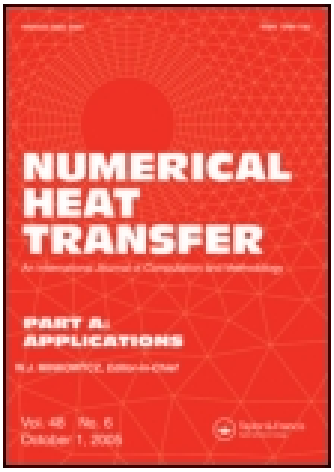

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The Temperature Effect on the Diffusion Processes of Water and Proton in the Proton Exchange Membrane Using Molecular Dynamics Simulation

Lei Chen [a], Ya-Ling He [a] & Wen-Quan Tao [a]
[a] Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, P. R. China
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THE TEMPERATURE EFFECT ON THE DIFFUSION PROCESSES OF WATER AND PROTON IN THE PROTON EXCHANGE MEMBRANE USING MOLECULAR DYNAMICS SIMULATION

Lei Chen, Ya-Ling He, and Wen-Quan Tao
Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, P. R. China

A molecular dynamics calculation model for the Nafion 117 membrane is constructed by Materials Studio (MS) software platform to study its transport properties. Cell structures of different water content of Nafion 117 membrane at 300 K and 353 K are obtained, respectively, and the predicted density values of simulated cell are in good agreement with available experimental data. It is found that at the same temperature, the predicted diffusion coefficients of both water molecules and hydrogen ions increase with the water content, and at the same water content the predicted diffusion coefficients of both water molecules and hydrogen ions increase with the temperature.

1. INTRODUCTION

The proton exchange membrane fuel cell (PEMFC) is considered as one possible substitute of fossil energy for its high efficiency and low pollution. In previous decades, great progress in the studies of PEMFC has been made, but there are still many key issues to be resolved before it can be cheaply applied to industries. One of them is a better understanding of the transport properties of PEM and their effects on battery performance. Because the hydrated membranes have higher proton conductivity, it is important to understand the transportive properties at different membrane temperatures.

The functional characteristics of PEM are mainly reflected on the nano-level [1], so to understand its microstructure and the relation between microstructure and transport properties, microscopic study is necessary. The molecular dynamics (MD) simulation is a useful method to study process in microstructure [2–6], especially for PEM [7–17]. Elliott et al. [7] used classical MD with a modified Dreiding force field [8] to study the dynamics of small molecules in a model Nafion

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Address correspondence to Wen-Quan Tao, Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, P. R. China, 710049. E-mail: wqtao@mail.xjtu.edu.cn

NOMENCLATURE

a	slope of the graph	θ,θ'	bond angle
A,B	parameters for van der Walls potential function	λ	water content
		ρ	density
b	bond length	ϕ	torsion angle
D	diffusion coefficient		
E	force field	**Subscripts**	
H	force constants of the bond potential	b	bond stretching term
k	force constants of the angle	*elec*	columbic interaction term
MSD	mean square displacement	*nb*	nonbonding term
n, x, y, z	chain length	x	cross term
N	number of atoms	h	hydronium ions
O	water molecule and hydronium ion	i, j	atom position
P	electric charge	w	water molecule
r	atom distance	θ	angle bending term
t	time	φ	torsion angle term
V	parameters in the torsion potential function	χ	out-of-plane bending term

membrane for $\lambda = 1$, 3.8, and 9.7, where λ is the ratio of the sum of the H_2O number and H_3O^+ number over the number of sulfonic groups. For example, if there are 40 sulfonic groups, 40 hydronium ions, and 72 water molecule, then $\lambda = 2.8$. Vishnyakov and Neimark [9] used a simplified united-atom force field in their MD simulation of hydrated Nafion with K+as the counterion for three different λ values. Urata et al. [10] also used a similar united-atom force field to model hydrated Nafion for $\lambda = 2.8$, 5.9, 13.3, and 35.4. Jang et al. [11] used an all-atom approach in their MD simulation of nanophase segregation and transport in Nafion for $\lambda = 16$. Charati and Stern [17] estimated diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 at 300 K in four silicone polymers by MD simulations. Hofmann et al. [18] discussed the results of extensive atomistic molecular dynamics investigations on the transport of different small molecules in flexible chain rubbery and stiff chain glassy polymers. However, all of the above references didn't consider the influence of temperature.

