EFFECTS OF PERFLUOROSULFONIC ACID SIDE CHAIN LENGTH ON PEM FUEL CELL CATALYST LAYER STRUCTURE: A MOLECULAR DYNAMICS APPROACH

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ABSTRACT

The effects of side chain (SC) length of perfluorosulfonic acid (PFSA) polymers on the structure of PEM fuel cell catalyst layer (CL) have been studied using molecular dynamics simulation. Two possible transport paths of reactant molecules towards platinum (Pt) surface are inferred based on the visualization of CL configurations. And the sandwich-like structure of CL is observed. Moreover, the results show that the short PFSA SCs will lead to the high accessibility of sulfonate acid groups, water molecules and hydronium ions to Pt particles, which can improve the transport of protons to Pt particles. Additionally, this paper has also found that PFSA SC length has little effect on the migration of hydronium ions.

Keywords: PEM fuel cell; Catalyst layer; Structure; Side chain length; Molecular dynamics simulation

1. INTRODUCTION

Proton exchange membrane (PEM) fuel cell is generally regarded as one of the most promising green power devices, and it has attracted considerable attention in many fields due to its many advantages such as low emissions, high power density, high efficiency and so on [1]. As one of the significant components in PEM fuel cell, the catalyst layer (CL) provide the site for electrochemical reaction. And CL composes of catalyst, catalyst support, electrolyte and so on, where the complex physical and chemical phenomena occur. Therefore, the investigates on CL is very necessary for developing PEM fuel cell.

Many researches have been carried out to explore the CL structure by molecular approach [2-6]. Cheng et al. [3] investigated the effects of platinum (Pt) particle size on CL structure and found that big Pt particle was beneficial to the protons transport in the region near Pt particles. He et al. [4-5] revealed the effects of hydration, ionomer thickness and carbon support oxidation on CL structure, and the effects of Pt particle shape and oxidation on the adhesion. Additionally, Malek et al. [6] have adopted coarse-grained molecular simulation to study CL structure.

As well known, the perfluorosulfonic acid (PFSA) is generally adopted as the electrolyte in CL. And many molecular simulation results demonstrated that the side chain (SC) length of PFSA has a strong effect on the bulk PFSA membrane [7-9]. But to the best of author's knowledge, the effects of PFSA SC length on CL structure have not ever been studied by molecular approach in previous researches. Therefore, this paper will carry out several simulation cases established carefully to reveal the effects of PFSA SC length on CL structure.

2. SIMULATION METHODE

In this simulation, the graphite is employed as the carbon support as Ref. [2,3]. And the platinum (Pt) particle is truncated octahedron shape [2] and approximately 3 nm width including 807 atoms. In addition, the internal structures of graphite sheets and Pt particles are regarded to be rigid. The perfluorosulfonic acid (PFSA) (Fig. 1) contains 10 repeated monomers that consist of 16 CF_2 groups and side chain (SC) with different length (m = 0, 1, 2). The potential models employed in this paper are from Ref. [5,7]. And the interactions between different atoms follow Lorentz-Bertelot mixing rule. The cut-off distance of Lennard-Jones (LJ) interactions without a truncation shift function is defined as 1.5 nm. Furthermore, particle-particle particle-mesh method (pppm) with the accuracy

of 0.0001 is used to calculate the long-range electrostatic interactions. The temperature is controlled using Nose-Hoover thermostat with relaxion time of 0.1 ps. All the MD simulations are carried out using LAMMPS package [10] with the time step of 1.0 fs.

$$CF_3\text{-}[(CF_2\text{-}CF_2)_7\text{-}CF_2\text{-}CF]_{10}CF_3$$
$$(O\text{-}CF_2\text{-}CF)_m\text{-}O\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$$
$$CF_3$$
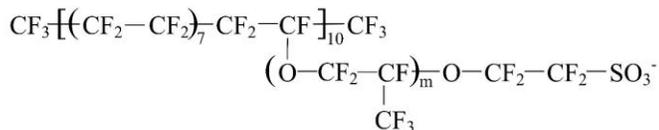
Fig. 1 Chemical structure of PFSA.

During simulation process, 15 PFSA chains, 150 hydronium ions and 1200 water molecules (corresponding to water content λ = 9) are randomly inserted around carbon-supported Pt. Then an annealing process is carried out to relax the original structures and eliminate the initial bias. And this annealing process includes a) NVT simulation for 3 ns at 1000 K using the LJ parameter (ε) within PFSA atoms reduced by two orders of magnitude; b) NVT simulation for 3 ns returning the LJ parameter (ε) to original value and the temperature to 353 K. Furthermore, another NVT simulation for 10 ns at 353 K is performed and the simulation results of last 5 ns are collected and analyzed. And in this process, a wall is placed at a high enough position to prevent the confined effect.

