Hydroxide ions transportation in polynorbornene anion exchange membrane

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\textbf{Abstract}

In this paper, a series of amorphous polynorbornene cells were constructed, and the microstructures of the membranes and the transports of OH- in the membranes were optimized at different temperatures and water contents. The relationships between the microstructure of polynorbornenes and the transport of hydroxide ions were investigated by molecular dynamic (MD) simulations. The mobility of hydroxide ions was studied by the mean square displacement (MSD) curves. The results of the radial distribution functions (RDFs) of quaternary ammonium groups indicated that the functional groups were evenly distributed around the water channels. The RDFs of the hydroxide ions and the water molecules suggested that the hydroxide ions were surrounded by two layers of water shells. The migration of hydroxide ions occurred between two layers of water molecules, depending on the interactions of the hydrogen bonding. As the kinetic energy of a molecule increased with increasing the temperature, hydroxide ions moved faster at higher temperatures.

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1. Introduction

Anion exchange membranes (AEMs) have attracted considerable attention as separators in alkaline membrane fuel cells (AMFCs) \cite{1}. Compared to proton exchange membrane fuel cells (PEMFCs), AEMFCs can work under alkaline conditions with much higher oxygen reduction kinetics, and can prompt to use of non-precious metal catalysts, greatly reducing the cost of fuel cell devices. Corrosion issues are less common in an alkaline environment \cite{2}. However, despite great promise, AMFC application has many technical problems that must be resolved before AMFC can be applied \cite{3}. The first is identifying the impact of water content on the microstructure of the membrane and transport limitations of hydroxide ions. During the normal operation of AMFCs, water is generated as a by-product at the anode, as hydroxide ions transport from the cathode, meet and react with hydrogen molecules. The ion conductivity of the membrane can be improved with a sufficient quantity of water. However, this causes the disadvantage of mechanical properties \cite{4–10}. Recognizing the impact of water content on the microstructure of polymer and transport mechanism of hydroxide ions is helpful not only to the design of polymer structure, but also to the efficient operation of fuel cells \cite{11}.

Molecular simulation has been applied to analyze the movement of ion and microstructure of polymer backbone in
membranes for years. Besides, the functional polymer can be designed and synthesized by molecular simulation. The ion conductivity mechanism and the properties of the various ion exchange membranes have been predicted [3,4,11–18]. With the molecular dynamic (MD) simulation, the reports [6] have constructed different molecular models of proton exchange membranes for understanding the relationship between the aggregation structures of the polymer membrane, and the transports of the protons amongst membranes through changing the temperatures. The previous works [5] displayed critical factors which influenced the distribution of particles, for example, the H2O around sulfonate sites inside the functional polymer membranes. Kim et al. [4] used MD simulations to study the ion exchange mechanism in the poly(ether ether ketone) (PEEK) ion exchange membrane. The simulation results were a validation for actual results of the cationic conductivity and ion exchange capacity (IEC). Oh and coworkers [17] reported the transported behavior of cation at different temperatures in fully hydrated Nafion membranes through devising cell model. They proposed that the distribution of H2O molecules in Nafion membrane was different from that of pure water clusters greatly, and similar to the distribution in hexagonal ice by using the relation between mean square displacement (MSD) and time.

The transmission mechanism of OH⁻ in AEMs is the same as cation exchange membrane. The factors of the relative humidity, the temperature, and pressure play on the important roles on the conductivity of OH⁻ [18–29]. Thus a reference has been provided for studying the OH⁻ conduction mechanisms [30–34]. Various mechanisms have been reported [24–29,35,36]. For example, Grothuss’ mechanism occurs attributed to the switching of covalent bonds and hydrogen, en masse diffusion means the OH⁻ around the quaternary ammonium side chains of the respective membrane. The migration and diffusion attributed to the concentration and potential gradient acting on the charged particles [35]. Ion transport is often the result of coordination of the several mechanisms. Unlike proton, the structural diffusion of hydroxide ions is few reported. As a note, the data refer to experimental technique can be not provided for confirming the detailed mechanism of the OH⁻ diffusion.

In the present work, amorphous cells composed of poly-norbornene chains, hydroxide ions, and water molecules were created by molecular modeling techniques to analyze that the transportation of hydroxide ions was related to the microstructure of anion exchange membranes. From the results of MD simulations, the calculated values for hydroxide ions were compared to the experimental values, the results from various water contents and temperature were also examined and used to predict the anion diffusivity and the interaction among the polymer chains and water molecules.

2. Experimental section

2.1. Stimulate software and parameters

Material Studio software package (Accelrys Inc., USA) was used for Molecular simulations. Fig. 1 shows the polynorbornene chemical formula (a) and repeat units (b). Both were used to build the unit cell of polymer (c). The degree of polymerization of polymer chains was set to 100. Polymer R2 and R3 including 198 and 150 functional groups were randomly arranged within the chains. The initial cell’s density was 1.0 g/cm³. The parameters for building the Model are shown in Table 1.

