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学位論文題目	Quantum-Classical Molecular Dynamics Study of Proton and Water Transport Mechanisms in the Nano/Meso Structure of Polymer Electrolyte Membranes
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論文内容要約

In this thesis, dynamic and structural properties of protons and water molecules in polymer electrolyte membranes (PEMs) have been studied using molecular dynamics simulations, to characterize the proton and water transport mechanisms in the nano/meso water cluster structures of PEMs.

Firstly, the Nafion systems have been constructed using the newly modified force field. The final density of the Nafion membrane agrees better with available experiment data within 1.5% for various water contents and the trends that density decreases with increasing hydration level are well reproduced. The diffusion coefficients of hydronium ions are consistent with the previous studies using the classical hydronium ions and those of water molecules are in good agreement with the experimental data, validating the dynamics of classical hydronium ions and water molecules in our modified Nafion model.

Secondly, the solvation structure and transport properties of protons in aqueous solutions have been examined to provide an accurate description of the excess proton mobility with the Grotthuss mechanism using classical molecular dynamics. A modified version of the two-state empirical valence bond (TS-EVB) model, anharmonic TS-EVB (*a*TS-EVB) model, was developed based on the WK model to improve the quantitative description of both the proton and water mobility in aqueous environments. The new *a*TS-EVB model was a substantial improvement over the WK model in terms of the proton transport (PT) properties. This was achieved by modifying the following aspects: (i) the water force fields used in the *a*TS-EVB model are the nonpolarizable anharmonic water force fields *a*SPC/FW, as an alternative to the original polarizable water model, which provides pronounced nuclear quantum effects for anharmonic potentials and reproduces water properties much better; and (ii) in the *a*TS-EVB model, the function $\Lambda(Q, R)$, an interaction matrix element in the Hamiltonian, was explicitly parameterized to reproduce the PESs calculated by the *ab initio* calculations for more reliable descriptions of the PT properties. The structural properties calculated from the RDFs are in good agreement with the experimental data obtained from the neutron and X-ray scattering measurements of the water structure factor, resulting in a significant improvement in water mobility over the WK model. The RDF between the excess protons and the

water molecules also yields the main feature of the experimental data, contributing to the improvement of the interaction between the hydronium ions and water molecules. The *a*TS-EVB model improves a description of PT via the Grotthuss hopping mechanism, giving a significantly enhanced transport, in comparison with the WK model. Specifically, given the proton concentration in the HCl solution calculated in this study, the self-diffusion coefficient is found to be within ~33% of the experimental value, giving a significantly enhanced transport. The classical activation energies for the proton and water were calculated from the Arrhenius equation between 298.15 and 340 K (the temperature range used in this study). The values calculated from the linear fit to the Arrhenius plots are found to be 0.090 eV and 0.17 eV for the proton and water, respectively, which are in excellent agreement with the experimental values of 0.093 eV and 0.17 eV. Although the *a*TS-EVB model underestimates the value of the hopping rate compared with that of the experimental values, the ratio between them is consistent with the difference between the diffusion coefficients for the *a*TS-EVB model and the experimental values, suggesting their strong correlation. Besides now being able to carry out simpler and faster calculations, with the new *a*TS-EVB model, it is now possible to obtain an accurate estimation of PT properties including the prediction of the absolute values of mobility within the simplicity of the theoretical framework, hence establishing an important link between proton mobility and its surrounding structures and environments. In this regard, the *a*TS-EVB model could attract wider usage and facilitate the efficient application of the PT phenomena to other longer simulations and larger systems in highly concentrated and confined heterogeneous multiproton environments, such as in polymer electrolyte membranes and along water wires in narrow pores.

Thirdly, a reactive molecular dynamics simulation has been performed to characterize the PT and cluster structures in PEMs at various water contents. The *a*TS-EVB model has been used to efficiently evaluate PT properties that include the Grotthuss hopping mechanism of bond formation and cleavage through the hydrogen bond network as well as vehicular mechanism.

The cluster size distribution shows that n_s can be fitted to the largest range of S at $\lambda = 5$ and $\lambda = 7$, suggesting that the percolation threshold is located in this range. The cluster structures were also studied by calculating the probability of finding water molecules and hydronium ions in a cluster of a certain size. The results show that at $\lambda = 3$ small isolated clusters with three or four solvent molecules are predominant, whereas at $\lambda = 5$ and $\lambda = 7$ clusters are increasingly of intermediate size and are frequently connected and disconnected by transient water bridges, leading to a wide distribution of S . This result suggests that a percolation threshold is close to these water contents. At $\lambda > 12$, a large spanning cluster with high connectivity of water molecules is observed. The distribution of mean cluster size, excluding the largest cluster, also shows that the percolation threshold lies between $\lambda = 5$ and $\lambda = 7$, which is related to an abrupt decrease in the average number of clusters when λ

