

MOLECULAR DYNAMICS SIMULATION OF WATER BEHAVIOR
AS A FUNCTION OF TEMPERATURES AND MONOMER NUMBERS IN NAFION 117

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ABSTRACT

The proton exchange membrane plays a critical role as an electrolyte for proton transports in the PEMFC. Generally, the membrane, such as Nafion 117, consists of a polytetrafluoroethylene (PTFE) backbone and side-chains terminated with a sulfonate group (SO_3^-). Operating the fuel cell, the membrane preferentially becomes hydrated by absorbing water. Then, the hydrogen atom on the SO_3^- part of the side-chain can detach from its own position and hop to the next SO_3^- site. The water management is the key to the efficient operation of the fuel cell, since the water content is the one of decisive factors for membrane's lifetime and efficient operations of fuel cells as well. In this report, we set up the molecular model for hydrated Nafion 117 and simulate the molecular movements for various temperatures and monomer numbers. Here, we obtain the mean square displacements of water molecules and estimate the self-diffusion coefficients of water in the Nafion 117.

N_w = number of water molecules

$R_i(t)$ = position of particle

SO_3^- = sulfonate ion molecule

t = time [ps]

Greek Symbols

λ = hydration degree

NOMENCLATURE

$D_{\text{H}_2\text{O}}$ = diffusion coefficient of water [cm^2/s]

H_2O = water molecule

H_3O^+ = hydronium ion molecule

$N_{\text{H}_3\text{O}^+}$ = number of hydronium ion molecule

INTRODUCTION

The polymer electrolyte membrane fuel cell (PEMFC) comes into notice as a highly promising power source for vehicles, mobile electronic equipments, and other applications. It is expected that the PEMFC will begin to replace the internal combustion engine within next decades.

In a PEMFC, a polymer membrane (e.g., Nafion® produced by DuPont) provides excellent performance such as a good chemical and mechanical stability, optional permeability, and very high proton conductivity in the presence of water by its characteristic structure.

A Nafion polymer molecule consists of a hydrophobic perfluorocarbon backbone with side chains terminated by the hydrophilic SO_3^- groups which is strong acidity with counterions $M^+ (\text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+)$ (See Fig. 1).

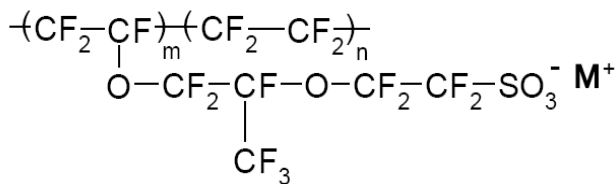


FIG. 1 CHEMICAL STRUCTURE OF NAFION 117 [1].

When the Nafion is exposed to water, it swells and goes through micro phase segregation. Water molecules and positively charged counterions are supposed to form aggregates or clusters, solvating negatively charged hydrophilic sulfonate groups. These hydrophilic clusters are embedded in the hydrophobic phase of fluorocarbon backbone [2], and then the proton conduction starts through the transport channels by some mechanisms [3-6]. Here, adequate water content of the Nafion is essential to make the conduction and maintain the conductivity of the polymer membrane. This has a strong influence on the fuel cell performance. However, excessive amounts of liquid water could interrupt mass transport within the membrane electrode assembly.

In this paper, we made the model based on the molecular dynamics (MD) for hydrated Nafion 117 and simulated for various temperatures and monomer numbers.

Also, we analyzed the movement of water molecules and determined the self-diffusion coefficients of water in the Nafion 117 using the mean-square displacement.

THEORY

In molecular dynamics, the diffusion coefficient can be determined by the following equation [7].

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \langle [R_i(t) - R_i(0)]^2 \rangle \quad (1)$$

In Eq. (1), the sum term on the right side is the mean-square displacement, α is the number of diffusing particles, t is time and $R_i(t)$ is the position vector of particle α at time t . It is crucial that Eq. (1) is reasonable only when the motion of the diffusing particle follows a random path. In other words, its moving is not related to its route at previous time. This means the Einstein diffusion is reached.

