

# A Molecular Dynamics Study of Proton Hopping in Nafion Membrane

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**Abstract** We have investigated the transport phenomena of hydronium ions and water molecules in the nanostructure of hydrated Nafion membrane by systematically changing the hydration level using classical molecular dynamics simulations. The new empirical valence bond (EVB) model is developed in order to improve the description of proton mobility in both aqueous and Nafion environments. The new EVB model predicts a significantly enhanced transport in comparison with previous hopping models as well as the classical hydronium diffusion, which largely improves the agreement with the available experimental data. We have determined diffusion coefficients of hydronium ions and water molecules in hydrated Nafion membrane as a function of hydration level to investigate the impact of the Grotthuss mechanism on the proton transport property. Proton hopping mechanism was found to become more significant at higher hydration levels. It was also found that a proton-hopping mechanism has a small effect on the diffusivity of water molecules for various hydration levels.

**Keywords:** Molecular Dynamics, Polymer Electrolyte Fuel Cell, Nafion

## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising power supply system because of the purity of its exhaust gas, the high power density, and the high efficiency. The heart of PEFCs is polymer electrolyte membrane (PEM) that separates the reactant gases and conducts protons. In the nanoscopic structure of the membrane, ion clusters are formed by water molecules gathered vicinity of sulfonate groups which are hydrophilic parts of a Nafion membrane, and proton transport are largely attributed to the nanoscopic structure of polymer membranes and water aggregations. Thus, many macroscopic simulations that are based on continuum theory have found it difficult to discuss the relation between the structural and dynamical properties of protons within the membrane in the previous experimental research (Wang et al., 2011). It is critical to understand the proton transport mechanisms through polymer membrane and clarify an important link between the

membrane nanostructure and the proton transport properties. In this study, a revised empirical valence bond (EVB) model has been developed based on the previous study of the two-state EVB model reported by Walbran et al. (Walbran and Kornyshev, 2001). We have investigated the impact of the proton hopping mechanism on the structure and dynamics properties of protons in hydrated Nafion membrane.

## 2. Simulation Methods

To reproduce the Grotthuss mechanism in our simulation, a new EVB model is developed. In the EVB model, we have considered a simplified cluster model of the Zundel ( $[\text{H} \cdot (\text{H}_2\text{O})_2]^+$ ) cation where a hydronium ion exchanges a proton with a neighboring water molecule, and employed a function of the proton transfer coordinate, defined as

$$Q \equiv |R_{O^*H}| - |R_{OH}| \quad (1)$$

where  $O^*$  and  $O$  are the oxygen of hydronium ion and water molecule, respectively. Also, a total potential energy of the  $H_5O_2^+$  complex  $V_{ad}$  is used as the following expression:

$$V_{ad} = \frac{(V_i + V_f) - \sqrt{(V_i - V_f)^2 + 4A(Q, R)^2}}{2} \quad (2)$$

where  $i$  and  $f$  stand for the “initial” and “final” states of the cluster. In the initial state,  $V_i$  is the energy of the cluster calculated under the assumption that the molecule labeled “ $H_3O^+$ ” is treated as hydronium model while the molecule labeled “ $H_2O$ ” is considered as the water model.  $A(Q, R)$  is a function of proton transport variable  $Q$  defined in Eq. (1) and  $R$  defined as the distance between  $O^*$  and  $O$ .  $V_{ad}$  is modified by parameterizing the function  $A$ , to fit it to the curves of the potential energy surface (PES) calculated by ab initio calculation (Park et al., 2012). Fig. 1 shows a comparison between the ab initio data (Park et al., 2012) and the results obtained with the EVB model for  $O^*-O$  separations corresponding to 2.2, 2.4, 2.6, and 2.8 Å, respectively. In all 4 distance cases, the results of EVB model are in good agreement with the corresponding ab initio data.

