Molecular Dynamics Study of Confined Structure and Diffusion of Hydrated Proton in Hyfion[®] Perfluorosulfonic Acid Membranes

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ABSTRACT. In polyelectrolyte membranes, hydrated protons and proton conductive channels have cooperative effect on proton conductivity, the mechanism of which is believed to involve the structure of hydrated proton being deformed to adapt the confining channel. To investigate the dependence of the structural and dynamical properties of hydrated protons in Hyfion[®] perfluorosulfonic acid membranes with various water uptake values on the channel size, a series of molecular dynamics simulations based on an all-atom force field were conducted. The water uptake dependence of the hydrated proton diffusivity determined from our simulations was consistent with the experimental results in literature, which verified the simulation systems. A probability distribution of the hydrated proton complex is proposed to characterize the confinement effect of the proton conductive channel on the hydrated proton structure in the membranes with different morphologies. By means of local structural properties and pair-potential energies, a reasonable hydrogen bond criterion was employed to characterize the structures of the hydrated proton complexes. It was found that the nanochannels confined the structure of the hydrated proton complex and that confined complexes of H_9O_4^+ , H_7O_3^+ and H_5O_2^+ were dominant. Weakening the

confinement by increasing the channel size was beneficial for the formation of the H_9O_4^+ complex, the probability distribution of which gradually became plateau. Thus, H_9O_4^+ can be considered the stable structure of the confined hydrated proton complex in polymer electrolyte membranes. This work is helpful in understanding the relationship between the structure of the confined hydrated proton and the proton conductive channel. It also provides potential guidance for improving the membrane performance in fuel cell.

Keywords: Hyfion[®]; Molecular dynamics simulation; Hydrated proton; Hydrogen bonding

1. Introduction

Polymer Electrolyte Membrane (PEM) fuel cells constitute an environmentally friendly and efficient power source that directly converts chemical energy into electrical energy. They have potential application as power sources for electric cars, submarines, portable mobile electronic devices, etc. (D'Urso et al., 2016; de Bruijn, 2005; Sagarik et al., 2008). Because of their low operating temperature, high power density, and rapid start-up, PEM fuel cells are believed to be an important technology in the future. The core component of PEM fuel cells is the polymer membrane between the anode and the cathode, which conducts protons and separates oxygen gas from the fuel (Hosseinzadeh et al., 2013; Li et al., 2008; Yousfi-Steiner et al., 2008; Zawodzinski et al., 1993). The characteristics of PEMs have significant effects on the fuel cell performance.

It has been reported that the nanostructure of PEMs is closely related to proton transfer through the membrane (Cui et al., 2007). Protons exhibit high conductivity and connectivity in larger proton conductive channels (PCCs). Several groups have experimentally modified PCCs to successfully enhance the proton conductivity of PEMs (Alberti et al., 2013; Li et al., 2011; Tran and Kalra, 2013). However, it was found that the increase in the proton conductivity of the commercial PEM Nafion[®] gradually decreased as the width of the PCCs increased (Wang et al., 2014). This is in agreement with the study that tuned the PCCs of Nafion[®] using the water content

(Kreuer, 1997). The results are also similar to those of a quasi-elastic neutron scattering study (Devanathan et al., 2013a), in which the diffusion coefficient of the proton was measured in order to characterize the proton conductivity of Nafion[®]. To elucidate the mechanism of the dependence of proton conductivity on the PCC width, it is important to investigate the structure of hydrated protons in the nanochannels of a membrane.

In bulk aqueous solutions, excess protons exist as hydrated complexes that take on several stable solvation structures such as Zundel (H_5O_2^+) (Zundel, 2000) and Eigen (H_9O_4^+) (Eigen and de Maeyer, 1958) cations. Hydrated complexes of protons have also been observed in the confined aqueous environment of PCC (Markovitch and Agmon, 2007; Marx et al., 1999). Hydrated complexes are the basic structures of proton in the PCCs, and their structures have inevitable effects on proton transport through the PEM. A wide PCC is needed for large hydrated protons to pass through. If the PCC is much wider than the hydrated proton being transported, proton conductivity will be blocked by the congestion of the hydrated protons. Fig. 1 illustrates the relationship between the PCC width and the proton structure. This mutual fit of proton to channel is suitable to both the vehicle mechanism and the Grotthuss mechanism. For example, in the Grotthuss mechanism, the hydrated protons in the broad PCC tend to form a three-dimensional hydrogen-bond network, greatly increasing the probability of proton transfer in directions other than that of the channel axis. As a result, the increasing negative effect on the proton transport reduces proton conductivity, as mentioned above. Because of the existence of hydrated protons, it is inferred that the mutual dependences of the hydrated proton structure on the PCC size determines the proton flux to a great extent. Therefore, in order to effectively regulate the microscale structure of PEMs, it is important to explore the stable structures of hydrated protons confined in PCCs.