In fact, there is a temperature difference in PEMFC [19], and many numerical simulations on fuel cell performance assume the thermal conductivity coefficients of the proton exchange membranes being constant. For example, in the three-dimensional transient model fully coupling the two-phase flow, species transport, heat transfer, and electrochemical processes developed by Wang and Wang [20], the thermal conductivity of the membrane is $0.95\,W/(m \cdot K)$. In Ye and Nguyen [21], the thermal conductivity of the membrane is $0.2\,W/(m \cdot K)$ in their three-dimensional simulation of liquid water distribution in a PEMFC; and in the three-dimensional transient model developed by Wu et al. [22], thermal conductivity of the membrane is assumed to be $0.445\,W/(m \cdot K)$. Although they have realized the essentiality of temperature action, in their models thermal conductivities are assumed to be a constant and only empirical relations on the diffusion coefficients of water are used.

In order to reveal the effect of temperature, in this article a molecular dynamics calculation model of the proton exchange membrane is established first according to the literature [17, 18] by Materials Studio (MS) software platform [24], and the diffusions of water molecules and hydronium ions in PEM are computed using classical

molecular dynamics simulation. Then, the diffusion processes of water and proton are analyzed at different water content and temperature. Finally, the numerical predictions are compared with relevant experimental results.

2. DETAILS OF NUMERICAL SIMULATION

2.1. Force Field

In the article, the COMPASS force field [24] is adopted in the molecular simulation. The bond stretching term(E_b), angle bending term(E_θ), torsion angle term (E_φ), out-of-plane bending term (E_χ), cross term (E_x), nonbonding term (E_{nb}), and columbic interaction term (E_{elec}) are defined as below.

$$E_b = \sum_b [k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_4(b-b_0)^4] \tag{1}$$

$$E_\theta = \sum_\theta [k_2(\theta-\theta_0)^2 + k_3(\theta-\theta_0) + k_4(\theta-\theta_0)^4] \tag{2}$$

$$E_\varphi = \sum_\varphi \{k_1[1-\cos(\varphi-\varphi_{0,1})]\} + k_2[1-\cos(2\varphi-\varphi_{0,2})] + k_3[1-\cos(3\varphi-\varphi_{0,3})] \tag{3}$$

$$E_\chi = \sum_\chi k_\chi \chi^2 \tag{4}$$

$$\begin{aligned} E_x = & \sum_{b,b'} k_{bb}(b-b_0)(b'-b'_0) + \sum_{\theta,\theta} k_{\theta\theta}(\theta-\theta_0)(\theta'-\theta'_0) + \sum_{b,\theta} k_{b\theta}(b-b_0)(\theta-\theta_0) \\ & + \sum_{b,\varphi} (b-b_0)[k_1\cos\varphi + k_2\cos 2\varphi + k_3\cos 3\varphi] \\ & + \sum_{b',\varphi} (b'-b'_0)[k_1\cos\varphi + k_2\cos 2\varphi + k_3\cos 3\varphi] \\ & + \sum_{\theta,\varphi} (\theta-\theta_0)[k_1\cos\varphi + k_2\cos 2\varphi + k_3\cos 3\varphi] \\ & + \sum_{\varphi,\theta,\theta'} k_{\varphi\theta\theta'}\cos\varphi(\theta-\theta_0)(\theta'-\theta'_0) \end{aligned} \tag{5}$$

$$E_{nb} = \sum_{i>j} \left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6}\right] \tag{6}$$

$$E_{elec} = \sum_{i,j} \frac{q_i q_j}{r_{ij}} \tag{7}$$

where k_i, $H_i (i = 2, 3, 4)$ are the force constants of the angle and the bond potentials; V_i and $\varphi_{0,\,i}$, $(i = 1, 2, 3)$ are parameters in the torsion potential function; θ and φ are the bond and the torsion angle; A_{ij} and B_{ij} are parameters for van der Walls potential

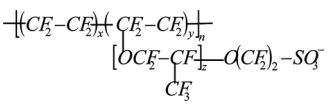

Figure 1. Chemical structure of Nafion.

function; and r_{ij} is the distance between atoms i and j. All of the parameters used for the potential functions are taken from reference [24].