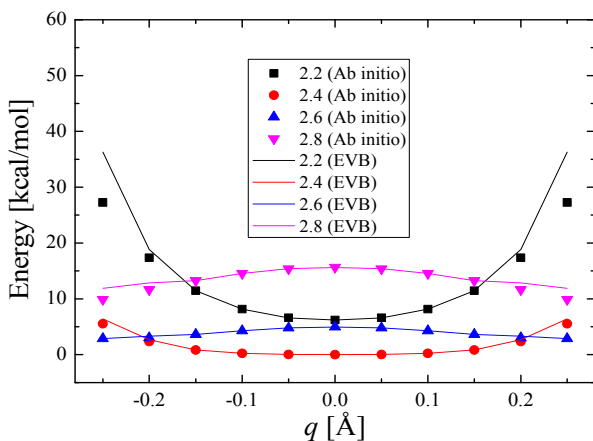


Fig. 1. Potential energy surface (PES) curves for the proton shuttling in the Zundel cation at  $O^*-O$  distances of 2.2, 2.4, 2.6, and 2.8 Å.

The Nafion membrane was used as PFSA

membrane. We generated Nafion by linking the polar monomeric unit (P) to the end of the nonpolar monomeric unit  $N_7$ , repeating the procedure 13 times to obtain  $(N_7P)_{13}$ . The potential model for Nafion was based on the DREIDING force field as referred to previous studies by other authors (Jang et al., 2004; Li et al., 2001). The aSPC/Fw model (Park et al., 2012) for hydronium ions and water molecule are employed. The initial configurations were generated by randomly placing 25 Nafion chains in a box with periodic boundary condition in all directions. To ensure charge neutrality, we added a total of 325 hydronium ions and considered hydration levels of  $\lambda = 3, 6, \text{ and } 12$ , where the parameter  $\lambda$  indicates the ratio of the number of water molecules to that of  $SO_3^-$  ( $N_{H_2O, H_3O^+}/N_{SO_3^-}$ ). The annealing procedure was carried out to eliminate the initial configurations and orientations of molecules, establishing the most stable equilibrium state. We used an annealing procedure based on previous studies (Ban et al., 2011; Karo et al., 2010). After equilibration, the  $NVT$  ensemble at 300 K was performed to collect a total of 1 ns simulation data for the vehicular model. The final structures for the vehicular model were then adopted as the initial structures in the EVB simulations. For the EVB system, an extra  $NVT$  ensemble for 500 ps was employed to relax the structures under the EVB potential. The final structures for the EVB model were then used for the  $NVT$  ensemble of 1 ns to collect simulation data for the EVB model. For each system, the trajectory of molecules was collected every 0.5 ps. The temperature was held by the Nosé-Hoover thermostat (Hoover, 1986), and the pressure was controlled by the Andersen method (Andersen, 1980).

### 3. Results and Discussion

Information on the proton solvation structure around sulfonate groups was obtained by the quantitative analysis of the excess proton distribution using the radial distribution function (RDF) shown as

$$g_{A-B}(r) = \left( \frac{n_B}{4\pi r^2 dr} \right) / \left( \frac{N_B}{V} \right) \quad (3)$$

where  $4\pi r^2 dr$  is the volume of a  $dr$  thick spherical shell at radius  $r$  from particle A,  $n_B$  is the number of B particles in the shell,  $V$  is the volume of the system, and  $N_B$  is the number of B particles in the whole system. Fig. 2. shows the RDFs,  $g_{S-O_h}(r)$ , between the sulfur atom of the sulfonate group and the oxygen atom of the hydronium ion (S—O<sub>h</sub>) for the EVB model (solid line) and vehicular model (dashed line) at each hydration level. For both models,  $g_{S-O_h}(r)$  shows a strong narrow peak at 4 Å with the first minimum at ~4.3 Å, suggesting the formation of solvation shell with a radius of  $r = 4.3$  Å. Interestingly, proton structure properties around the sulfonate groups are found to be very similar between the EVB model and vehicular model. This implies that the proton-hopping transport has a low impact on the proton dissociation from the sulfonate groups.