Fig. 1 Schematic diagrams of the probable structures of the hydrated proton complexes in PCCs of different sizes

In recent years, there has been an increasing interest in understanding the relationship between the membrane structure and proton conductivity. Experimental studies on the water uptake of membranes (Bharath et al., 2016), water self-diffusion (Ochi et al., 2009), and membrane microstructure (Darden et al., 1993) have been implemented to understand the proton conduction mechanism. Progress in molecular modelling technology and simulation methodology has also made it possible to obtain reliable information on the structure of PEMs and hydrated protons on a molecular level using molecular simulation techniques such as classical molecular dynamics (MD) simulation, *ab-initio* molecular simulation, and density functional theory (DFT) (Abdolmaleki et al., 2016; Kim et al., 2008; Paddison et al., 2001). Paddison and Elliott (Paddison and Elliott, 2005, 2006) and Paddison et al. (Paddison et al., 2006) performed first-principles-based molecular modeling to investigate the effects of the side chains in Nafion[®] and Hyfion[®] on the structure of the hydrated proton. Because of the high computational cost, only a fragment with two side chains was used to model the membrane. The results showed that the structure of the hydrated proton is dependent on the properties of the side chains. Devanathan (Devanathan et al., 2013b) carried out *ab-initio* molecular simulations to study proton hopping in a Nafion[®] membrane under different hydration levels. It was found that the hydrated protons mainly existed as complexes of H_5O_2^+ , H_7O_3^+ and H_9O_4^+ . Classical MD is well adapted

for characterizing the structure of hydrated protons in the PCCs of PEMs (Liu et al., 2015; Spohr et al., 2002; Xie et al., 2016). Cui et al. (Cui et al., 2007; Cui et al., 2008) employed classical MD simulation to study the local structure of hydrated protons inside PEMs under different hydration levels. The formation of hydrated hydronium ions was determined by a defined distance from the radial distribution function between the oxygen atoms of hydronium and those of water. It is well known that the hydrogen bonding interaction between water and protons governs the formation of hydrated proton (Eigen, 1963). Thus it is necessary to adopt a reasonable hydrogen bond criterion to explicitly characterize the structures of the hydrated hydronium ions. Karo et al. (Karo et al., 2010) employed classical MD simulations to investigate the structures of hydrated protons in PEMs with different side-chain lengths. It was shown that the distributions of hydrated proton species were quite different for different hydrogen-bond criteria, which only included the $\text{H}\cdots\text{O}$ distance. Thus, a more explicit hydrogen-bond criterion is needed to investigate the hydrated proton structure.

Perfluorosulfonic acid (PFSA)-based membranes, such as Nafion[®] and Hyfion[®], are widely used in PEM fuel cells. In this work, a Hyfion[®] membrane was studied by classical MD simulations in order to elucidate the structural and dynamic properties of hydrated protons in the PCC. Several simulations were carried out with five water content values and three temperature values for the Hyfion[®] membrane. This paper is organized as follows: Section 2 provides details of the model and simulation methods; Section 3 discusses the results obtained from MD simulations for various hydration levels at the temperatures of 298, 325, and 353 K. The dynamical behaviors of water and hydronium were characterized by self-diffusion coefficients. Structural properties including radial distribution functions, hydrogen bonding network, and hydrated hydronium complexes, were also analyzed to describe the interaction between water and hydronium. Section 4 summarizes the findings of the present study. The current study helps us to understand the mechanism of proton transfer and develop PEMs with high performance.