2.2. Computation Model and Procedure

The chemical structure of Nafion membrane is shown in Figure 1, where x varies between 6 and 10 and $y = z = 1$ [13]. In this article, MD study is conducted for Nafion 117 membrane with $x = 7$ and $n = 10$. The system simulated by Materials Studio software consists of several Nafion chains forming a porous structure with the water and protons inside. Figures 2*a* and 2*b* are water molecule model and hydrogen ion model, respectively. Figure 3 provides Nafion 117 chain, where oxygen atom, hydrogen atom, sulfur atom, fluorine atom, and carbon atoms are, respectively, represented in red, offwhite, yellow, lightblue, and gray balls. The cell simulated consists of 4 Nafion 117 chains and 0–640 H_2O. The number of water molecules depends on the values of λ. The total number of atoms in four Nafion chains is 2,728. To keep the cell being neutrality in charge, another 40 H_3O^+ are added.

The cell models of hydrated Nafion 117 membrane for $\lambda = 3.5$, 7, 12.5, and 17 are constructed by MS software platforms at 300 K and 353 K, respectively. Here, 300 K is the room operation temperature of PEMFC, and 353 K is almost up to its upper limit temperature. The concrete steps to construct the cell model are as follows.

- Via the Materials Visualizer, the Nafion 117 chain and the structure models of water molecules and hydronium ions, are established, as shown in Figures 2 and 3, and energy optimization is carried out.
- The cell structure models consisting of four Nafion 117 chains, 40 hydronium ions, and a certain amount of water molecules are constructed.
- The cell structure models are optimized to minimize their energies by the steepest descent method, and the overall minimum energy conformations are obtained by simulated annealing method. The simulated annealing steps are as follows.

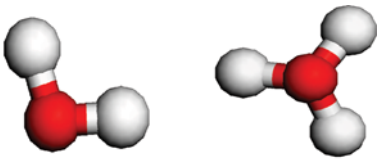

Figure 2. Structure models of water and hydrogen ion (color figure available online).

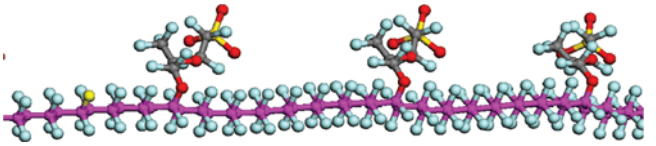

Figure 3. Nafion 117 chain (color figure available online).

- MD simulation is conducted for 100 ps at 300 K, and an NPT (constant number of particles, constant pressure, and constant temperature) ensemble is adopted.
- MD simulation is conducted for 50 ps with the temperature increasing from 300 K to 600 K, and an NVT (constant number of particles, constant system volume, and constant temperature) ensemble is adopted.
- MD simulation is conducted for 50 ps at 600 K and an NVT ensemble is adopted.
- MD simulation is conducted for 50 ps with the temperature lowered from 600 K to 300 K, and an NVT ensemble is adopted.

Repeat the above process three times to obtain the lowest energy structure, and take the final structure as the initial configuration.

After that, the final eight cell structure models are generated by equilibrating the above initial configuration using molecular dynamics simulation for 250 ps and conducting the NPT ensemble at 300/353 K, $\lambda = 100$, 240, 460, and 640, respectively. Figure 4 shows the simulated models for different water content of Nafion 117 membrane after equilibrating at 353 K.

In this article, MD simulations are performed for each of the eight models, three-dimensional periodic boundary conditions are applied, and temperature is controlled by the velocity scale heat bath method.