On the other hand, if the surroundings prohibit the free movement of the particle, (for example the movement of particle is limited by the polymer chain) this is called anomalous diffusion. In this case, $\langle [R_i(t) - R_i(0)]^2 \rangle \propto t^n$

where $n < 1$, and Eq. (1) is not valid. The movement of the particle is not by diffusion but by some other transport mechanism, if $n < 1$ in $\langle [R_i(t) - R_i(0)]^2 \rangle \propto t^n$.

It is easy to test the region in which Eq. (1) is valid by plotting $\log(MSD)$ against $\log(t)$ (See Eq. 2). In the case of the Einstein diffusion, the slope of the curve is one [8].

In this study, we assumed that the diffusing molecules in the Nafion diffuse as the Einstein diffusion because the slope in the simulation varies from 0.56 to 1.24.

$$\frac{\Delta \log(MSD)}{\Delta \log(t)} = 1 \quad (2)$$

Note, the Einstein relation always yields a vanishing self-diffusion coefficient for a fluid confined in a cell of finite size, provided that the observation time is unlimited.

In real MD simulations the observation time is limited, and the dependence of the mean-square displacement on time might show standard features with a linear interval, which allows one to estimate the self-diffusion coefficients even in the systems of limited size [14-15].

MODELS AND SIMULATIONS

In the study, the molecular model of the Nafion 117 including main and side chains has been used and shown in Fig. 2; the same set of intramolecular and intermolecular interaction parameters has been used as those given in Refs [9-11].

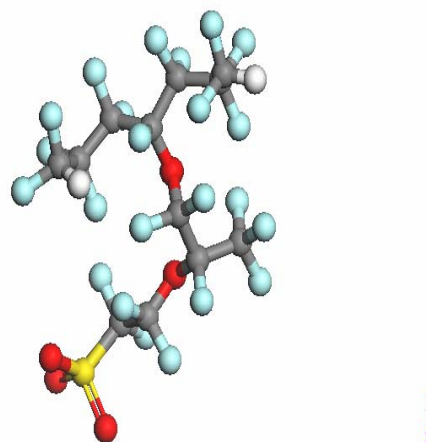


FIG. 2 A SNAPSHOT OF NAFION 117. FLUORINE ATOMS ARE IN BLUE, OXYGEN IN RED AND CARBON IN DARK GRAY, AND SULFUR IN YELLOW.

We, especially, considered that the combination between the ions: SO_3^- and H^+ . Operating the fuel cell, it is supposed the hydrogen ions are moved by three mechanisms which are the hopping from one SO_3^- site to next site; the interactions of H_2O and H_3O^+ ; the moving between water molecules and sulfonate groups.

If the hydrogen ion in the modeling is attached to all of SO_3^- of Nafion, an electric charge of the side chain is zero, which means it couldn't react according to the water molecules, and then the hydrogen ions lose the way to move through the side chains. We'd not, therefore, put the H^+ on the sulfonate groups in our molecular model and it also has the hydronium ions (H_3O^+) in the model.

Optimizations and calculations were made on the server which is composed of 8 Xeon[™] processors of Intel[®]. The used software are Amorphous Cell[®] program and Discover[®] molecular modeling system which made by Accelrys Inc.

Two systems were simulated in the two different parameters which are the number of monomers and the temperatures with periodic boundary conditions, as described in Table 1.

TABLE 1 SUMMARY OF PERFORMED SIMULATIONS

Run	Number of			Temperature [K]	Initial Configuration
	Monomers	H_2O	H_3O^+		
1	1	50	50	353	Random
2	2	100	100		
3	3	150	150		
4	4	200	200		
5	5	250	250		
6				283	
7	3	150	150	293	Random
15				373	

The cells, in the first system, of five different number of monomers was made with the hydration degree λ which defined as the ratio of H_2O or H_3O^+ and the sulfonate group in the polymer, $(n_{H_2O} + n_{H_3O^+}) / n_{SO_3^-}$, is 10.

In the other system, the temperature was changed from 283K to 373K, and another parameter was fixed such as the monomer number is 3, water and hydronium molecules are 150 each ($\lambda = 10$).

The cell sizes were varied from 14613.76\AA^3 for 1 monomer to 72935.08\AA^3 of 5 monomers to keep the density of system as 1 g/cm^3 and snapshots of the systems are shown in Fig. 3.

The PCFF force field was used for all calculations. The cells were first minimized using two methods: steepest descents and conjugate gradients, until the maximum derivative reached the value of $1.0 \times 10^{-5} \text{ kcal}/(\text{mol} \cdot \text{\AA})$.

