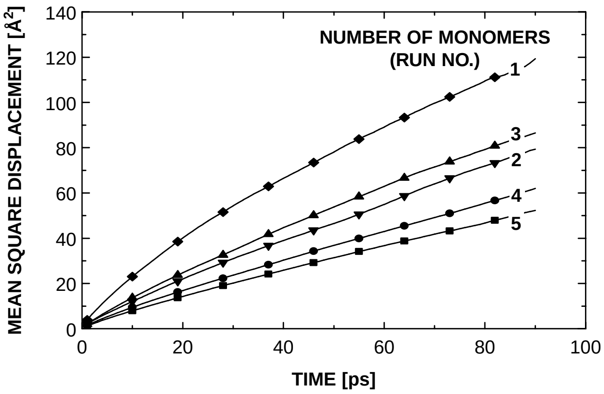

Figure 5. MSD of water molecules in Nafion with respect to simulation times under the simulation conditions as explained in Table 1.

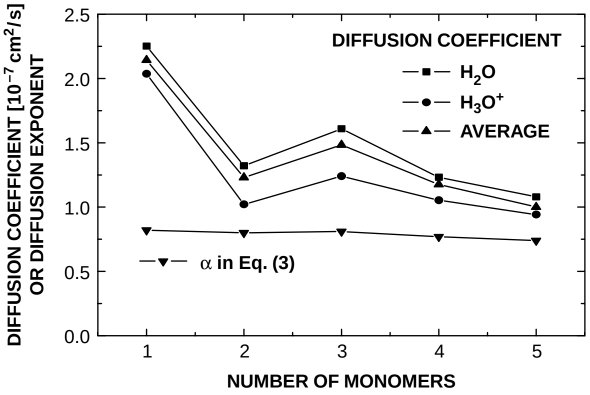

Figure 6. Self-diffusion coefficients of water and hydronium molecules in Nafion estimated from the MSD for different monomer number systems of one Nafion molecule and diffusion exponents in Equation (3).

At the temperature of 353 K, the self-diffusion coefficient values are $2.14 \times 10^{-7}\,\mathrm{cm^2/s}$ for one monomer and $1 \times 10^{-7}\,\mathrm{cm^2/s}$ for five monomers and they are in the range of the experimental estimates of $1.8 \times 10^{-6}\,\mathrm{cm^2/s}$ $-5 \times 10^{-8}\,\mathrm{cm^2/s}$, [31,32,58,59].

Equation (3) implies that the slope of log–log plots of MSD could describe the diffusion mechanism in another aspect. The slope of MSD of one in log scale means the normal diffusion representing the general diffusion of fluid, and slopes smaller than one indicate the inhibited diffusion due to obstacles interfering with fluid movements. Here, we have calculated the slope of MSD in log scale for pure water and the slope is around 0.98 indicating, that the pure water transport is under the normal diffusion. On the contrary, the slopes of water molecules in the Nafion range between 0.74 in five monomers and 0.82 in one monomer, as shown in Figure 5. It seems that the water movement becomes retarded by the interaction with Nafion molecules.

For increased temperatures, the MSD and self-diffusion coefficient values increase accordingly, as shown in Figures 7 and 8. The self-diffusion coefficient values of water vary from $1.58 \times 10^{-7}\,\mathrm{cm^2/s}$ at 333 K to $1.74 \times 10^{-7}\,\mathrm{cm^2/s}$ at 353 K, which is the general operation temperature range of the PEMFC.

After simulation runs, the structures of water molecules in Nafion were investigated using the pair correlation functions and Voronoi tessellation. This may lead to an understanding of how the specific molecules in the system are specifically distributed.

Figure 9 compares the pair correlation functions of oxygen atoms in pure water and water molecules in Nafion at 353 K and shows that the local structures of the latter molecules are completely different from those of the former

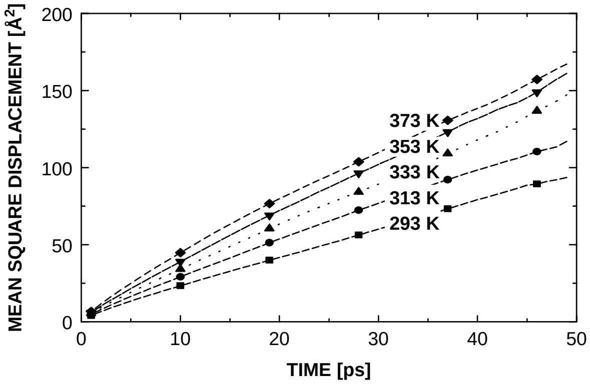

Figure 7. MSD of water molecules in Nafion with respect to simulation times at various temperatures.

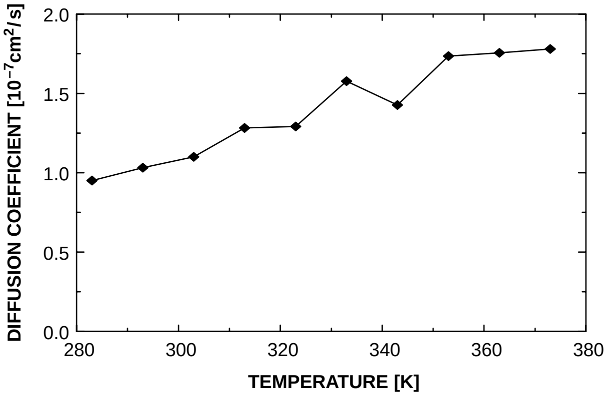

Figure 8. Self-diffusion coefficients of water molecules in Nafion estimated from the MSD at various temperatures.