2. Methodology

2.1 Simulation details

A Hyfion[®] polymer with ten monomers was employed for each system in this study. It was found that neither the number of Hyfion[®] chains nor the number of monomers in each chain had a significant effect on the simulation results of the studied systems, as shown in the Supplementary data (Figs. S1 and S2). Fig. 2 depicts the chemical structure of the Hyfion[®] chain, a monomer of which has a molecular weight of 997 Da. Hydronium was selected as the basic complex of the hydrated proton in the simulation. MD simulations were started from the initial configuration comprising eight Hyfion[®] chains and water with an additional eighty hydronium ions. This number of hydronium ions was adopted in order to maintain the system in electric neutrality. The number of water molecules used was determined according to the desired water contents ranging from $\lambda = 3$ to 17, where λ indicates the ratio of summation of the water and hydronium numbers over the number of sulfonic groups. The initial configuration of the membrane was randomly mixed. It has been reported that $\text{CF}_3\text{SO}_3\text{H}$ is ionized to CF_3SO_3^- and H^+ when $\lambda \geq 3$ (Wang et al., 2011), and hence the sulfonate groups of Hyfion[®] are considered as the ionized form SO_3^- in the present paper.

Fig. 2 Chemical structure of a Hyfion[®] chain. The blue and black fragments denote the hydrophobic and hydrophilic groups, respectively.

All molecules were modelled with all-atom force fields described by a combination of bond, angle, dihedral, Lennard–Jones (L–J), and Coulombic potentials. The geometric parameters of Nafion 117 reported by Vishnyakov and Neimark (Vishnyakov and Neimark, 2001) were adopted to build Hyfion[®]. The potentials of the side-chains were described using the $-\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_3^-$ part of the Nafion[®] side-chain with modification of the oxygen charge from -0.2742 to -0.6879 e (Brandell et al., 2007; Jang et al., 2004). All the intermolecular interactions are presented with a combination of Coulombic and L–J potentials. The parameters characterizing van der Waals and other intra-molecular interactions were taken from the previous reports (Jang et al., 2004; Tasaki et al., 1993). Water molecules were modeled using the TIP3P potential (Jorgensen et al., 1983) to describe the transport properties. The smallest stable hydrated form of hydronium (H_3O^+) was used to model the excess protons. Hydronium ions are described using the four-site model with the parameters reported by Jang et al. (Jang et al., 2004). Rigid bonds were applied to water and hydronium molecules.

The molecular dynamic simulations were carried out using the package NAMD 2.9 (Phillips et al., 2005) at 298, 325, and 353 K. To achieve equilibration, each simulation box was relaxed in the NVT ensemble by triplicate annealing procedures. The annealing procedure consisted of increasing the temperature from 300 to 600 K and then decreasing the temperature from 600 to 300 K. Then, each simulation cell was minimized for 2 ps and equilibrated for 10 ns in an isothermal–isobaric (NPT) ensemble. Data sampling was performed for another 200 ps, during which the system was in equilibrium. The sampling frequency was 10 time steps with a time step of 2 fs. A cut-off distance of 12 Å was adopted in both switching and shifting functions. Full electrostatic interactions were solved using the particle mesh Ewald (PME) method (Darden et al., 1993) with a grid spacing of 1.0 Å in each direction.

2.2 Data analysis

(a) Radial distribution function. The radial distribution function (RDF) provides a method to describe the structure on a molecular scale. The RDF between two species A and B can be calculated by the following equation:

$$g_{A-B}(r) = \frac{dN_B}{\rho 4\pi r^2 dr} \quad (1)$$

where ρ is the average density of species A in the system, dN_B is the number of species B located in a shell of thickness dr with distance r to species A. $g_{A-B}(r)$ provides the spherically averaged distribution of interatomic distance r between species A and B.

(b) Self-diffusion coefficient. The mean square displacement (MSD) according to the Einstein–Smoluchowski relation was adopted to calculate the self-diffusion coefficients for water (D_w) and hydronium (D_h).

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

where $\vec{r}_i(t)$ and $\vec{r}_i(0)$ are the position vectors of the center of mass of the i th molecule at times t and 0, respectively; the bracket $\langle \dots \rangle$ denotes the ensemble average. D_w and D_h can be evaluated from the slope of MSD as a function of simulation time, which in three dimensions reads

$$D = \lim_{t \rightarrow \infty} \frac{1}{6N_w t} \left\langle \sum_{i=1}^{N_m} \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle \quad (3)$$

where N_w is the number of molecules.