3. RESULTS AND DISCUSSION

The final configurations of CL with different PFSA SC length are shown in Fig. 2. And the Pt particles are mostly covered as expected, nevertheless there is still a part of Pt surface directly exposed to the gas region, especially for shorter PFSA SC. Therefore, the reactant molecules can be directly adsorbed onto Pt surface. Besides, there are extensive pores/cracks between PFSA backbone. And the reactant molecules can be also adsorbed by those pores/cracks and then migrate towards Pt surface. But the resistance of the second transport path may be very high due to the low permeability for reactant molecules in electrolyte. Therefore, the long PFSA SCs tend to increase the transport resistance of reactant molecules as indicated in previous experiments [11], due to the low possibility of the exposure of Pt to the gas region.

The distributions of C atoms of PFSA backbone and water molecules along the direction perpendicular to carbon support for different PFSA SC length are plotted in Fig. 3 (a). It is evident that the water molecules are mostly distributed in the middle, whereas PFSA backbone is dispersed close to the carbon support or gas region. Furthermore, the peak location of water molecule number distribution is gradually far from carbon support with the increment of PFSA SC length. In addition, Fig. 3 (b) shows that the number distribution of sulfonate acid groups and SC orientation angle (θ) at SC length m = 1. It can be found that the sulfonate acid groups are also mostly in the middle as same as the water molecules. And the SC orientation angle (θ) are defined as the angle between the normalized orientation vector of O-C-C-S and normal vector to carbon support. As shown in Fig. 3 (b), the cosine of SC orientation angle (θ) changes from positive number to negative number around the peak location of water molecule number distribution, which indicates that the orientation of sulfonate acid groups tends to point to the water clusters.

The radial distribution function (RDF) is defined as:

$$g_{A-B} = \left(\frac{n_B}{4\pi r^2 dr}\right) \Big/ \left(\frac{N_B}{V}\right)$$

where n_B is the number of B particles in the dr-thick spherical shell at radius r from A particles, $4\pi r^2 dr$ the volume of the shell, N_B the total number of B particles, and V the volume of simulation box. And g_{Pt-S}, g_{Pt-OW} and g_{Pt-OH} (the RDFs between Pt atoms and S atoms in PFSA, O atoms in water molecules and O atoms in hydronium ions) are plotted in Fig. 4. It can be found for short PFSA SC, the accessibility of sulfonate acid groups, water molecules and hydronium ions to Pt particles is higher. It may be because that the sulfonate acid groups in long PFSA SCs can extend far from PFSA backbone adsorbed on Pt particles. And water molecules and hydroniums
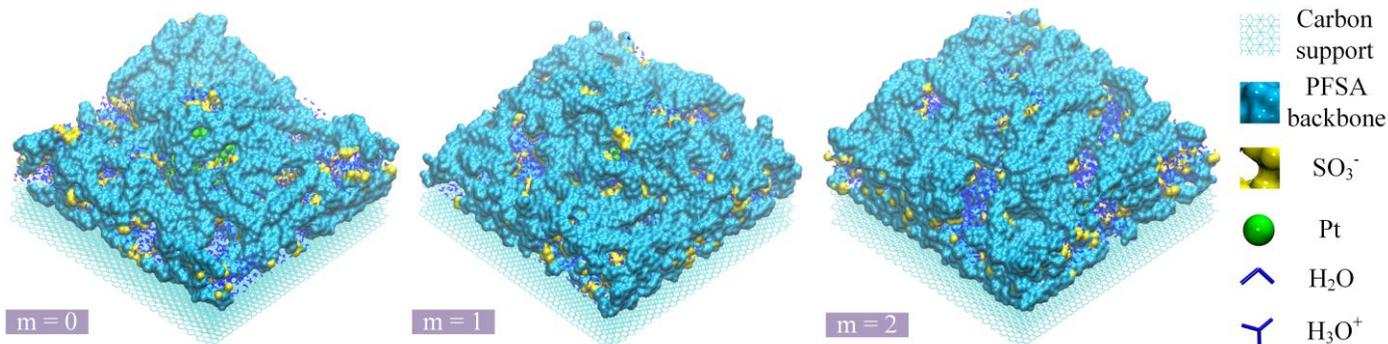
Fig. 2 The final configurations of CL with different PFSA SC length.

ions also tend to stay far from Pt particles owing to their strongly binding to sulfonate acid groups. As well known, the protons migrate along the conducting network provided by water molecules and PFSA SCs. Therefore, the short PFSA SCs enhance the proton transport to Pt particles, thereby increasing the electrochemical surface area (ECSA) of catalyst layer as demonstrated in the experiments by Park et al. [12].

