A Revised EVB Model for Proton Transport in Hydrated Nafion Membrane

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Polymer electrolyte fuel cells (PEFCs) are highly expected as a next-generation power supply system due to the purity of its exhaust gas, its high power density and high efficiency. The heart of PEFCs is polymer electrolyte membrane (PEM) that separated the reactant gases and conducts protons. Perfluorosulfonic acid Membranes, such are Nafion developed by DuPont, are the most widely used for PEM. In the nanoscopic structure of the membrane, ion clusters are formed by water molecules gathered vicinity of sulfonate groups which are hydrophilic parts of Nafion membrane, and protons transport inside of these water aggregations. The molecular level structure and transport mechanism of protons are important factors contributing to dynamic properties of protons in the membrane. Thus, it is critical to understand an important link between Nafion membrane nanostructure and the dynamics of water molecules and hydronium ions to enhance proton transport.

In the bulk aqueous solution, the porton transport process has been investigated trough both experiment and quantum simulations. It is observed that proton mobility is roughly 5 times higher than other cations such as K^+ which have an ionic radius similar to the hydronium ions and this dynamic property of proton is attributed to the Grotthuss mechanism as well as Vehicular mechanism. It has been generally accepted that the proton transport process thorugh the Grothuss mechanim or proton hopping is enhanced significantly between two distinct proton hydration structures, the Eigen and Zundel cations.

In Nafion membranes, it is considered that proton hopping still takes place although the water dynamic property in the bulk aqueous solution is inhibited by a lack of bulklike water structure at low water contents. However, the correlation between the Grotthuss mechanism and Vehicular mechanism components of proton diffusion in Nafion is yet to be clearly understood.

In this study, a revised empirical valence bond (EVB) model is developed based on the the previous study of EVB model reported by Walbran et al.[1] in order to improve the description of proton mobility in both aqueous and Nafion environments. The new EVB model shows a larger proton diffusion coefficient, which is 0.72 ± 0.05 $Å^2$/ps and is within ~21% of the experimental value of 0.94 ± 0.01 $Å^2$/ps[2], than previous models of multistate EVB[3, 4]. The calculated result of MSDs of the hydronium ion and water molecules in bulk aqueous solution are shown in Fig. 1. The result of hopping rate considered both the forward-hop to the new donor and backward-hop to the last donor indicates a significantly lage value of 1.04 ps^{-1} compared with the previous work value of 0.16 ps^{-1}[4].

In addition, We have applied the new EVB model to Nafion system and performed an atomistic analysis of the transport of hydronium ions and water molecules in the nanostructure of hydrated Nafion membrane by systematically changing the hydration level using classical molecular dynamics simulations with DREIDING force field. After annealing procedure, the simulated density agreement with experiment is within 1.3 % for various water contents and the trends that density decreases with increasing hydration level are reproduced. A snapshot of water aggregation in Nafion membrane in our simulation are shown in Fig. 2. In addition to determination of diffusion coefficients of hydronium ions and water molecules as a function of hydration level as a dynamical analysis calculated by mean square displacement, we have also calculated radial distribution functions of hydronium ions and water molecules around the first solvation shell of sulfonate groups for structural analysis.

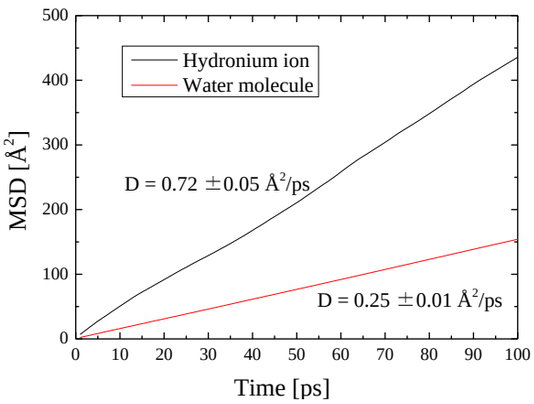

Fig. 1 MSDs of the hydronium ion and water molecules in bulk aqueous solution.

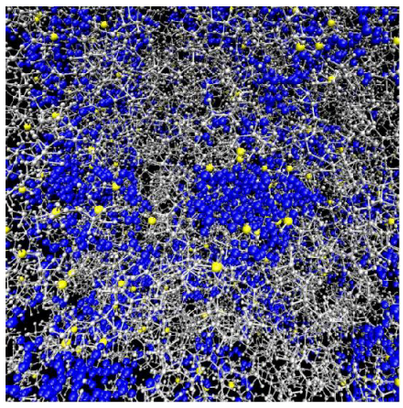

Fig. 2 Snapshot of water aggregations (in blue) and S of sulfonate groups (in yellow) in Nafion membrane at λ = 6.

References

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