(c) Hydrogen-bond criterion. To identify hydrogen bonds between two molecules, a hydrogen-bond criterion should be defined. The most widely used hydrogen-bond criteria are the geometric, energetic and hybrid criteria. The geometric criterion of hydrogen bonds (H-bonds) is defined as two atoms satisfying a constraint on the spatial position. The geometric criterion for determining one H-bond $O-H \cdots O$ involves the distance $O \cdots O$, the H-bond length $O \cdots H$, and the angles $O-H \cdots O$, $H-O \cdots O$ and $O \cdots O-H$. The symbol “—” stands for the covalent bond and the symbol

“...” represents a non-bonded interaction. In our paper, the geometric criterion is based on the following:

1) The distance R_{OO} between the donor and acceptor is less than the threshold value

R_{OO}^C ;

2) The distance R_{OH} between the acceptor and the hydrogen of the donor is less than R_{OH}^C ;

3) The H—O...O angle α is less than the threshold angle α^C .

The thresholds R_{OO}^C and R_{OH}^C can be determined by the positions of the first minima in the oxygen–oxygen and oxygen–hydrogen RDFs. The value of α^C is usually determined by computing the angle (α) distribution.

MD simulation provides an opportunity to obtain detailed information about the atoms in the system, including position, velocity, energy, and their evolution over time. The pair-interaction energy, E_{ij} , which characterizes the intermolecular interaction between two molecules, can be evaluated by the summation of the Lennard–Jones potential, U_{ij} , and the electrostatic energy, Q_{ij} (Kalinichev et al., 1999). If the pair-interaction energy between two molecules, E_{ij} , is less than the threshold energy, which can be determined according to the distribution of the pair-potential energy of two molecules, they are considered to be hydrogen bonded. The hybrid geometric and energetic criterion is defined as mentioned above.

3. Results and discussion

3.1 Membrane morphology

Fig. 3 Snapshots of the configurations of the Hyfion® ionomer with $\lambda = 5.8$, 12.9, and 16.9 at temperatures of (a) 298 K and (b) 353 K, respectively. The ionomers are not shown in order to clearly exhibit the water channels. Hydronium ions are denoted in green and the hydrogen and oxygen atoms of water are denoted in white and red, respectively.

Fig. 3 shows snapshots of equilibrated configurations with different hydration levels at temperatures of 298 and 353 K. The figures show that the hydrated Hyfion® membranes are segregated into hydrophobic and hydrophilic regions, which is consistent with the hypothesis of the Gierke model (Gierke et al., 1981). Many nanoscale water clusters are connected within 1 nm channels in the hydrated membrane. Visual inspection of the snapshots for $\lambda = 5.8$ shows that the connectivity of the water clusters is poor and that the hydroniums expose to the surface of the water clusters. As the water content increases, the channels in the membrane gradually fill

with water, and the connectivity of the water clusters also increases. Despite the addition of water molecules, most hydroniums are still exposed to the surface of the water clusters. This implies that hydronium ions prefer to remain in the vicinity of the channel surface of the membrane. Several computations will be implemented in the following sections to quantitatively characterize the structure of the hydrophilic region of the membrane.

3.2 Water-channel topology

Free water and bound water present different structures within a perfluorinated sulfonic acid polymer (Awatani et al., 2013; Schmidt-Rohr and Chen, 2008). The local structure of water and hydronium in the hydrated Hyfion[®] was characterized by the RDFs. The RDFs of the S-S, S-O_w, S-O_h, O_w-O_w, O_h-O_h and O_w-O_h pairs were computed from the simulation results sampled over 2 ns after equilibration. The characters “S” and “O” denote sulfur and oxygen atoms, respectively, and the subscripts “w” and “h” are the abbreviations for water and hydronium, respectively. Figs. 4 and 5 plot these RDFs for different hydration levels at temperatures of 298 and 353 K.