2.3. Diffusion Coefficients Computation

There are two kinds of diffusion coefficients in multi-mixture: self diffusion and mutual diffusion [25, 26]. Self diffusion describes the diffusion motion of the molecules without the driving force (for example, the concentration gradient). It is caused by Brownian motion of molecules, and can be applied to both pure substances and certain components in the mixture. In this article, the self diffusion refers to the diffusion of water molecules in the mixture and the diffusion of hydronium ion in the mixture. Mutual diffusion for binary mixtures describes the diffusion motion ability of component A through component B. It is related to the mass, the molar flux, and so on. The mutual diffusion is not studied here.

The atom in the molecular dynamic calculation system is conducting a non-stop movement from the initial position, so it has a different location at different time. Let $\vec{r}_i(t)$ represent the location of particle i at t time. The mean value of square displacement of a particle is defined as the mean square displacement (MSD); that is,

$$MSD = \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle \tag{8}$$

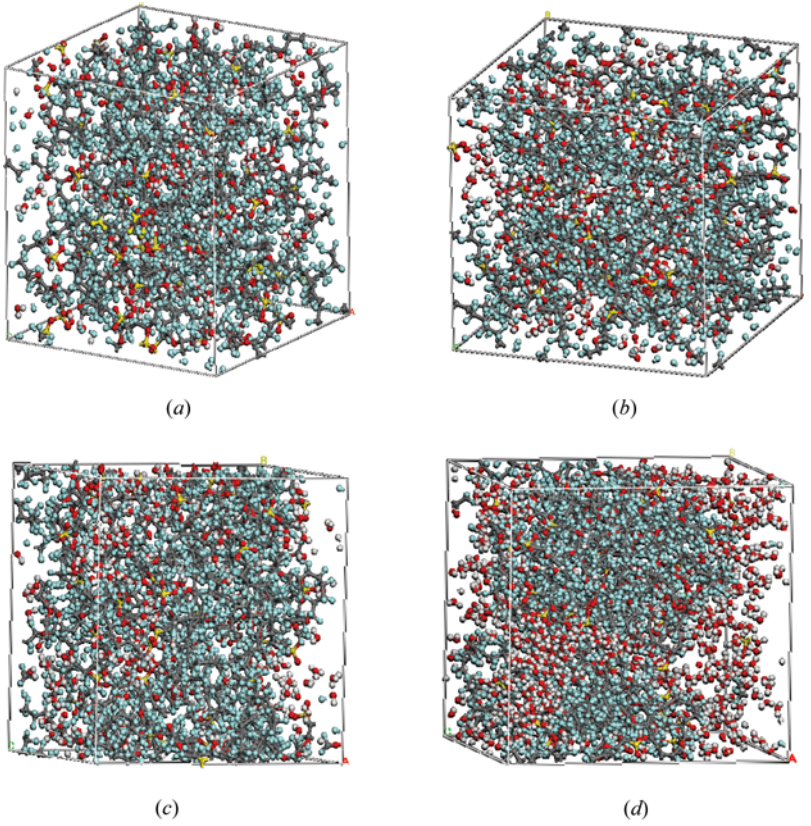

Figure 4. Final cell structure of hydrated Nafion for (*a*) $\lambda = 3.5$, (*b*) $\lambda = 7$, (*c*) $\lambda = 12.5$, and (*d*) $\lambda = 17$, at 353 K (color figure available online).

where $< >$ represents the mean value and $\overrightarrow{r}(0)$ represents the initial position. From Eq. (8), it can be seen that the values of MSD represent the moving activity of a particle. The bigger the MSD value, the larger the distance the particle travels within a certain time period.

According to Einstein's diffusion law [2],

$$\lim_{t\to\infty}\left\langle \left|\vec{r}(t) - \vec{r}(0)\right|^2 \right\rangle = 6Dt \tag{9}$$

where D represents self diffusion coefficient.