(a)

(b)
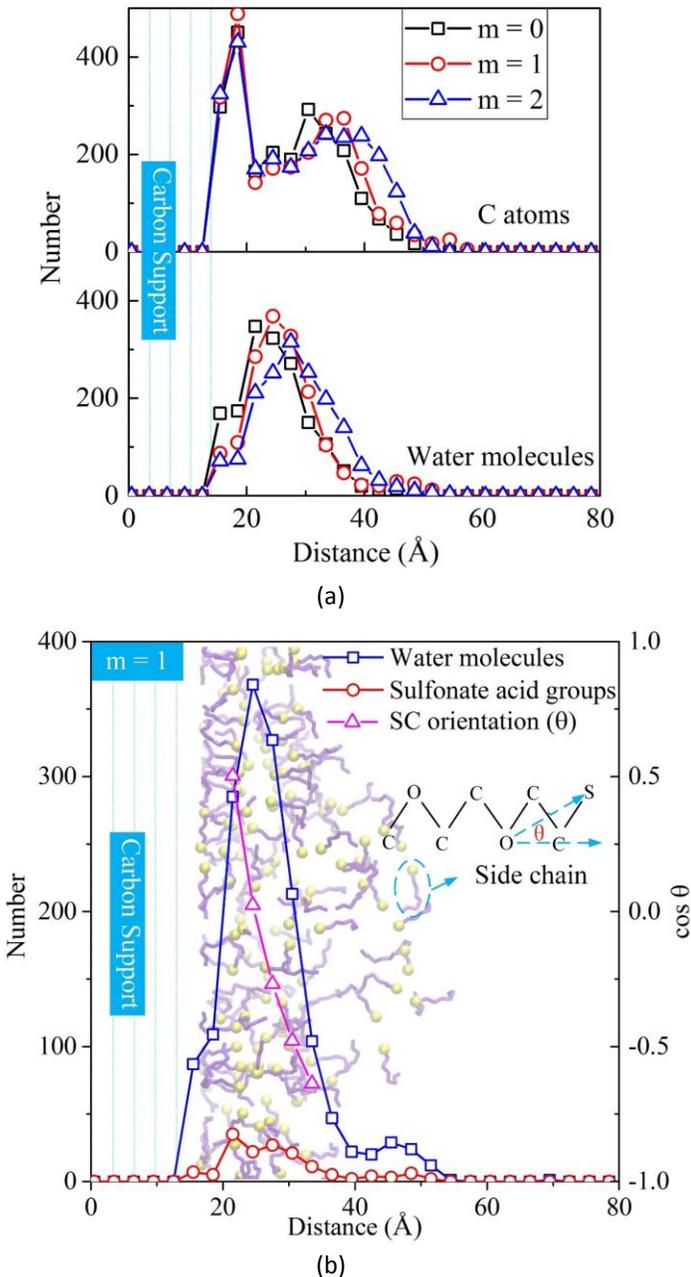
Fig. 3 The number distributions of C atoms in PFSA backbone, water molecules (a) and sulfonate acid groups, and PFSA SC orientation (b).

(a)

(b)