The summation method was the atom based method for the minimization and the cell multiple method during the simulation [12]. The system temperature was controlled by the Anderson method [13].

For the first system, the equilibrium time was 15 ps, and 100ps for the dynamic time with the NVT ensemble at 353K. The other system was simulated for 3ps for the stability and for 50ps as estimating the properties.

RESULTS AND DISCUSSION

The mean-square displacement (MSD) is a measure of the average distance a molecule travels. As the result for the same value of the hydration degree in our simulation, the mean-square displacement of H_2O and H_3O^+ was decreased along with increase of monomer numbers, as shown in Fig. 4.

During 100 ps simulation time, the MSDs of water molecule range from 146\AA^2 to 98\AA^2 , corresponding to one monomer with 100 water molecules and five monomer with 500 ones, respectively, as described in Fig. 4.

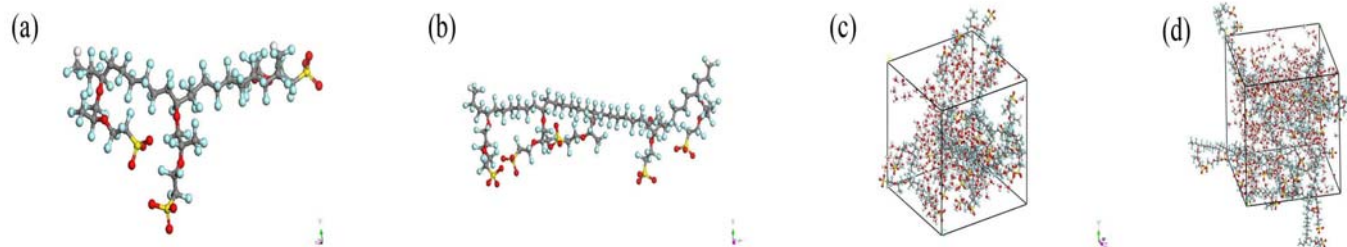


FIG. 3 SIMULATION SNAPSHOTS: (A) NAFION MOLECULE OF 3 MONOMERS, (B) NAFION MOLECULE OF 5 MONOMERS, (C) $50 H_2O$, $50 H_3O^+$, 10 NAFION OF 1 MONOMER, (D) $250 H_2O$, $250 H_3O^+$, 10 NAFION OF 5 MONOMER

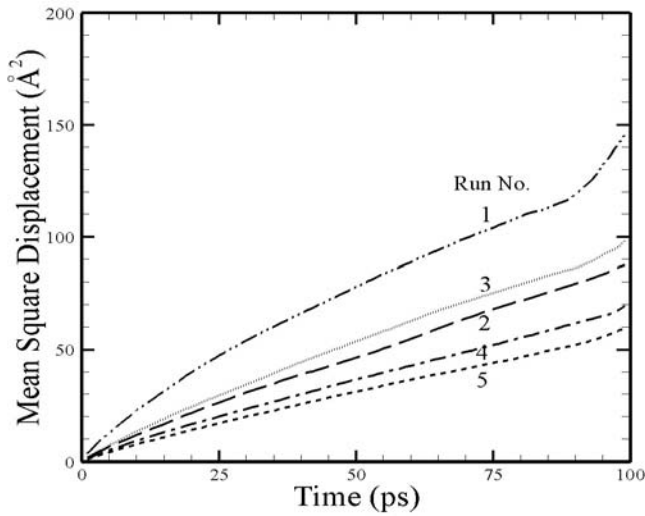


FIG. 4 MEAN-SQUARE DISPLACEMENTS OF THE WATER AND HYDRONIUM MOLECULES.