In the MS software, the diffusion coefficient is calculated by the following equation,

$$D = \frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\sum_{i=1}^{N}\left([r_i(t) - r_0(t)]^2\right) \tag{10}$$

where N is the number of atoms diffusively moving in the system.

The differential term of Eq. (10) can be replaced by the ratio of MSD over time difference; that is, the slope of the curve of MSD with time. MSD has been divided by the number of diffusion atoms, so the above formula can be simplified as follows.

$$D = \frac{a}{6} \tag{11}$$

where a is the slope of the graph.

Thus, the diffusion coefficients of water molecules and hydrogen ions can be obtained, respectively, by dynamically calculating the locations of the cell structure model and analyzing according to the above method. In this article, MD simulation is performed on the DELL 7400 workstation with 16 cores for 200 ps, and the temperature is set at 300 K and 353 K, respectively; NVE ensemble is adopted. In, the simulation, the time step is set at 1 fs and the frame output is every 200 steps. Then, we analyzed the trajectory files via the Analysis Dialog in the Discover Module of MS software and calculated the diffusion coefficient according to the calculation method mentioned above. In the simulation process, whether or not the system achieves the equilibrium state can be estimated by monitoring the change of interval energy. If the change of energy with time is minute, as is shown in Figure 5, the system can be regarded in equilibrium state.

The simulation process is as follows. First, mark water molecules and hydronium ions through oxygen atoms, denoted by O_w, O_h, respectively; second, analyze the trajectory files by the module Analysis in DISCOVERY of MS; and finally, calculate the diffusion coefficients of water molecules and hydronium ions according to the method mentioned above.

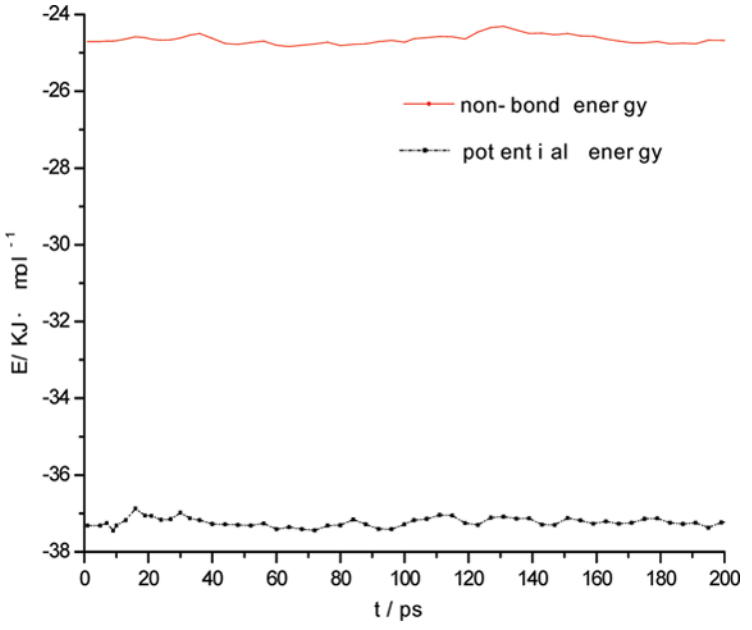

Figure 5. Energy change for $\lambda = 7$ at 300 K (color figure available online).

3. SIMULATED RESULTS AND DISCUSSION

3.1. Cell Density

We can obtain the sizes (length, breadth, and height of cell) of eight models from MS and the volume equals length × breadth × height. The simulated volumes of the cell at 353 K for $\lambda = 3.5$, 7, 12.5, and 17 are as follows: 3.392 nm × 3.392 nm × 3.392 nm; 3.546 nm × 3.546 nm × 3.546 nm; 3.754 nm × 3.754 nm × 3.754 nm; and 3.922 nm × 3.922 nm × 3.922 nm, respectively. The volumes of cell at 300 K for the four values of λ are 3.382 nm × 3.382 nm × 3.3 82 nm; 3.507 nm × 3.507 nm × 3.507 nm; 3.702 nm × 3.702 nm × 3.702 nm; and 3.805 nm × 3.80 nm × 3.805 nm, respectively. It shows that the volumes of cells at higher temperature are slightly bigger than that at lower temperature under the same water content, which illustrates that the PEM will expand along with the increasing of temperature.