increases from 3 to 7. To identify the percolation threshold, the probability R of finding an infinite cluster was examined. The fit of the simulation data to the Boltzmann function locates a percolation threshold at $\lambda = 5.7$, which is in good agreement with our estimations observed earlier. Furthermore, the hydrogen bond number distribution shows a significant difference between λ values above and below the percolation threshold. The PT properties were analyzed based on the total proton diffusion and on the diffusion contribution of each component of the Grotthuss and vehicle mechanisms. The proton diffusion coefficients were found to be in good agreement with experimental data for the studied water contents, which is a significant improvement over the results obtained using the classical hydronium ion model. The total proton diffusion coefficient was increased by more than an order of magnitude when crossing the percolation threshold with increasing λ from 3 to 7, revealing the strong correlation between the PT properties and the water percolation. In addition, whereas both components of the vehicle and Grotthuss mechanisms contribute almost equally to the increase in total proton diffusion when λ is increased from 3 to 7, the contribution of the Grotthuss mechanism becomes more important at higher water contents. The present study provides direct, quantitative evidence of the influence of water percolation on PT properties, and demonstrates the suitability of the *a*TS-EVB model for providing an accurate estimation of PT properties within the simplicity of the theoretical framework. By taking advantage of the present approach, further understanding and characterization of PT properties in different types of PEMs will be explored.

In addition to the characterization of the PT and cluster structures, the nanoscopic structural properties of water and hydronium ions in the vicinity of the sulfonate groups in the hydrated Nafion membrane have also been investigated using classical molecular dynamics simulations to clarify their correlation with the vehicular diffusivity of hydronium ions. Our finding of the average number of solvent molecules reveals that the solvent molecules in the overlapped area and in the isolated area within the first solvation shell clearly show different dynamic properties at the studied water contents. The mean residence time analysis has demonstrated the correlations between those two different areas and the residence time of solvent molecules. The results indicate that the increase in the vehicular diffusion coefficients of solvent molecules with increasing water content are largely affected by the diffusivity increase of solvent molecules in the first solvation shell rather than in the second solvation shell. The mean residence time of solvent molecules in the overlapped area was found to decrease monotonically in comparison with that in the isolated area, suggesting that the change in the diffusivity depending on water content is larger in the overlapped area than in the isolated area. It was also found that the diffusivity of hydronium ions in both the overlapped area and the isolated area increases with increasing water content. The simulation results suggest the influence of the two different areas in bound on the vehicular transport of hydronium ions: the diffusivity of hydronium ions in the overlapped area dominates their total

diffusion at lower water contents ($\lambda \leq 6$), while that in the isolated area dominates their diffusion at higher water contents ($\lambda > 6$). The present simulations have demonstrated a very detailed analysis of the structural properties of the sulfonate groups in terms of the isolated and the overlapped areas in the first solvation shells. The understanding of the coordination properties of the sulfonate groups achieved by this work could help in the design of new polymer electrolyte membranes having additional desirable properties.

Finally, another reactive molecular dynamics simulation has been performed to investigate the polymer structure dependence of the electroosmosis in various EWs membranes, 900, 1100, and 1300. The *a*TS-EVB model has been employed to describe efficiently accurate PT behavior involving both the vehicular mechanism and the Grotthuss mechanism. The proton and water distributions around the sulfonate groups were examined at each EW. It was found that at lower EWs, the first solvent shells are saturated with a smaller number of solvents by overlapping and sharing the same solvents with multiple solvation shells nearby, which leads to a larger number of protons and water molecules in the free water region. The water cluster structures in terms of the average number of clusters and the connectivity of clusters were also investigated at each EW to describe the correlation between the water domain structure and the electroosmosis. The average number of clusters increases and the connectivity of the largest clusters decreases with increasing EW. These results suggest that a spanning water cluster with a continuous hydrogen-bonded network is formed at low EW corresponding to 900 EW, while a larger number of isolated small clusters are observed at high 1300 EW. The electroosmotic drag coefficients, K_{drag} , for each EW were evaluated from the mean velocity of protons and water molecules induced by an electric field. A decrease in both K_{drag} and proton and water mobility was found, which can be reasonably correlated with the observed water cluster structure changes. The present simulations provide important insight into the direct link between electroosmosis and water domain structure in different polymer structures.

Besides now being able to carry out simpler and faster calculations, with the new *a*TS-EVB model, it is now possible to obtain an accurate estimation of proton transport properties including the prediction of the absolute values of mobility within the simplicity of the theoretical framework. The present simulations have demonstrated a very detailed analysis of the structural properties of PEMs, revealing quantitative evidence of the influence of water cluster structures on proton transport and electroosmosis properties. Such simulation can therefore provide important insight into the direct link between the proton/water transport mechanisms and the structural properties of PEMs, which may help in both the understanding and optimization of morphology of new PEMs that have additional desirable properties.