3.2.1 Local structure of sulfonate group

As shown in Figs. 4(a) and 4(b), the S-S RDFs at 298 and 353 K, respectively, present broad peaks at approximately 5 Å under different hydration levels. The sulfonate groups present local aggregation despite electrostatic repulsion. This is similar to the results reported by Urata et al. (Urata et al., 2005). As the water content increases, the first peak height of the S-S RDF decreases. This implies that the aggregation of sulfonate group clusters was gradually disrupted, resulting in swelling of the membrane with the channel expansion.

The S-O_w RDFs at 298 and 353 K in Figs. 4(c) and 4(d), respectively, show one evident peak at 4 Å. This is consistent with the report by Cui et al. (Cui et al., 2007). The height of the peak decreases with increasing hydration level. The peaks of the S-O_w RDFs illustrate the existence of a hydration shell around the sulfonate group. At

a hydration level of 3.2, the peak height of the S-O_w RDFs at 298 K is higher than that at 353 K. As the hydration level increases, the temperature effect on the peak height gradually decreases. At low hydration levels, high temperatures strengthen the ability of water to escape the attraction of the sulfonate groups, thereby reducing the water distribution in the vicinity of the sulfonate groups. If there are enough water molecules in the membrane, the temperature-dependent escape of water from the sulfonate groups will be compensated for by the surrounding water molecules. Thus, temperature has little effect on the peak height for systems at high hydration levels.

Figs. 4(e) and 4(f) show the S-O_h RDFs at 298 and 353 K, respectively. For each hydration level, the RDF presents two peaks at 4 and 6 Å. It is noted that the S-O_w and S-O_h RDFs exhibit similar positions for the first peak and minimum. This implies that the sulfonate group attracts both water and hydronium. As the water content increases, the first peak declines and the second peak rises. This may be due to the fact that several hydronium ions are no longer attracted to the sulfonate group, and the escaped hydroniums diffuse from the first hydration shell to the second one. The space left by the escaped hydroniums in the first hydration shell is compensated for by the water in the second shell. The “free hydronium” contributes to the increase of the second peak of the S-O_h RDF. The S-O_w and S-O_h RDFs indicate that the water and hydronium ions attracted by the sulfonate groups form a hydrophilic region, as shown in Fig. 3.

Fig. 4 RDFs for the S-S, S-O_w and S-O_h pairs with five hydration levels at 298 and 353 K

3.2.2 Local structure of water and hydronium

As shown in Figs. 5(a) and 5(b), the positions of the peaks in the O_w-O_w RDFs at

298 and 353 K, respectively, are located at 2.8 Å. It is observed that increasing the hydration level from 3 to 17 reduces the peak height. The peaks shown in the O_w-O_w RDFs reflect the local aggregation of water in Hyfion[®] facilitating the formation of water clusters through which water and hydronium ions can migrate (Bahlakeh et al., 2013). It can be seen in Figs. 5(c) and 5(d) that the O_h-O_w RDFs for each hydration level at 298 and 353 K, respectively, show the first peak at 2.7 Å and the second peak at 5 Å, respectively. For the corresponding hydration level, the first peak for 298 K is higher than that for 353 K due to the thermal motion. With increasing water content, the decrease in the height of the first peak suggests that the number of the water molecules surrounded by hydronium ions decreases. Figs. 5(e) and 5(f) show the O_h-O_h RDFs at 298 and 353 K, respectively, with the evident peaks located at 6.8 Å. Similarly, the peak height decreases as the hydration level increases. This implies that the hydronium ions are gradually dispersed with the increasing water content in the channels.

Fig. 5 RDFs for the O_w-O_w , O_h-O_w and O_h-O_h pairs under five hydration levels at 298 and 353 K

3.3 Diffusion of water and hydronium

Molecular thermodynamic movement leads to the self-diffusion of hydronium and water, as well as to membrane fluctuation. Here, we primarily focus on the molecular