The simulated densities of the cell at 300 K and 353 K are shown in Figure 6, and the figure also shows the experimental data of density measured by Mirris and Sun [27]. From the figure, the following features may be noted. First, the predicted variation trends of density with water content represented by the value of λ at the same temperature are consistent with the measured data, and with the increase in λ the membrane content decreases; at the same water content, the higher the temperature, the lower the density, especially for the higher values of λ. As far as the absolute values are concerned, the predicted densities values at 300 K deviate from the experimental data with the maximum deviation of 8%. Generally speaking, the MD predicted results are agreeable with the available test data, and with the

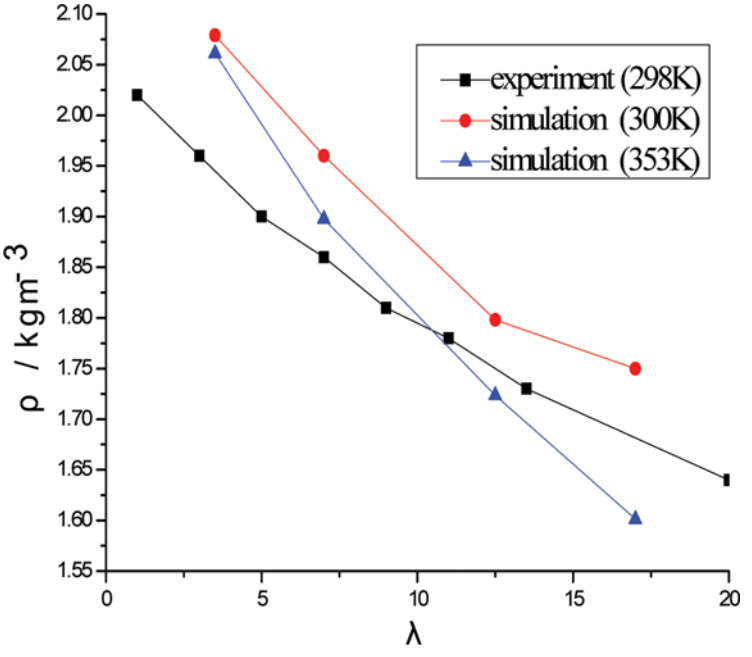

Figure 6. Density versus water content (color figure available online).

fact that the PEM will slightly expand at higher temperature under the same water content.

3.2. Diffusion Coefficient

Figures 7 and 8 show the MSD of the water molecule (MSD of O_w) and the MSD of the hydronium ion (MSD of O_h), respectively, for various water contents ($\lambda = 3.5$ to $\lambda = 17$) at 300 K, where O_w and O_h are the water molecule and hydronium ion respectively. From the figures it can be seen that the MSD of O_w and MSD of O_h increase with the water content, and the increasing rate of MSD of O_h is smaller than that of O_w. That is to say, the motions of water molecule and hydronium ion are accelerated because of the increase of water content, and accelerating action is more obvious for the MSD of O_w. The major role of PEM is to transport the proton. From the aspect of particle moving activities, a higher value of MSD is in favor of transporting the proton. Thus, increasing the water content of PEM can improve the proton conductivity, especially at lower values of λ.

In Figures 9 and 10, the variations of diffusion coefficients of water molecules and hydronium ions with the water content at 300 K are presented, which are qualitatively consistent with the experimental results [28]. Both experimental and numerical results show that the more water content, the greater diffusion coefficient. The figures also show that at the same water content, the predicted diffusion coefficients of both water molecules and hydrogen ions increase with the temperature. According to vehicular mechanism [29] on the proton conduction in the proton exchange membrane, hydronium diffuses through the aqueous medium in response to the electrochemical difference. Meanwhile, hydronium forms more easily when