(c)
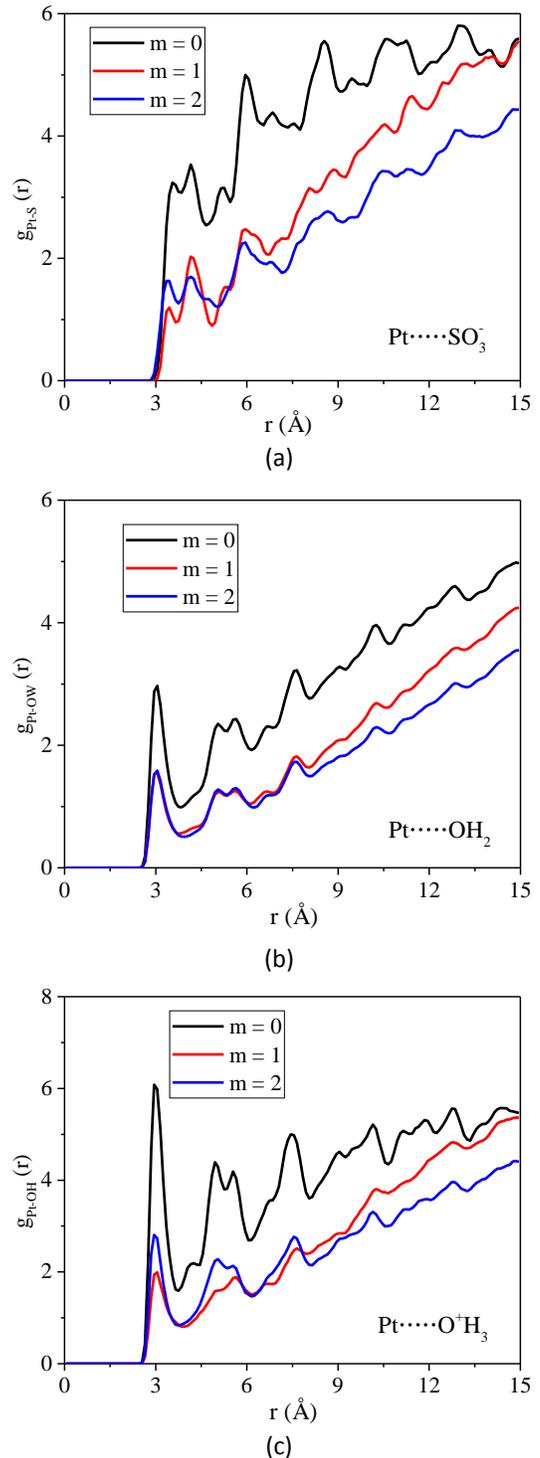
Fig. 4 The RDFs of g_{Pt-S} (a), g_{Pt-OW} (b) and g_{Pt-OH} (c) for different PFSA SC length.

Fig. 5 shows the mean square displacement (MSD) of hydronium ions along the plane parallel to carbon support (In-plane) and along the direction perpendicular to carbon support (Through-plane). It can be found that In-plane MSD is obviously higher than Through-plane MSD, which means that the hydronium ions mainly migrate along the plane parallel to carbon support. And the migration along the direction perpendicular to

carbon support is severely confined by the ionomer thin film. In addition, the effect of PFSA SC length on the migration of hydronium ions is observed to be not obvious.
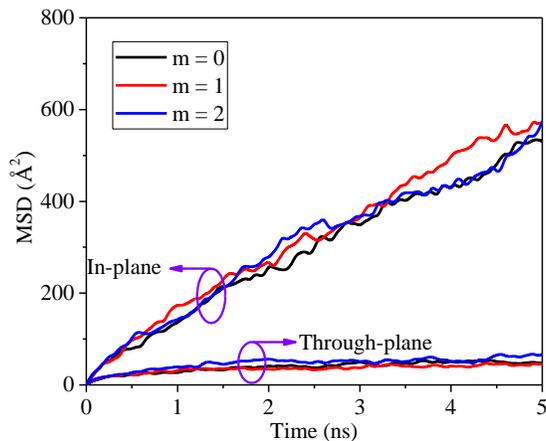
Fig. 5 Mean square displacement (MSD) of hydronium ions along the plane parallel to carbon support (In-plane) and along the direction perpendicular to carbon support (Through-plane).

4. CONCLUSIONS

In this paper, the configurations of catalyst layer (CL) consisting of graphite (carbon support), Pt particle, PFSA (electrolyte), water molecules and hydronium ions are founded. And the effects of PFSA side chain (SC) length on CL structure are investigated using molecular dynamics simulation. Based on the visualization of CL configurations, two possible transport paths towards Pt surface for the reactant molecules are inferred: a) directly adsorbed by the exposed Pt surface, b) firstly adsorbed by PFSA pores/cracks and then migrating towards Pt surface. Moreover, the CL configurations are sandwich-like, where the PFSA backbone is dispersed on both sides (close to carbon support or gas region) with water molecules in the middle. Additionally, the possibility of sulfonate acid groups, water molecules and hydronium ions around Pt atoms for short PFSA SC is higher, which can enhance the transport of protons to Pt particles. Moreover, the hydronium ions mainly migrate along the plane parallel to carbon support, and PFSA SC length has little effect on the migration of hydronium ions.

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