

Molecular Dynamics Simulation Study of Proton Diffusion in Sulfonated Polyphenylene Oxide Membranes: Postprint

Authors: Han Xuhui, Zhang Peng, Ma Yue, Li Jia, Wang Yuxiang, Zhou Qiong, Zhou Guang-Gang, Lu Guiwu

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Abstract

To investigate the properties of sulfonated polyphenylene oxide (SPPO) for proton exchange membrane fuel cells (PEMFCs), we studied the molecular diffusion characteristics of water and hydronium ions inside the SPPO membrane. Molecular structural models of SPPO membranes with different water contents were constructed, and molecular dynamics (MD) was employed to study the static structure of the equilibrium model; it was found that the density of the unit cell decreases with increasing water content; simultaneously, by analyzing the radial distribution function (RDF), it was found that water molecules aggregate around the sulfur atoms on the sulfonate groups on the SPPO chains, playing a role in water absorption and conduction, and hydronium ions also tend to aggregate near the sulfonate groups. Through analysis of the molecular motion trajectories, the diffusion coefficient D and conductivity of water and hydronium ions in the SPPO membrane were calculated. The research results indicate that the conductivity of the SPPO membrane increases with increasing water content within the membrane, yielding results in good agreement with experiments.

Full Text

Preamble

Molecular Dynamics Simulation Study of Proton Diffusion in Sulfonated Poly(phenylene oxide) Membranes

Han Xuhui, Zhang Peng, Ma Yue, Li Jia, Wang Yuxiang, Zhou Qiong, Zhou Guanggang, Lu Guiwu

(College of Science, China University of Petroleum (Beijing), Beijing 102249)

Abstract

To investigate the properties of sulfonated poly(phenylene oxide) (SPPO) for application in proton exchange membrane fuel cells (PEMFCs), we studied the molecular diffusion characteristics of water and hydronium ions within SPPO membranes. Molecular models of SPPO membranes with varying water contents were constructed, and molecular dynamics (MD) simulations were employed to analyze the static structure of equilibrated systems. The results reveal that the simulation cell density decreases with increasing water content. Radial distribution function (RDF) analysis demonstrates that water molecules aggregate around the sulfur atoms of sulfonate groups on SPPO chains, facilitating water absorption and proton conduction, while hydronium ions also preferentially cluster near sulfonate groups. By analyzing molecular trajectories, we calculated the diffusion coefficients (D) of water and hydronium ions and the conductivity (σ) of SPPO membranes. The findings indicate that SPPO membrane conductivity increases with water content, yielding results that agree well with experimental data.

Keywords: Proton exchange membrane; Sulfonated poly(phenylene oxide); Proton diffusion; Molecular dynamics simulation

Introduction

Fuel cells have become a major research focus in the global energy field due to their safety, high efficiency, pollution-free operation, wide applicability, and low noise characteristics [1-2]. Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have attracted particular attention [3].

Proton exchange membranes are cation-exchange films made from polymer materials containing ion-exchange groups. In PEMFCs, they serve the critical functions of proton conduction, fuel separation (e.g., hydrogen and methanol from oxygen), and electron insulation, making them a key focus of PEMFC research [4-5].

Currently, only perfluorosulfonic acid membranes (commercially known as Nafion) are used in practical fuel cell applications. However, their high methanol permeability, poor thermal stability, and high cost are major obstacles for application in direct methanol fuel cells (DMFCs) [6-7]. Sulfonated poly(phenylene oxide) (SPPO) membranes have attracted considerable attention due to their unique properties [8]. Previous research on SPPO membranes has primarily focused on their use as gas separation membranes in reverse osmosis applications [9-10], though an increasing number of studies have investigated their potential as electrolyte materials for fuel cells [11-12].

In recent years, numerous molecular dynamics simulation studies on proton exchange membranes have been reported [13-15]. Theoretical simulation and

prediction of SPPO membrane properties have become increasingly necessary [16]. In this work, we utilized the Materials Studio (MS) software platform to construct structural models of SPPO membranes with different water contents, simulated the diffusion behavior of water molecules and hydronium ions within the membranes, and calculated the corresponding conductivity values.

[Figure 2: see original paper] The cell structure for $\lambda=5$ (a), 8(b), 11(c), 14(d)

1. Computational Model and Simulation Methods

To investigate the conduction characteristics of water and hydronium ions within SPPO membranes, we constructed SPPO chains with a sulfonation degree of 50% and a polymerization degree of 10, as shown in Figure 1. Figures 1(a) and 1(b) display the structural models of non-sulfonated and sulfonated SPPO monomers, respectively, while Figure 1(c) shows the SPPO chain configuration.

[Figure 1: see original paper] Chemical structures of non-sulfonated (a) and sulfonated (b) SPPO monomers used in the simulation, and SPPO chain (c) molecular model

The Amorphous Cell module was used to construct the proton conduction system for SPPO membranes. Figure 2 presents molecular models of SPPO membranes with water-to-sulfonic acid ratios (λ) of 5, 8, 11, and 14 (where $\lambda =$ number of water molecules / number of sulfonic acid groups). The specific cell parameters are listed in Table 1 .

All model optimization and molecular dynamics simulations were performed using the Forcite module in MS software with the COMPASS force field. COMPASS is an ab initio-based force field that combines quantum mechanical calculations with empirical methods to determine force field parameters. It represents the first molecular force field to unify organic and inorganic molecular systems, enabling simulation of organic and inorganic small molecules, polymers, metal ions, and metal oxides [17].

