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Understanding of imidazolium group hydration and polymer structure for hydroxide anion conduction in hydrated imidazolium-g-PPO membrane by molecular dynamics simulations

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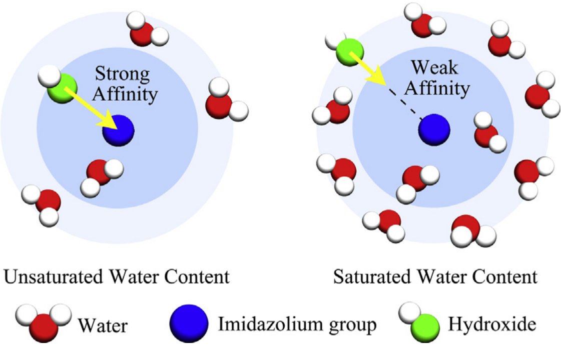
HIGHLIGHTS

- We investigated imidazolium-grafted PPO membrane with various water uptake.
- We described the effect of water uptake on the hydration structure of imidazolium group.
- Enhancing the hydration structure of the imidazolium group could weaken the affinity to the surrounding OH^-.
- Critical water saturation of imidazolium group could produce proper affinity to the surrounding OH^-.

GRAPHICAL ABSTRACT



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ABSTRACT

In an anion exchange membrane, OH^- conduction is closely related to the affinity of the functional group and membrane morphology. This relationship can change when the water uptake of the membrane varies. To explore the effect of the water uptake on the affinity of the functional group to OH^- and the membrane morphology, a series of molecular dynamics simulations based on an all-atom force field were performed for the imidazolium-grafted PPO (Im-g-PPO) membranes with different water uptakes. The simulation results of the membrane density, water and OH^- self-diffusivity, and OH^- conductivity verify the accuracy of the simulation systems. The local distributions of OH^- and water around the imidazolium group indicate that increasing water uptake enhances the hydration structure of the imidazolium group and weakens the affinity of the imidazolium group to OH^-. The critical water saturation of imidazolium group could produces suitable affinity to the surrounding OH^-. When the imidazolium group is water saturated, further increasing water uptake is not conducive to retaining the affinity to OH^-. As a result, the critical water saturation of the imidazolium group balances between the affinity to OH^- and the transfer of OH^- in the hydrated Im-g-PPO membrane. Furthermore, it also produces a percolated hydrophilic channel and maintains a relatively high mechanical strength of the Im-g-PPO membrane. Therefore, the imidazolium groups should be maintained under the critical water saturation, where two and eight water molecules are retained in the first and second hydration shells, respectively. This work provides a molecular-level understanding of the effect of the hydration structure of the imidazolium group on OH^-

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conduction and the morphology of the Im-g-PPO membrane. It also provides potential guidance for maintaining high performance in anion exchange membrane fuel cells.

1. Introduction

The anion exchange membrane fuel cell (AEMFC), which uses non-noble metal catalysts and has high oxygen reduction reaction (ORR) kinetics at the cathode, is considered to be a promising electrochemical energy storage and conversion device (He and Frank, 2014; Kusoglu and Weber, 2017; Nykaza et al., 2016; Varcoe et al., 2014). The anion exchange membrane (AEM) conducts hydroxide ions (OH^-) from the cathode to the anode (Pham et al., 2017; Shin et al., 2017), and thus determines the performance of the AEMFCs. The OH^- conductivity in AEM is closely related to the functional group (Park et al., 2017) and the membrane channel (Ge et al., 2016). An *ab initio* molecular dynamics study (Castañeda and Ribadeneira, 2015) showed that the affinity of the functional group to OH^- depends on the surrounding water. Water is involved in the interaction between OH^- and the functional group (Wang et al., 2018). Moreover, atomic force microscopy (AFM) results revealed that water uptake plays a key role in tuning the morphology of the membrane channel (Lin et al., 2013). To enhance OH^- conductivity, it is necessary to understand the mechanism of the water content effect on the functions of the cationic group and the membrane channel.

It was observed that the water uptake of the membrane fluctuates during the AEMFC operation (Jiao and Li, 2011). In particular, membrane dehydration results in ohmic losses and electrical resistance (Ji and Wei, 2009), while excessive water uptake inevitably gives rise to excess membrane swelling (Ge et al., 2015). For high OH^- conductivity, reasonable water content should be maintained to produce suitable hydrated cationic groups and a hydrophilic channel in the membrane. Thus, an adequate understanding of the water effect is beneficial for enhancing OH^- conduction in AEM.