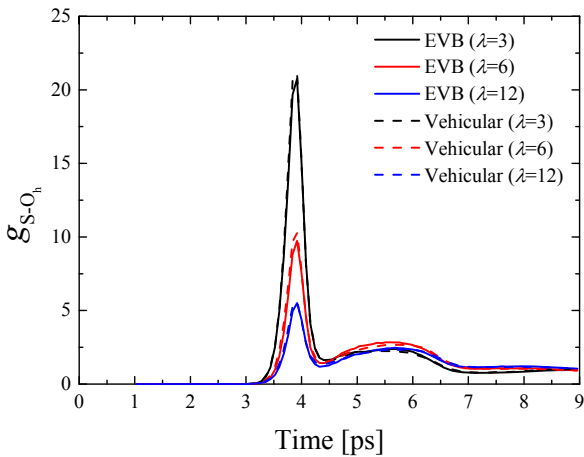


Fig. 2. RDF of sulfur-hydronium oxygen for the EVB model (solid line) and vehicular model (dashed line) at hydration level 3, 6, and 12.

The mobility of hydronium ions and water molecules was analyzed by calculating the mean square displacements (MSDs) of hydronium ions and water molecules during the simulations. We determined the diffusion coefficients,  $D$ , for hydronium ions and water

molecules using MSDs to satisfy the Einstein-Smoluchowski function written as

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle \quad (4)$$

where  $t$  is the diffusion time,  $r(t)$  is the position vector of hydronium ion and water molecule. Fig. 3. shows the MSDs of O<sub>h</sub> (in part a of Fig. 3.) and O<sub>w</sub> (in part b of Fig. 3.) for the EVB model (solid line) and vehicular model (dashed line) as a function of time for the hydration level of  $\lambda = 3, 6$  and 12. The diffusion coefficients of hydronium ions and water molecules were then estimated by the linear regime of these MSD curves from 300 to 500 ps at each hydration level. Fig. 4. shows the diffusion coefficients of hydronium ions (in part a of Fig. 4.) and water molecules (in part b of Fig. 4.) for the EVB model and vehicular model from the present simulation. Experimental measurements (Zawodzinski et al., 1991) are also plotted in part a of Fig. 4.. In part a of Fig. 4., the diffusion coefficients of the vehicular hydronium model are in good agreement with the classical hydronium model previously reported by Devanathan et al. (Devanathan et al., 2007) for the studied hydration levels, testifying the validation of our vehicular model. With the EVB model, the simulation results were found to be in good agreement with experimental measurements (Zawodzinski et al., 1991) for the studied hydration levels. In addition, the MSDs of the EVB model for hydronium oxygen are larger and increase faster than those of the vehicular model as the hydration level increases as shown in part a of Fig. 3.. Thus, the simulation results indicate that proton hopping mechanism becomes more significant at higher water contents. In part b of Fig. 4., the diffusion coefficients are compared with the experimental values of  $D_{H_2O}$  obtained from experimental measurements of nuclear magnetic resonance (NMR) (Zawodzinski et al., 1991) and quasi-elastic neutron scattering (QENS) (Perrin et al., 2007). The simulation results are in good agreement with experimental data for the studied hydration levels. It should be noted that because the

differences between  $D_{\text{H}_2\text{O}}$  values for the EVB model and vehicular model are small, a proton-hopping mechanism has a low impact on the diffusivity of water molecules for various hydration levels.