After initial model construction, the molecular conformations were not at their minimum energy states, necessitating optimization through an annealing process. The steepest descent method was employed to optimize the energy and geometry of the cell structures, and the annealing module was used to simulate the annealing process to locate the minimum energy conformations. Finally, molecular dynamics simulations of proton conduction in SPPO membranes were conducted in the canonical ensemble (NVT) at a system temperature of 298 K for 1.5 ns. A time step of 1 fs was used for all simulations.

The dynamic trajectories of models with different water contents were obtained through these procedures. Analysis of the final structures and trajectories yielded the cell density, volume, and mean square displacement (MSD) data.

2. Results and Discussion

2.1 Cell Density Analysis

For molecular dynamics simulations of amorphous cells, ensuring that the simulation cell reaches a fully equilibrated state is crucial to guarantee adequate diffusion of water molecules and hydronium ions within the SPPO membrane. To verify equilibrium, we monitored parameters including temperature, total energy, and density. Figure 3 [Figure 3: see original paper] shows the fluctuation curves of system temperature (T) and total energy (E) over time (t). The minimal fluctuations indicate that both temperature and total energy remained essentially constant. Table 2 presents the volume and density of the simulated cells. Both Figure 3 and Table 2 confirm that the systems had reached equilibrium.

[Figure 3: see original paper] Temperature and total energy of the dynamic simulation system as a function of time

Density and volume of cell

2.2 Static Structure Analysis

Figures 4(a), (b), and (c) show the radial distribution functions (RDF) for the SPPO-5 membrane ($\lambda = 5$). The sulfur atoms on sulfonate groups are labeled as S, oxygen atoms on water molecules as Ow, oxygen atoms on hydronium ions as Oh, carbon atoms on methyl groups as Cm, and carbon atoms on benzene rings as Cb. Comparing the two curves in Figure 4(a), we observe distinct peaks for both S-Oh and S-Ow, with the S-Oh peak being higher than the S-Ow peak. This occurs because the positively charged hydronium ions are electrostatically attracted to the negatively charged sulfonate groups, resulting in a higher concentration of hydronium ions near sulfonate groups. Comparing Figure 4(a) with Figure 4(b) reveals that hydronium ions preferentially accumulate around sulfonate groups rather than near hydrophobic groups such as methane and benzene rings. In Figure 4(c), the cutoff radii for S-S and Oh-Oh extend beyond 0.4 nm, whereas those for S-Oh and S-Ow in Figure 4(a) are at 0.4 nm, further demonstrating the mutual attraction between sulfonate groups and hydronium ions. Similar patterns were observed in RDF curves for SPPO membranes with $\lambda = 8, 11, \text{ and } 14$.

[Figure 4: see original paper] (a) RDF of S-Oh and S-Ow in SPPO membrane; (b) RDF of Cb-Oh and Cm-Oh in SPPO membrane; (c) RDF of S-S and Oh-Oh in SPPO membrane

2.3 Diffusion Coefficient Calculation for Water and Hydronium Ions in the Membrane

After 1.5 ns of dynamics simulation, the trajectory segment from 100 ps to 1200 ps was analyzed to generate the mean square displacement (MSD) plots shown in Figure 5 [Figure 5: see original paper]. Due to the small size of water

and hydronium ions, oxygen atom positions were tracked to calculate diffusion coefficients, with oxygen atoms in water (Ow) and hydronium ions (Oh) being separately identified.

[Figure 5: see original paper] (a) MSD of water at different water content; (b) MSD of hydronium ions at different water content

The diffusion coefficient D is calculated using the relationship between MSD and time. In Equation (1), parameter a represents the slope obtained by fitting the MSD versus time curve to a linear function. Substituting a into Equation (1) yields the diffusion coefficient D .

The conductivity σ is calculated using the Nernst-Einstein relation [3] shown in Equation (2), where k is the Boltzmann constant, n is the number of hydronium ions in the cell, T is the absolute temperature, and e is the elementary charge. By substituting D into Equation (2), the system conductivity can be determined.

Table 3 presents the final diffusion coefficients for water molecules and hydronium ions, along with the calculated conductivity values. The results show that both diffusion coefficients increase with water content, reflecting the physical reality that higher water content leads to more hydrated membranes and greater proton conductivity. The conductivity values calculated from hydronium ion diffusion coefficients range from 0.0056 to 0.0382 S/cm. Gong Chunli et al. [11] experimentally measured a conductivity of 0.0116 S/cm for an SPPO membrane with 40.1% sulfonation degree, which agrees well with our simulation results.

Diffusion coefficient of water and hydronium ions and conductivity

Conclusion

Molecular dynamics simulations of SPPO membrane cells demonstrate that membrane density decreases with increasing water content. Sulfonate groups play a crucial role in proton conduction, with hydronium ions preferentially aggregating near these groups. The study reveals that diffusion coefficients of both water molecules and hydronium ions increase with water content, leading to higher membrane conductivity. These trends are consistent with experimental observations.

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Author Information

Corresponding Author: Zhang Peng, Professor

Address: Room 111, Building B, College of Science, China University of Petroleum (Beijing), No. 18 Fuxue Road, Changping District, Beijing

Phone: 15010939211

Email: 836385794@qq.com

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