vehicular diffusivities in the membrane without considering Grotthus proton hopping. Fig. 6 depicts the self-diffusion coefficients D_w and D_h of water and hydronium, respectively, as a function of hydration level. The simulated values of D_w were $0.11 \times 10^{-5} \text{ cm}^2/\text{s}$ for $\lambda = 3.2$ and $0.37 \times 10^{-5} \text{ cm}^2/\text{s}$ for $\lambda = 5.8$. These values are quite similar to the experimental results of $D_w = 0.073 \times 10^{-5} \text{ cm}^2/\text{s}$ for $\lambda = 3.0$ and $0.36 \times 10^{-5} \text{ cm}^2/\text{s}$ for $\lambda = 6.0$ (Zawodzinski et al., 1993). The calculated D_w and D_h values are also consistent with the simulation results reported by Sunda and Venkatnathan (Sunda and Venkatnathan, 2013). In the studied conditions of hydration level and temperature, the largest value of D_w was approximately 30 times higher than the smallest value. Because of membrane blockage, water diffusivity in the membrane was significantly reduced as compared to bulk water (Wang and Hou, 2011). Also, both D_w and D_h increased with increasing temperature and hydration level. For all systems, the self-diffusion coefficient of hydronium in the membrane was approximately 3–10 times lower than that of water. This is similar to previous reports about Nafion[®] (Mabuchi et al., 2013). The diffusivity of hydronium ions in particular was even slower than that of water at a lower hydration levels. The electrostatic interaction between hydronium ions and the sulfonate groups weakened the proton transfer into the water channel. It is worth noting that the variations of D_w and D_h with water content correspond to the morphology of the water channel in the membrane. These results are consistent with those of our previous study by experimental and simulation methods (Wang et al., 2014).

Fig. 6 The self-diffusion coefficients of (a) water and (b) hydronium ions as a function of hydration level for three temperatures. The statistical errors are 3–4 orders of magnitude smaller than the corresponding data of D_w and D_h , and thus they are not shown in the figure.

3.4 Hydrogen-bonding analysis

In the hydrated membrane, the hydrogen bonding network plays a critical role in facilitating proton transfer (Bahlakeh and Nikazar, 2012; Clark Ii and Paddison, 2012; Hayes et al., 2009; Wang and Paddison, 2013). It is therefore necessary to study the structure of these H-bonds in the channels of hydrated Hyfion[®]. Herein, we focus on the water–water and water–hydronium H-bonds. In order to study the H-bond statistics, it is important to determine the definition of H-bonds. Geometric (Sarkisov et al., 1974) and energetic criteria (Frank H. Stillinger and Rahman, 1972) are two widely used methods to identify H-bonds.

3.4.1 Geometric criterion

For the water–water H-bonds, a threshold R_{Oo}^{c} of 4.0 Å was adopted based on the minimum position of the $\text{O}_{\text{w}}\text{--}\text{O}_{\text{w}}$ RDFs (Fig. 5) and R_{OH}^{c} of 2.3 Å was used according to the minimum position of the $\text{O}_{\text{w}}\text{--}\text{H}_{\text{w}}$ RDFs [Fig. 7(a)]. The angle cutoff, α^{c} , was obtained according to the distribution of angle α , shown in Fig. 8(a). It is observed that the cumulative distribution of angle α in a range below 40° was as much as 97.0–97.5 % that of systems with different water contents. Thus, the H-bonds among water molecules are identified when $R_{\text{Oo}} \leq 0.40$ nm, $R_{\text{OH}} \leq 0.23$ nm, and $\alpha \leq 40^{\circ}$.

Fig. 7 RDF of (a) O_w-H_w and (b) O_w-H_h with five hydration levels at 353K.

Similarly, the R_{OO} and R_{OH} were determined according to the O_h-O_w [Fig. 5] and O_w-H_h RDFs [Fig. 7(b)], respectively. α^c was obtained by the angular distribution

shown in Fig. 8(b). Finally, the geometric criterion for the water–hydronium H-bonds was adopted as $R_{OO} \leq 0.35$ nm, $R_{OH} \leq 0.22$ nm, and $\alpha \leq 40^\circ$.

Fig. 8 Distributions of angle α represented by the snapshots for the (a) water–water and (b) water–hydronium pairs.