2.2. Stimulation methods

This hydrophobic and hydrophilic three-dimensional (3-D) microstructure can be determined in this simulation. It was made up of polymer backbone as the hydrophobic components and the hydrophilic channels with different sizes. And the mobilized charge groups transported across the hydrophilic channels. In this simulation, amorphous cells containing various amount of water were used to analyze the ion diffusivities at different temperatures.

First, polymer chains, H2O molecules and OH⁻ were constructed by a Visualizer module. There are three polymer chains in each cell. Next, the geometry of the cell was optimized by smart algorithm, and the simulated annealing was used for the design of global minimum configuration. Then the target temperature was cooled down to 300 K, the structure came back to over 50 ps of the initial volume. This procedure was adopted with heating and cooling from 300 to 600 K repeatedly. This procedure was repeated 5 times until the structure showed no significant changes [3].

Furthermore, the temperature and energy of the Forcite module were the equilibrium criteria in the cell. In this step, NPT canonical ensemble was applied to calculation. The 1 fs time step and the total simulation time was set as 500 ps NPT at 300 K and 330 K, respectively. The Ewald summation was used for molecular simulations with the 0.001 kcal/mol. The temperature and the pressure were controlled during the simulations with a decay constant of 0.1 ps. After that, the system was up to the equilibrium by maintaining the density and energy of the cells constantly. Then, MSD and radial distribution function (RDF) were calculated based on the molecules motion trails.

The dynamic molecules were predicted through the simulation of the MSD. The result confirmed the diffusion of OH⁻ and H2O distributed in the AEMs. The simulated data of the diffusion coefficient was obtained from Equation (1) [27]:

\[
D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{j=1}^{N} \left( r_j(t) - r_j(0) \right)^2 = \frac{1}{6} \lim_{t \to \infty} \frac{dMSD(t)}{dt}
\]  

(1)
where the parameters of the diffusion coefficient and the number of diffusing particles are \( D \) and \( N \) in the equation, \( r_j(t) - r_j(0) \) represent the distance of the molecule motion at different time, and mean square displacement abbreviate to MSD.

The calculated data illustrated that the particles were related to the distribution of the particles in the polymer. The RDF could describe the structural characteristics accurately and provide the cluster status and coordination number. The RDF was calculated according to Equation (2) [39]:

\[
g_{A-B}(r) = \frac{V}{N_B n_B} \int_0^r \frac{n_B}{4\pi r'^2} dr' \tag{2}
\]

where \( g_{A-B} \) represents the occurrence probability of particle B around particle A, \( V \) represents the total volume of the system, parameter of the amount of particle B is \( N_B \), and \( n_B \) is the amount of particle B at the distance \( r \) around A.

3. Results and discussion

3.1. Water content

The mean square displacement curves (MSDs) of hydroxide ions in R2-50 and R3-30, which were selected based on the experimental IEC and water content, were analyzed. R2-50 had a higher IEC and water content than R3-30. The water content was increased when the number of functional groups was high [37], because of the interaction between quaternary ammonium groups and water molecules. AEMs, which contain high IEC and water absorption, had high ion conductivity. The curves shown in Fig. 2 suggest that the slope of the MSD curve of the hydroxide ions in R2-50 is larger than that in R3-30 at 300 K. This result indicates that the hydroxide ions in a cell with 50 wt% water uptake had a longer trajectory and a better mobility at 300 K. The simulated data of hydroxide ions in membranes displayed the same trend as that of the practical data [37], Fig. 3. R2-50 had a greater percentage of quaternary ammonium groups than R3-30. The water content of R2-50 was larger than that of R3-30, due to the interaction between quaternary ammonium groups and water molecules. The calculated diffusion coefficients by Equation (1) were 34.83 and 17.17 \( \times 10^{-3} \) cm\(^2\)/s for R2-50 and R3-30, which were in accordance with the tendency of ion conductivity in this experiment. The calculated diffusion coefficients are the positive role for the preparation of anion exchange membranes.

In order to scrutinize the impact of water content on the ion conductivity, R2-10, R2-30 and R2-50 were selected for dynamic analysis. Fig. 4 shows the MSD curves of hydroxide ions. The comparison of results suggested that R2-50 had a maximum slope, followed by R2-30, and then R2-10. The mobility of hydroxide ions increased from R2-10 to R2-50. The diffusion coefficients were calculated by Equation (1) and the results were 8.16, 14.25 and 34.83 cm\(^2\)/s in R2-10, R2-30 and R2-50, respectively. The higher water content a cell contained, the better mobility the hydroxide ions performed.