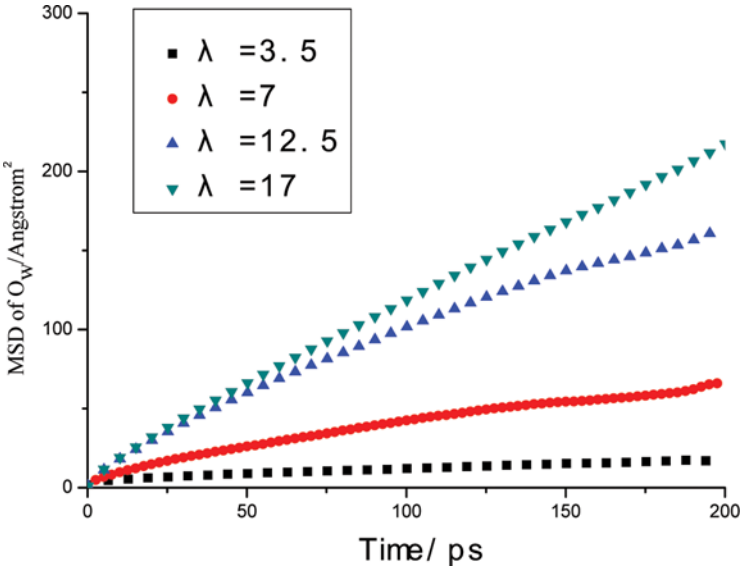

Figure 7. MSD of water molecular in Nafion for hydration level (λ) indicated by the legend at 300 K (color figure available online).

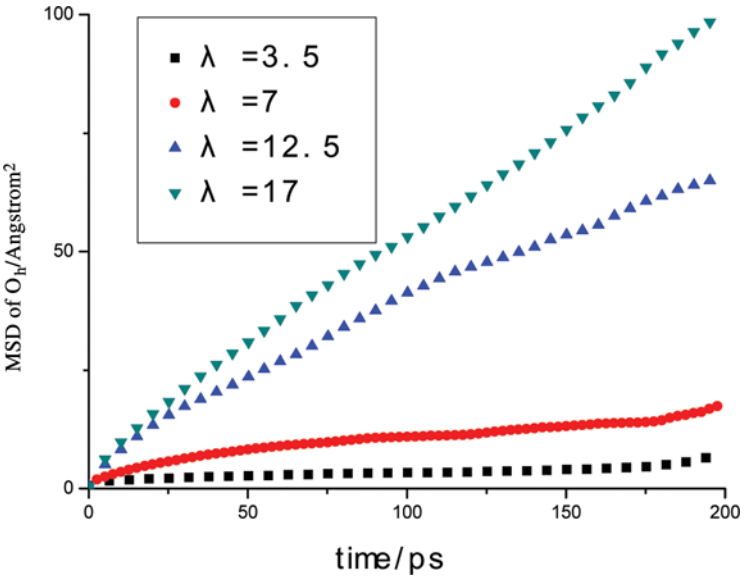

Figure 8. MSD of hydronium ions in Nafion for hydration level (λ) indicated by the legend at 300 K (color figure available online).

more water molecules are in PEM. Therefore, proton conductivity is higher when hydronium diffuses much more strongly; and at a higher temperature, the void of PEM expands which is useful to transport proton. Besides, comparison of the diffusion coefficients of water molecules with that of hydronium ions at 300 K shows