Experimental studies (Bender et al., 2003; Dong et al., 2005) have been carried out to observe the water distribution in the polymer electrolyte membrane (PEM) by examining the electrochemical impedance spectroscopy (EIS) distribution. Several other experimental methods can also be used for investigating water behaviors inside the fuel cells (Jiao et al., 2010; Stumper et al., 1998). However, the application of the experimental measurements inevitably modifies the cell assembly and the system structure, resulting in unrealistic operating conditions. To overcome this deficiency, Weinzierl and Krewer (2016) constructed a general mathematical model for analyzing the influence of the operational conditions on the water transport through AEM. However, mathematical models cannot provide microscopic evidence regarding the hydrated structure of the functional groups and the morphology of the membrane channel. Molecular dynamics (MD) simulations based on empirical or semi-empirical force fields have been widely used for better understanding of water behaviors inside the hydrated AEM (Chen et al., 2016; Han et al., 2014; Zhang and van Duin, 2015). Chen et al. (2017) reported that the cationic group has strong electrostatic interaction with OH^-, helping to improve the OH^- conductivity under a low water uptake. Vishnyakov and Neimark (2014) used dissipative particle dynamics (DPD) simulations to enlarge the spatial and time scales. It was found that a high water uptake gives rise to excess water content in the membrane and reduces its mechanical strength.

In this study, we focus on the widely used membrane of poly (2,6-dimethyl-1,4-phenylene oxide) (Ran et al., 2012; Wu et al., 2015) grafted with imidazolium groups (i.e., Im-g-PPO) due to its excellent OH^- conductivity (Lin et al., 2013) and physicochemical stability (Mohanty et al., 2016) as well as low cost. Although the dimethylimidazolium (DIm) membrane has higher alkaline and thermal stabilities, the methyl group of the DIm group increases the steric hindrance and keeps OH^- away from the nitrogen atom of the DIm group. To explore the effect of the nitrogen atom of the Im group on OH^- conduction, it is necessary to focus on the Im-g-PPO membrane without considering the interference due to the steric hindrance. In this work, classical MD simulations were adopted to investigate the effect of the water uptake on the affinity of the Im group and the hydrophilic channel of the Im-g-PPO membrane. The rest of the paper is organized as follows. Section 2 presents a detailed description of the model and the simulation methodology and confirms that the models are reasonable. Section 3 discusses the results of the MD simulations for six hydrated Im-g-PPO membranes at atmospheric pressure and 353 K. Section 4 summarizes the results and discussions of this study. The present work provides an understanding of the membrane channel morphology and the theoretical guidance for the development of high-performance AEM.

2. Simulation methods

2.1. Atomistic models construction

A series of MD simulations were performed to elucidate the mechanism of OH^- conduction inside the hydrated Im-g-PPO membrane. Each MD simulation was started with an initial configuration consisting of an Im-g-PPO membrane and water molecules with additional OH^-. The number of OH^- was chosen so as to achieve overall electric neutrality. The water amount was determined according to the desired water uptake that corresponds to the hydration level as listed in Table 1. The hydration level λ was defined as the ratio of the total number of water and OH^- molecules to the number of Im groups. The Im-g-PPO membrane consists of ten Im-g-PPO chains with the substitution degree of 50%. The chemical structure of the Im-g-PPO polymer is depicted in Fig. 1, and the compositions of the six systems are listed in Table 1.

All molecules were described by an all-atom force field as a function of bond, angle, dihedral, improper, Lennard-Jones (L-J), and Coulombic potentials. The CHARMM force field was used to describe the Im-g-PPO polymer (MacKerell et al., 2000). Partial charges of the Im-g-PPO polymer were optimized using the Mulliken population analysis of the results of the density functional theory (DFT) calculations at the B3LYP level using the 6-311+G(d, p) basis set. Water molecules were described by the TIP3P model (Jorgensen et al., 1983), and the OH^- were modeled using the parameters reported by Jang et al. (Han et al., 2014). The relevant force field parameters are listed in Supporting Information (Tables 1–3).

2.2. Computational details

MD simulations were performed using the NAMD 2.9 package (Phillips et al., 2005) with periodic boundary conditions imposed in three dimensions. To ensure the system equilibrium, the initial structure of each system was relaxed using the following annealing procedure (Jang et al., 2004): (I) the system volume was gradually