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

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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 within SPPO membranes. Molecular structure models of SPPO membranes with different water contents were constructed, and the static structure of the equilibrium models was investigated using molecular dynamics (MD). 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 of the sulfonate groups on the SPPO chains, playing a role in water absorption and conduction, while hydronium ions also tend to aggregate near the sulfonate groups. Through analysis of the molecular trajectories, the diffusion coefficient D and conductivity of water and hydronium ions within the SPPO membrane were calculated. The results show 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

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

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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 different water contents were constructed, and molecular dynamics (MD) simulations were employed to examine the static structure of equilibrated systems. The results reveal that the simulation cell density decreases with increasing water content. Analysis of radial distribution functions (RDFs) 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 exhibit a strong tendency to cluster near sulfonate groups. By analyzing molecular trajectories, we calculated the diffusion coefficients (D) of water and hydronium ions and the conductivity ( ) of SPPO membranes. The findings indicate that the conductivity of SPPO membranes increases with water content, yielding results in good agreement with experimental data.

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

Introduction

Fuel cells have emerged as a focal point of energy research worldwide due to their safety, high efficiency, environmental friendliness, broad applicability, and low noise operation [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, these membranes serve critical functions: proton conduction, separation of reactants (e.g., hydrogen and methanol from oxygen), and electronic 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 present significant obstacles for application in direct methanol fuel cells (DMFCs) [6-7]. Sulfonated poly(phenylene oxide) (SPPO) membranes have garnered considerable interest due to their unique properties [8]. Previous research on SPPO membranes primarily focused on their use as gas separation membranes for reverse osmosis applications [9-10], though increasing attention has been directed toward their potential as electrolyte materials for fuel cells [11-12].

In recent years, numerous molecular dynamics simulation studies have been reported for proton exchange membranes [13-15]. Theoretical modeling and prediction of SPPO membrane properties have become increasingly important [16]. In this work, we utilized the Materials Studio (MS) software platform to construct structural models of SPPO membranes with varying water contents, simulated the diffusion behavior of water molecules and hydronium ions within the membranes, and calculated the corresponding conductivity values.

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1. Computational Model and Simulation Methods

To investigate the conduction characteristics of water and hydronium ions in 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) illustrates the SPPO chain configuration.

Fig. 1 [**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 employed to construct proton conduction systems for SPPO membranes. Figure 2 presents molecular models of SPPO membranes with water-to-sulfonic acid ratios ( ) of 5, 8, 11, and 14 (where = number of water molecules / number of sulfonic acid groups). Detailed cell parameters are provided in Table 1 .

Fig. 2 [**Figure 2: see original paper**] The cell structure for = 5 (a), 8 (b), 11 (c), and 14 (d).

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].

Following initial model construction, the annealing process was applied to optimize the models, as the initial molecular conformations were not at energy minima. The steepest descent method was used to optimize the cell structure energy and geometry, and the annealing module simulated the annealing process to locate the lowest-energy conformations. Finally, molecular dynamics simulations of proton conduction in SPPO membranes were conducted in the canonical ensemble (NVT) at 298 K for 1.5 ns. A simulation time step of 1 fs was used throughout this study.

Dynamic trajectories for models with different water contents were obtained through the above procedure. Analysis of the final structures and trajectories yielded cell densities, volumes, and mean square displacements.

2.1 Cell Density Analysis

For molecular dynamics simulations of amorphous cells, ensuring the simulation cell reaches complete equilibrium is crucial to guarantee that water molecules and hydronium ions can diffuse adequately within the equilibrated SPPO membrane. To verify equilibrium, parameters including temperature, total energy, and density were monitored. Figure 3 [Figure 3: see original paper] shows the fluctuation curves of system temperature (T) and total energy (E) as functions of time (t). The minimal fluctuations indicate that both temperature and total energy remain essentially constant. Table 2 presents the volumes and densities of the simulated cells. These results collectively demonstrate that the systems have reached equilibrium.

Fig. 3 [Figure 3: see original paper] Temperature and total energy of the dynamic simulation system as functions of time.

Table 2 Density and volume of cell.

2.2 Static Structure Analysis

Figures 4(a), (b), and (c) display the radial distribution functions (RDFs) for the SPPO-5 membrane (= 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 curves, with the S-Oh peak being more pronounced. This indicates that the electrostatic attraction between positively charged hydronium ions and negatively charged sulfonate groups leads to a higher concentration of hydronium ions near sulfonate groups. Comparison of Figure 4(a) with Figure 4(b) reveals that hydronium ions preferentially accumulate around sulfonate groups rather than near hydrophobic moieties such as methane and benzene rings. In Figure 4(c), the cutoff radii for S-S and Oh-Oh interactions extend beyond 0.4 nm, whereas those for S-Oh and S-Ow in Figure 4(a) are around 0.4 nm, further confirming the mutual attraction between sulfonate groups and hydronium ions. Similar patterns are observed in RDF curves for SPPO membranes with = 8, 11, and 14.

Fig. 4 [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 atoms, oxygen atom positions were tracked to calculate diffusion coefficients, with oxygen atoms in water (Ow) and hydronium ions (Oh) being separately identified.

Fig. 5 [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 Equation (1), where *a* represents the slope obtained from linear fitting of the MSD versus time curve. Substituting *a* into Equation (1) yields the diffusion coefficient D.

The conductivity is calculated using Equation (2) [3]:

$$= (n e^2 D) / (kT)$$

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 conductivities. 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 calculated conductivities range from 0.0056 to 0.0382 S/cm, increasing with diffusion coefficient. Gong et al. [11] experimentally measured a conductivity of 0.0116 S/cm for SPPO membranes with 40.1% sulfonation degree, which aligns well with our simulation results.

Table 3 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 showing a greater tendency to aggregate 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—a trend consistent with experimental observations.

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Note: Figure translations are in progress. See original paper for figures.