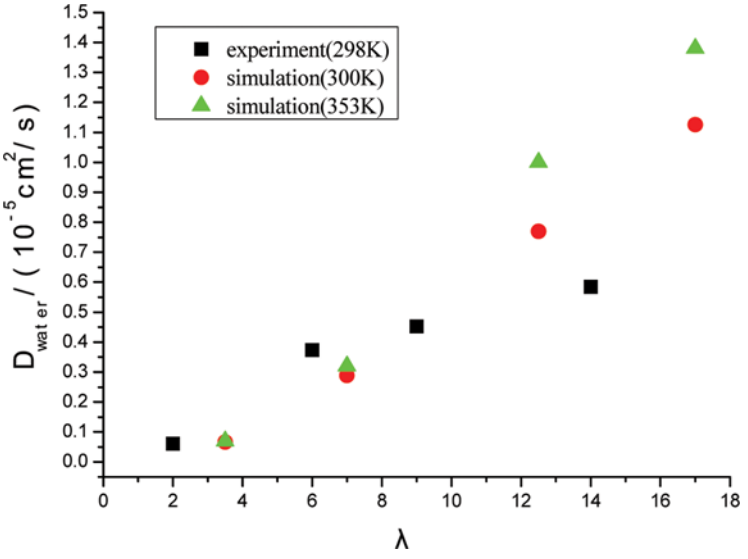

Figure 9. Diffusion coefficient of water molecules at different water content (color figure available online).

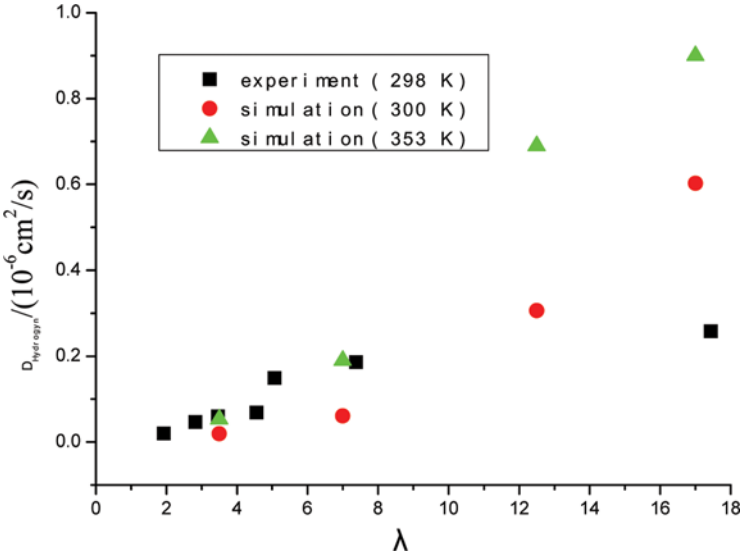

Figure 10. Diffusion coefficients of hydronium ions at different water content (color figure available online).

that the former is almost five times of the diffusion coefficient of the latter for $\lambda = 7$; but for $\lambda = 17$, the ratio is reduced to about two. This reveals that water molecule transports faster than hydronium ion and sulfonic acid group has a stronger action with hydronium ion at low water content. So, generally speaking, the temperature effect on diffusion processes of water and hydronium in the proton exchange membrane of PEMFC cannot be neglected. The present widely-adopted macro-models about PEMFC can be improved by modifying the water molecule diffusion coefficients according to the water content and temperature in PEM.

As can be seen in Figures 9 and 10, the deviation between predicted and measured data is somewhat significant, not only in the absolute value but also in the variation trend. It may be partially attributed to the periodic boundary conditions applied in our simulation for the Nafion 117 membrane because of the limitation of computing capability. The periodic boundary condition is just an ideal treatment for an infinite system. However, in the literature [28], the experimental results were obtained by describing the diffusion process through Gassian statistics in a restricted geometry with ill-defined boundaries at 298 K.

4. CONCLUSION

In this article, molecular dynamics simulations for hydrated Nafion 117 at various hydration levels and temperatures are performed by Materials Studio software.

The cell structure model of proton exchange membrane Nafion 117 is first constructed. The densities of various hydrated proton exchange membrane cell are obtained at 300 K and 353 K, respectively. It is found that at the same temperature, the cell density deceases with the increase of water content; at the same water content, the cell density decreases with the increase in temperature. The predicted

cell density is consistent with the experimental data, with the maximum deviation being 8%.

The simulated diffusion coefficients of both water molecules and hydrogen ions increase with the water content at the same temperature (300 K and 353 K), and at the same water content, the predicted diffusion coefficients of both water molecules and hydrogen ions increase with the temperature. So, the proton conductivity can be enhanced by increasing the water content, and temperature is a significant factor affecting diffusion characteristics for PEM.

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