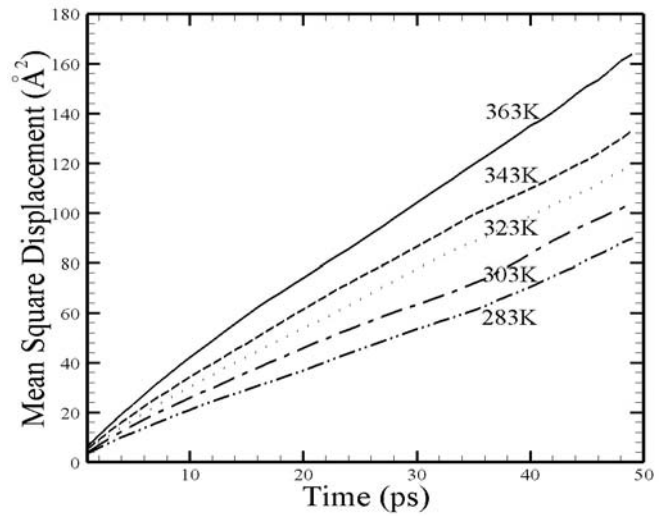


FIG. 5 MEAN-SQUARE DISPLACEMENTS WITH RESPECT TO TEMPERATURES.

Even though the number densities in the simulations of Run No. 1 to 5 are equal to each other, the MSD decreases significantly, that might be due to the size effect.

The diffusion coefficients are in proportion to the gradient of the MSD as formulated in Eq. (1). As the same as MSD, the diffusion coefficients decreases as the cell size increases.

At 353K, the diffusion coefficients are $2.1424 \times 10^{-7} \text{ cm}^2 / \text{s}$ for one monomer and $1.0011 \times 10^{-7} \text{ cm}^2 / \text{s}$ for five monomers, as shown in Table 2. Average of the current estimation is $1.38 \times 10^{-7} \text{ cm}^2 / \text{s}$, which agrees well with the experimental estimate of $1.2 \times 10^{-7} \text{ cm}^2 / \text{s}$ [15-17].

As the temperature rises, the MSD also increases proportionally, as shown in Fig. 5. The diffusion coefficients of water vary from $1.67 \times 10^{-7} \text{ cm}^2 / \text{s}$ at 333K to $1.83 \times 10^{-7} \text{ cm}^2 / \text{s}$ at 353K, which is the general operation temperature range of PEMFC (see Fig. 6).

TABLE 2 DIFFUSION COEFFICIENTS OF WATER MOLECULES FOR VARIOUS MONOMER NUMBERS

Number of Monomers (Run No.)	1	2	3	4	5
D_{H_2O} ($10^{-7} \text{ cm}^2 / \text{s}$)	2.1424	1.1097	1.4826	1.1754	1.0011

CONCLUSIONS

We design the molecular models for the fully hydrated Nafion membranes to understand the movement of water molecules in the membrane.

The molecular model composed of H_2O , H_3O^+ and Nafion unit molecules was simulated for a various monomers and for various temperatures. The diffusion coefficients were calculated using the mean-square displacement of water and hydronium molecules.

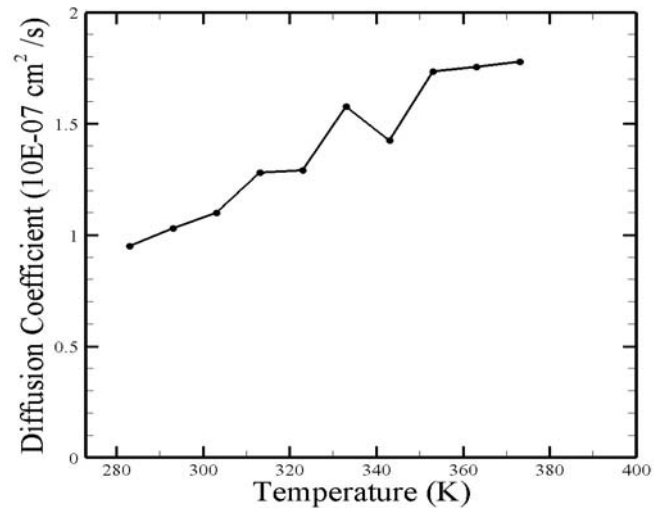


FIG. 6 DIFFUSION COEFFICIENTS OF WATER WITH RESPECT TO TEMPERATURE.

The average diffusion coefficient of water molecules in Nafion at 354 K was estimated as $1.38 \times 10^{-7} \text{ cm}^2 / \text{s}$. This value agrees well with the experimental estimate of $1.2 \times 10^{-7} \text{ cm}^2 / \text{s}$.

The diffusion coefficients were almost proportional to the temperatures in the temperature ranges between 280 and 380 K, which is the typical operational range of the PEMFC.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the Micro Thermal System Research Center sponsored by the Korean Science and Engineering Foundation.

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