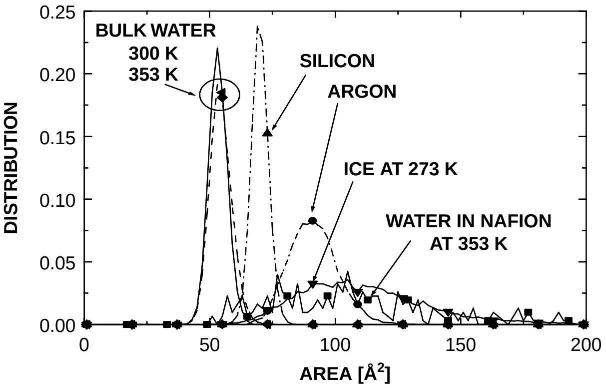

Figure 10. Surface area distributions of Voronoi polyhedra for bulk water, water in Nafion, ice, silicon and argon.

ones. For pure water molecules at 353 K, the peaks around 3, 5, 8 and 10 Å indicate that the pure water molecules are spatially distributed along almost regular intervals and each water molecule has a weak polarity caused by two hydrogen molecules leaning to the partial site of oxygen molecule. The net result is that the opposite site of oxygen molecule is negatively charged [50]. On the other hand, water molecules in Nafion reveal a totally different trend. The first peak at 3 Å is similar to that of pure water induced by clustering due to their dipole moments. The next peaks, however, are different from those of pure water. The second peak is located at nearly 6 Å and the noticeable peaks are not detected after the second peak.

To further understand the local structures of water molecules in Nafion, the Voronoi tessellation analysis is applied. Figures 10 and 11 compare the distributions of surface area and volume of Voronoi polyhedron for pure water, water in Nafion, ice, silicon and argon molecules. As expected, the distributions of water molecules in Nafion completely deviate from those of pure water and are rather very close to those of ice at 273 K in which the dominant structure is hexagonal.

Table 2 shows the estimates of asphericities in this study for different phases of water molecules from Voronoi tessellations. The asphericity of pure water molecules at 300 K is 1.62, which agrees well with the results of other researches (1.61 by Shih et al. [50], 1.7 by Ruocco et al. [51] and 1.59 by Jedlovszky [52]). The present study obtains 2.49 for the asphericity

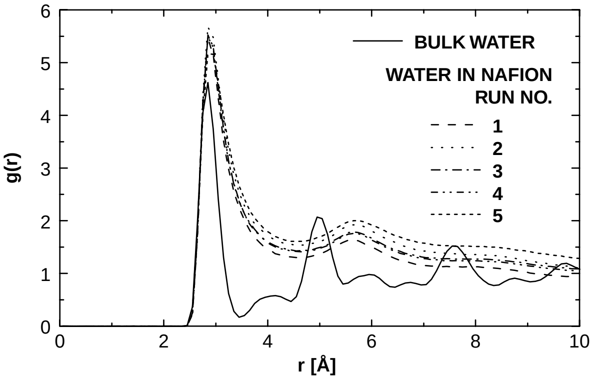

Figure 9. Pair correlation functions of oxygen–oxygen within water molecules at 300 K under various conditions.

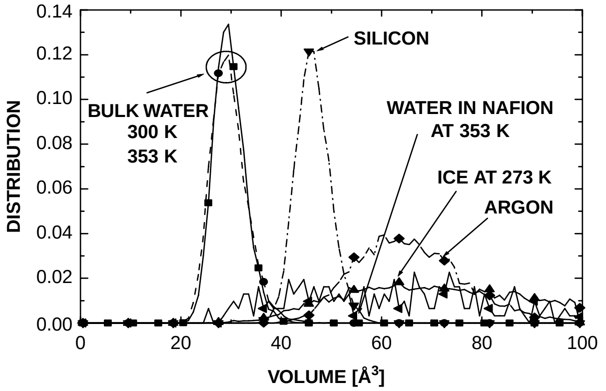

Figure 11. Volume distributions of Voronoi polyhedra for bulk water, water in Nafion, ice, silicon and argon.

Table 2. Asphericities for different phases of water molecules estimated from Voronoi tessellations.

	Surface area (Å^2)	Volume (Å^3)	Asphericity
Pure water (300 K)	54.46	29.66	1.62
Ice (273 K)	112.2	76.21	>2.15
Water in Nafion (300 K)	110.7	69.41	2.49

of water molecules in Nafion, which is considerably close to that of the hexagonal ice structure [46–48]. The present finding indicates that the phase of water in Nafion at 353 K is close to hexagonal ice at 273 K, implying that water molecules form a kind of ice-like crystalline structure in the Nafion membrane.

4. Conclusions

We have devised molecular models for fully hydrated Nafion membranes for understanding the transports and structures of water molecules in the membranes. The behaviour of molecular models composed of H_2O, H_3O^+ and Nafion unit molecules are simulated for various monomers and for various temperatures.

Diffusion coefficients are calculated from the MSD of water molecules. The mean diffusion coefficient of water molecules in Nafion is estimated at 1.83×10^{-7} cm^2/s at 353 K. This value agrees well with the experimental observations. The diffusion coefficient values are almost proportional to the temperature in the temperature range between 283 and 373 K, which is the typical operational range of the PEMFC.

Simple estimation using the relation between MSD and time indicates that the diffusion exponents for water molecules in Nafion molecules are much smaller than one and shows that the diffusion is significantly inhibited, comp to that for pure water.

Voronoi tessellation analysis shows that the distribution of water molecules in the Nafion membrane is quite different from that of pure water molecules, but is quite close to the distribution in hexagonal ice.

Acknowledgements

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