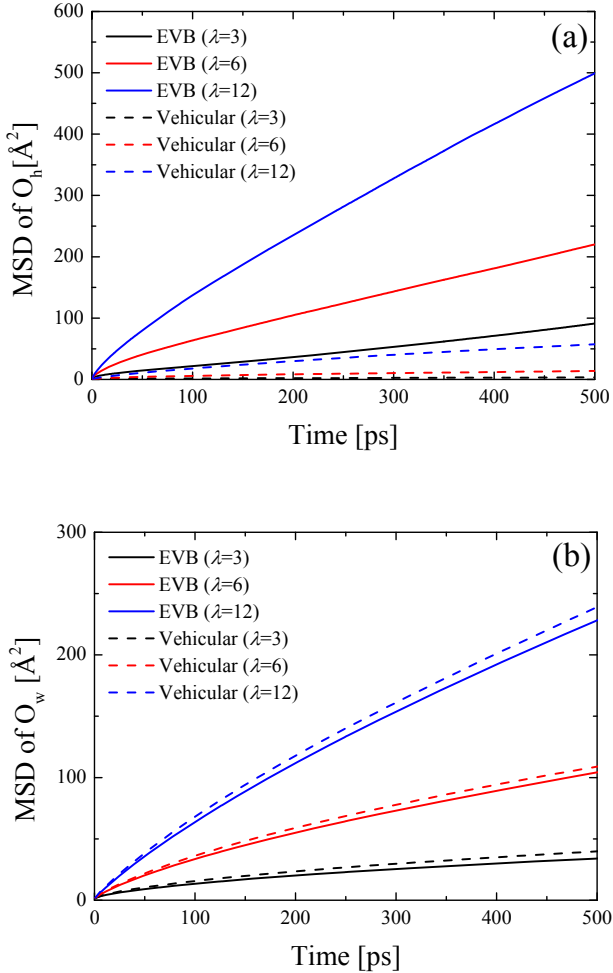


Fig. 3. (a) MSDs of hydronium ion oxygen for EVB model (solid line) and vehicular model (dashed line) at hydration level of 3, 6, and 12. (b) MSDs of water oxygen for EVB model (solid line) and vehicular model (dashed line) at hydration level of 3, 6, and 12.

#### 4. Conclusions

We have performed an atomistic analysis of hydronium ions and water molecules transports in the nanostructure of hydrated Nafion membrane by systematically changing the hydration level using classical molecular dynamics simulations. The new EVB model is developed to improve the description of proton

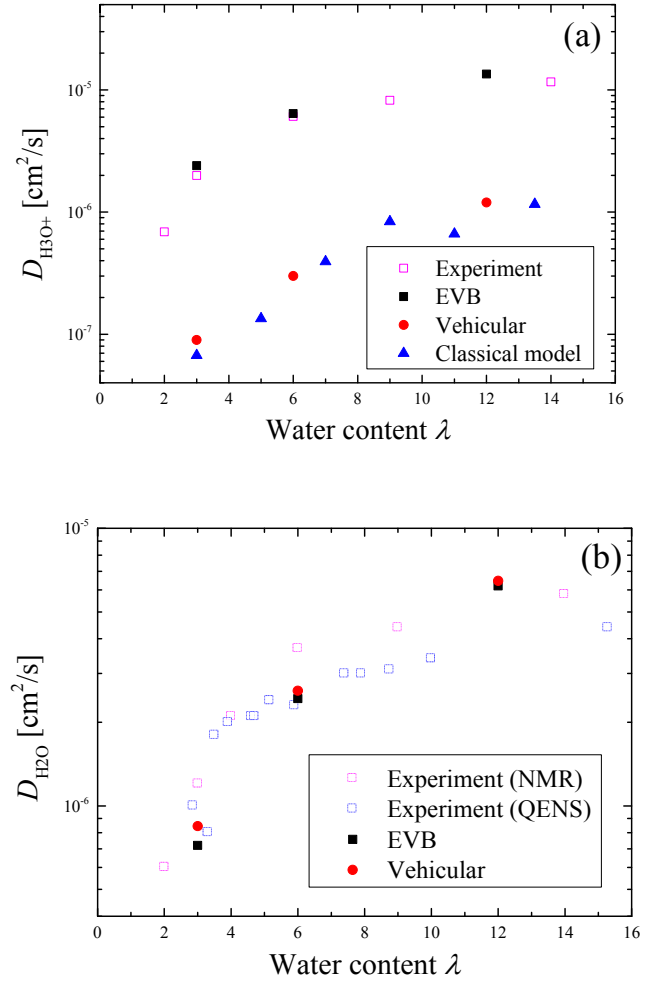


Fig. 4. (a) Diffusion coefficient of hydronium ions as a function of  $\lambda$ . Results are compared with experimental data taken from (Zawodzinski et al., 1991) and classical hydronium model taken from ref 11. (b) Diffusion coefficient of water molecules as a function of  $\lambda$ . Results are compared with experimental measurements of NMR taken from (Zawodzinski et al., 1991) and QENS taken from (Perrin et al., 2007).

mobility in the Nafion membrane. We have calculated MSDs to determine the diffusion coefficients of hydronium ions and water molecules as a function of hydration level. The results demonstrated the significant impact of Grotthuss mechanism on the transport property of hydronium ions and yet testified the validation of our simulation by comparing with the experimental data of diffusion coefficients.

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