3.4.2 Energetic criterion

The E_{ij} values of the water–water and water–hydronium pairs, shown in Fig. 9, were

characterized by a well-known bimodal curve (Jorgensen, 1980). It is observed that most interactions in the system involving pairs of non-neighboring molecules result in the main spike of the distribution at approximately 0 kJ·mol⁻¹. There are also low-energy minima at approximately -8 and -18 kJ·mol⁻¹ for the water–water and water–hydronium pairs, respectively. These features are significantly associated with the interactions of the hydrogen-bonded molecules. In general, the low-energy minimum can be used to determine the threshold energy employed in the energetic criterion (Shilov, 2014). Thus, two molecules are considered to be hydrogen bonded if the pair-interaction energy $E_{ij} \leq -8$ kJ·mol⁻¹ for the water–water pair and $E_{ij} \leq -18$ kJ·mol⁻¹ for the water–hydronium pair.

Fig. 9 Distributions of the pair-potential energies for the (a) water–water and (b) water–hydronium pairs.

In order to evaluate the geometric criteria as defined above, Fig. 10 shows the distributions of the pair-interaction energies, E_{ij} , of the hydrogen-bonded molecules determined by the distance and angle thresholds. It was found that approximately 10% of the water–water pairs exhibited the pair-interaction energy larger than $-8 \text{ kJ}\cdot\text{mol}^{-1}$. Therefore, the hybrid geometric and energetic criterion was employed with $R_{\text{OO}} \leq 0.40 \text{ nm}$, $R_{\text{OH}} \leq 0.23 \text{ nm}$, $\alpha \leq 40^\circ$, and $E_{ij} \leq -8 \text{ kJ}\cdot\text{mol}^{-1}$ to identify the water–water H-bonds. Only approximately 3 % of the water–hydronium pairs showed a pair-interaction energy larger than $-18 \text{ kJ}\cdot\text{mol}^{-1}$. Thus, the purely geometric criterion with $R_{\text{OO}} \leq 0.35 \text{ nm}$, $R_{\text{OH}} \leq 0.22 \text{ nm}$, and $\alpha \leq 40^\circ$ was adopted for the water–hydronium H-bonds.

Fig. 10 Distributions of the pair-potential energies of the hydrogen-bonded pairs of (a) water–water and (b) water–hydronium according to the geometric criteria.

3.4.3 Hydrogen-bonding statistics

The H-bond statistics provide the information about the number of H-bonds between different molecular pairs (Zhang et al., 2013). Figs 11(a) and (b) show the average numbers of H-bonds per water $\langle n(HB)_w \rangle$ and per hydronium $\langle n(HB)_h \rangle$, respectively,

with their corresponding statistical errors. The statistical errors were obtained from five simulation runs of different initial configurations. For the low hydration level, $\lambda = 3.2$, $\langle n(HB)_w \rangle$ and $\langle n(HB)_h \rangle$ for different temperatures are approximately 1.0 and 1.4, respectively. As the hydration level increases, the values of $\langle n(HB)_w \rangle$ and $\langle n(HB)_h \rangle$ also increase. Increasing the water content promotes the formation of H-bonds and enhances the connectivity of the H-bond network in Hyfion[®] membrane, providing good proton transfer channels. This conclusion is verified by the above results of the relationship between the self-diffusion coefficient of hydronium ion and the water content. This is also consistent with the previous findings (Prater, 1990). It is also shown that the dependence of $\langle n(HB)_w \rangle$ and $\langle n(HB)_h \rangle$ on water content gradually decreases with the increasing hydration level. For example, the value of $\langle n(HB)_h \rangle$ increased by 0.8 from 1.4 to 2.2 as λ increased from 3.2 to 10.5, and $\langle n(HB)_h \rangle$ increased to 2.4 when λ reached 16.9. Thus, it is inferred that one hydronium ion could form the hydrated complexes, $H_3O^+ \cdot (H_2O)_n$, where $n = 1-3$, which is further analyzed in the next section. Additionally, the value of $\langle n(HB)_w \rangle$ decreased as the temperature increased, and $\langle n(HB)_h \rangle$ showed irregular dependence on temperature.

Fig. 11 (a) The average numbers of the H-bonds (a) per water molecule $\langle n(HB)_w \rangle$ and (b) per hydronium ion $\langle n(HB)_h \rangle$ under different hydration levels and temperatures.

