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Proton conduction of fuel cell polymer membranes: Molecular dynamics simulation

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ABSTRACT

Fuel cell polymer membrane as the core of the proton exchange membrane fuel cell (PEMFC) plays an important role in maintaining high intrinsic proton conductivity and insulating electrode. To investigate the effect of crosslinking formation on proton conduction, the proton mobility and ion conduction were calculated and analyzed by using molecular dynamics (MD) simulation. As the crosslinking number increased, the proton diffusion coefficients increased at first and then decreased. The results indicated that the formation of crosslinked bonds was beneficial for opening new channels to enhance the proton conductivity. But too many crosslinking also can decrease proton diffusivity due to the blocking along the chain backbone. Besides, the proton conduction was better at 350 K than at 300 K. It can be concluded that temperature also had a significant impact on diffusivity and conductivity.

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1. Introduction

PEM is the core of proton exchange membrane fuel cells (PEMFCs) [1,2]. Proton conduction is the primary function of ionomer in the catalyst layers (CLs) of the polymer electrolyte fuel cell [3,4]. In common CLs, commercial PEMs such as Nafion, Dow, Aciplex membranes were used widely, which have been investigated widely. Many researchers [5–12] have studied the dynamic properties such as ion diffusion, proton conductivity and thermal properties such as thermal conductivity of PEM. Cui et al. [9] performed classical MD simulations to analyze the effect of the length of the side chain on hydrated morphology and hydronium ion diffusion in Nafion and the SSC PFSA membranes. They concluded that the diffusion coefficient of water and hydronium ions are both slightly lower in the SSC PFSA membrane when compared to Nafion, which can suggest that structural diffusion by proton hopping may account for the observed higher conductivities in the SSC PFSA membrane.

To enhance the mechanical properties and improve conductivity, the membranes were modified through experiment [13–21] and MD simulation [22] methods for further study. Han et al. [13] prepared a series of novel organic-inorganic crosslinked hybrid proton exchange membranes. The crosslinked hybrid membranes exhibited excellent mechanical properties and high proton conductivity due to the inorganic phase and crosslinked structure. Song et al. [14] prepared acid-base ionic crosslinking sulfonated poly composite membranes. Highly Sulfonated poly (ether ether ketone) (SPEEK) membrane doped with moderate polybenzimidazole (PBI) formed ionic crosslinking bonds which can improve conductivity, mechanical strength and thermal stability. In addition to the experimental method, Li et al. [22] prepared a novel polymer material which was intended to be used as PEMs based on polynorbornenes via ring-opening metathesis polymerization (ROMP) by MD simulation. They investigated the feasibility of the designed structure membrane by calculating the ion diffusion coefficient and proton conductivity. Kikugawa et al. [23] performed MD simulations on amorphous polyethylene and polystyrene with varying crosslinking concentrations to investigate the effect of crosslinking between polymer chains and heat conduction. They revealed that crosslinking has effect on thermal conductivity and the increase in thermal conductivity was dominated by the contribution of energy exchange by bonded interaction. Bahlakeh et al. [24–26] employed MD simulations to elucidate the effect of the degree of sulfonation (DS) on structural and dynamical characteristics of SPEEK and sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes at different temperatures. The simulated ionic conductivities had qualitatively agreement with the experimental data.

In our previous works [27], we investigated the proton mobility and thermal conductivities of Nafion, Dow, and Aciplex membranes. In this paper, we employed MD simulation to elucidate the effect of crosslinking formation on proton diffusivity and conductivity in PEM. We calculated the radial distribution functions (RDFs), the coordination numbers (CNs), mean square displacements (MSDs), and free volumes to gain a quantitative understanding of the relationship between crosslinking and proton conduction in the micro mechanism.

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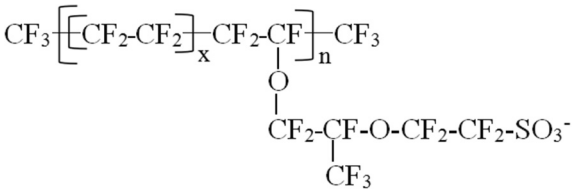

Fig. 1. Chemical structure of the membrane polymer.

2. Models and computational details

2.1. Models

All atomistic MD simulation models were carried out on manually constructed 3D amorphous cells containing six polymer chains (the chemical structure of polymer as shown in Fig. 1, where takes x = 7 and n = 10), 60 hydronium ions in order to keep the cells neutral and 900 water molecules to make water content k = 16 so that fuel cell in optimum operating condition. Fig. 2 is the initial model schematic of the five simulation systems with crosslinking number of 0, 5, 11, 20, 27, respectively, and named C0, C5, C11, C20, C27, correspondingly.