The RDFs of quaternary ammonium groups and water molecules were calculated by Equation (2). As shown in Fig. 5(a), it was found that the first and largest peak of N-H\(_2\)O (quaternary ammonium groups and water molecules) occurred in the range of 4.1–4.3 Å, possibly owing to the interactions of hydrogen bonding between water molecules and quaternary ammonium groups. The distribution of quaternary ammonium groups indicated that the functional groups were evenly distributed around the water channels, forming the walls of the water channels. The amount of water concentration was increased, meanwhile the intensity of the peaks were decreased. The results indicated that the interaction between cation (quaternary ammonium groups) and anion (OH\(^{-}\)) was weakened with increasing the water content and cationic site content. Fig. 5(b) shows the RDFs and the electrostatic interaction

<table>
<thead>
<tr>
<th>Cell</th>
<th>Temperature</th>
<th>number of particles</th>
<th>% of water</th>
<th>density (g/cm(^3))</th>
<th>Volume of cell (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>R2-10</td>
<td>300 K</td>
<td>198</td>
<td>198</td>
<td>260</td>
<td>10</td>
</tr>
<tr>
<td>R2-30</td>
<td>300 K</td>
<td>198</td>
<td>198</td>
<td>780</td>
<td>30</td>
</tr>
<tr>
<td>R2-50</td>
<td>300 K</td>
<td>198</td>
<td>198</td>
<td>1300</td>
<td>50</td>
</tr>
<tr>
<td>R3-30</td>
<td>300 K</td>
<td>150</td>
<td>150</td>
<td>700</td>
<td>30</td>
</tr>
<tr>
<td>R2-50</td>
<td>330 K</td>
<td>198</td>
<td>198</td>
<td>1300</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 1 Description of the simulated cells.
between the hydroxide ions and the quaternary ammonium groups. The $g(r)$ of N-OH (quaternary ammonium groups and OH$^-$) was weakened with increasing the water uptake of the membrane through solvation. Hence, the correlation of quaternary ammonium sites with OH$^-$ decreased, and thus the hydroxide ions could spread broadly in the water channel. In conjunction with Fig. 4, it could clearly be observed that the mobility of hydroxide ions took a positive correlation to the water content and a negative correlation to the interaction between the hydroxide ions and the quaternary ammonium groups [3].

The RDFs of hydroxide ions and water molecules had two peaks for hydroxide ions and water molecules, which were shown in Fig. 5(c). The first peak appeared at 1.3 Å, and the second one appeared at 2.6 Å. It meant that the hydroxide ions were surrounded by two layers of water shells. It might be hydrogen bonding, by which hydroxide ions were well solvated in the water phase. In the previous work [38,39], triple and quadruple hydrogen bonds can be formed in a hydroxide ion and donate one in aqueous solvent. Meanwhile, Merinov et al. asserted that the hydroxide ion was coordinated with multiple hydrogen bonds and one donated hydrogen bond among water molecules [3]. Combining with simulation data as shown in Fig. 5(c), the OH$^-$ anions were considered to be surrounded by two-layer water shells. The first layer of water molecules can be related with the hydroxide ions by strong and short hydrogen bonding, and the second layer of water molecules is located 2.6 Å away from the hydroxide ions. When the hydroxide ion moves closer to the second layer of water molecule by vibration, the hydrogen bond becomes shorter and stronger. Simultaneously, the formerly adjacent hydrogen bond elongates, forming a new water cluster.

### 3.2. Temperature

According to the observed experiment phenomena [26], the higher ion conductivity occurred with increasing the temperature, increasing the water content, and enlarging the transport channel size inside the membrane. Two corresponding cells were selected and compared with experiment data. R2-30 contained 30 wt% water content at 300 K, R2-50 contained 50 wt% water content at 330 K. The diffusion coefficients of simulation cells were calculated by Equation (1), as depicted in Fig. 6. The results of the diffusion coefficients of simulation cells are consistent with the experimental data [26]. The slopes of MSDs for hydroxide ions of these two cells are illustrated in Fig. 7. The MSD of hydroxide anions with 50 wt% water content at 330 K was larger than that with 30 wt% water content at 300 K. This indicated that the hydroxide ions in the cell with 50 wt% water content at 330 K had a longer trajectory and a better mobility.

Despite of the effect of differing water contents, the MSDs of hydroxide ions with 50 wt% water content at different temperatures were depicted in Fig. 8. It revealed that the slope of curve at 330 K was higher than that at 300 K, meaning that the hydroxide ion moved faster at 330 K than that at 300 K in an equal time. This demonstrated that the mobility of hydroxide ions was related to the temperature. High temperature increased the kinetic energy of molecules and thus the hydroxide ions moved a further distance.

### 4. Conclusion

The structures of H$_2$O, OH$^-$, and polymer backbone were built and optimized. Molecular models for anion exchange membranes were designed for understanding the microstructures of the membranes and the transport of the OH$^-$ in the membranes at
different temperatures and water contents. After MD simulations, the MSDs of OH- and RDFs of N-H₂O, N-OH and OH-H₂O were calculated to analyze the impact of water content and temperature on the transport of hydroxide ions. According to the simulation results, the OH⁻ diffusion likely combined both the mass diffusion and Grotthuss mechanisms in the hydrated membranes. Hydroxide ions were surrounded with two-layer water shells via the interaction of hydrogen bonding. The first water cluster was located just at 1.6 Å from hydroxide ion by strong and short hydrogen bonding, while the second cluster had a weaker and longer hydrogen bond, 1.6 Å from hydroxide ion by strong and short hydrogen bonding.

**Author contribution**

Chao Wang and Biming Mo contributed equally to this work.

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**References**