3.4.4 Hydrated hydronium complexes

The hydronium ion, H_3O^+ , presents several degrees of hydration in hydrated PEM (Selvan et al., 2008). To further understand the hydrated hydronium complexes, Fig. 12 shows the possible structures and the corresponding distributions of the hydrated hydronium complexes for different hydration levels at a temperature of 353 K. Fig. 12(a) exhibits three typical structures of hydrated hydronium complexes, including the $H_7O_3^+$ complex, formed by one hydronium ion with two water molecules, the $H_5O_2^+$ complex, denoted as the Zundel ion (Zundel and Metzger, 1967), and the $H_9O_4^+$ complex, denoted as the Eigen ion (Eigen, 1963). Fig. 12(b) shows the probability of the water number, n , for the hydrated complexes $H_3O^+ \cdot (H_2O)_n$. For $\lambda = 3.2$, hydronium ions prefer to form $H_5O_2^+$ and $H_7O_3^+$ ions. As the hydration level increases, the number of $H_9O_4^+$ ions increases and the number of the $H_5O_2^+$ ions decreases. These results are consistent with previous results reported by Cui et al. (Selvan et al., 2008). In that study, the authors reported that as the water content increased, the hydration

distribution shifted to a higher value in all regions. The hydration histogram in Fig. 12(b) shows that the aqueous domains are less connected at low hydration levels because fewer water molecules have a higher probability of being surrounded by hydronium ions. It is noteworthy that the number of H_7O_3^+ ions had no significant impact on the water content. This indicates that H_7O_3^+ ions are a relatively stable complex. A small number of $\text{H}_{11}\text{O}_5^+$ ions are observed in the membrane with a high water content. As mentioned above, the proton transfer channel expands as the water content increases, as shown in Fig. 4. Thus, water content and membrane structure have a cooperative effect on the structure of hydrated hydronium complexes.

Fig. 12 (a) The structures of the hydrated hydronium complexes $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$, where $n = 1, 2, 3$. (b) The probability distributions of the hydrated hydronium complex $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ as a function of hydration level at 353 K.

4. Conclusion

Classical molecular dynamic simulation was used to investigate the structural and dynamical properties of water and hydronium ions in a Hyfion[®] membrane at hydration levels of 3.2, 5.8, 10.5, 12.9, and 16.9 and at temperatures of 298, 325, and 353 K. In the hydrated Hyfion[®] membrane, the phase separation into hydrophilic and hydrophobic regions clearly produced water networks with a wide range of topologies. The results in the study demonstrate that the water-channel topology and connectivity are strongly dependent on water content and that the temperature and water content have significant effects on the self-diffusion of water molecules and hydronium ions. The simulation results show that the self-diffusion coefficients of water and hydronium ions increased with the increasing hydration level and temperature. The analysis of the RDFs and H-bonds of various atom pairs provided insight into the local structure and

morphology of the hydrated Hyfion[®] membrane. The S–S RDFs indicated that the sulfonate groups aggregate within a distance of 5 Å. This aggregation of the sulfonate groups is gradually disrupted by increasing hydration levels. As the hydration level increases, the number of “free hydronium ions” increases. For characterizing the water channels in the hydrated membrane, the H-bonds networks of water–water and water–hydronium in the channels were primarily studied in our work. A geometric criterion for the water–hydronium pair and a hybrid geometric and energetic criterion for the water–water pair were determined in order to accurately describe the H-bond network. Increasing water content promoted the formation of water–water H-bonds and enhanced the connectivity of the H-bond network in the Hyfion[®] membrane, providing good proton transfer channels. The hydrogen bonding interaction between water and hydronium led to the formation of the hydrated hydronium complexes, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, where $n = 1, 2, 3$. Hydronium ions preferred to form complexes of H_5O_2^+ and H_7O_3^+ at low hydration levels and complexes of H_7O_3^+ and H_9O_4^+ at high hydration levels. This work provides a basic understanding of the proton transfer process in Hyfion[®] membranes, which should contribute to optimizing the operating conditions. The mobility of the hydrated hydronium complexes will be further investigated to obtain insight into the mechanism of proton transfer in Hyfion[®] membranes. This paper deepens our understanding of the fundamental characteristics of the membrane structure and their relationship to the structure of the hydrated proton.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6A

Figure 6B

Figure 7A

Figure 7B

Figure 8A

Figure 8B

Figure 9A

Figure 9B

Figure 10A

Figure 10B

Figure 11A

Figure 11B

Figure 12A

Figure 12B