2.2. Computational details

In this article, the ab initio COMPASS force field [28] and three-dimensional periodic boundary conditions were adopted. Firstly, the final structures obtained from the geometry optimization step were heated from 200 to 500 K over a period of 500 ps in NPT ensemble and 1000 ps in NVT ensemble. The annealing procedure was repeated five cycles. After that, using the final structures obtained from the annealing procedure to perform the following dynamic simulation: 1000 ps NPT dynamics simulation and 2000 ps NVT dynamics simulation, which used to study the dynamic properties of these cells. In the simulation procedure, temperature

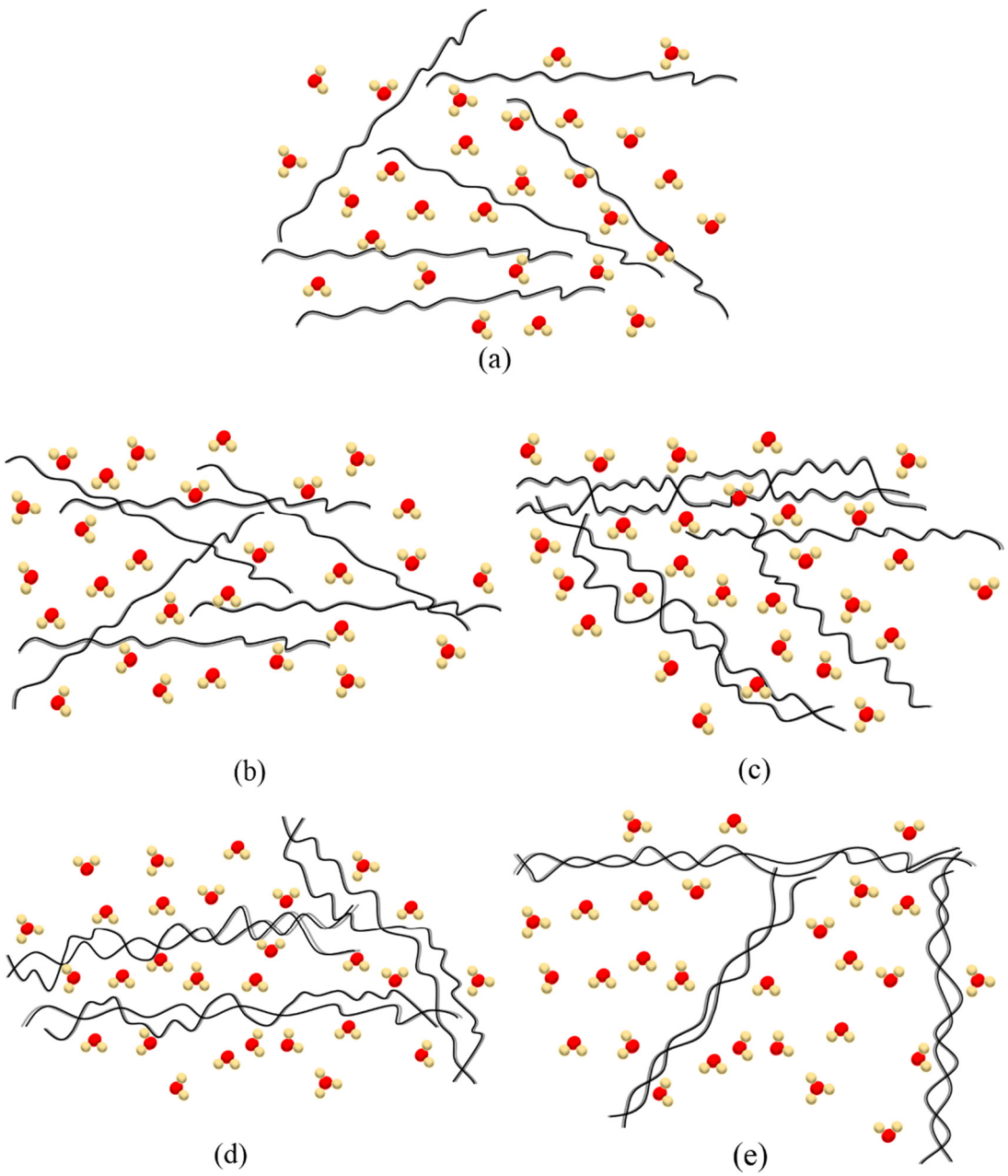

Fig. 2. The initial model schematic of C0, C5, C11, C20, C27 systems, corresponding (a)–(e).

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