V.P.4 The Study of Proton Transport Using Reactive Molecular Dynamics

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Objectives

The objective of this work is to develop a model capable of describing the molecular mechanisms of proton transport in highly confined and highly acidic environments. Specifically, we seek to develop a molecular-level understanding of how confinement and acidity impact both the vehicular and structural components of proton transport. To this end, we develop a Reactive Molecular Dynamics (RMD) algorithm that is capable of describing both components of proton transport, with sensitivity for each component to the local environment. We apply this RMD algorithm to describe proton transport in four systems: (1) bulk water, (2) bulk HCl solutions, (3) carbon nanotubes, and (4) hydrated perfluorinated sulfonic acid (PFSA) proton exchange membranes (PEMs). These four systems allow us to decouple the effect of confinement and acidity on vehicular and structural components of proton transport.

Technical Barriers

This work is motivated by practical technical barriers and addresses theoretical technical barriers. On the practical side, the structure-property relationships obtained from a fundamental understanding of the molecular mechanisms of proton transport in highly confined and highly acidic environments would provide guidance for the development of next generation PEMs. On the theoretical side, the hydrated PEM in a fuel cell contains phenomena that occur over disparate time scales. At the shortest time scale, there is the description of a single proton hopping event, occurring on the order of femtoseconds (10^{-15} s) and best described by quantum mechanical techniques; while at the next time scale, vehicular diffusion may take 10s or 100s of nanoseconds, which requires classical molecular dynamics simulation.

The RMD algorithm provides an efficient procedure for including both structural and vehicular diffusion in a simulation.

Abstract, Progress Report and Future Directions

Proton transport in aqueous solutions occurs through a combination of mass diffusion and structural diffusion. The structural diffusion of a proton, as a reaction, can be given as

$$H_3O^+ + H_2O \xleftrightarrow{\ 4\,H_2O\ } H_2O + H_3O^+$$
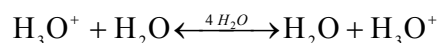
Transport of the proton by Grotthuss mechanism was implemented using a newly devised reactive molecular dynamics (RMD) algorithm. In this approach, a three step procedure was incorporated to the existing classical molecular dynamic simulation to allow the explicit proton transfer from a hydronium ion to a water molecule based on quantum mechanical transition and ground state configurations to reproduce macroscopic reaction properties. The reactive part of the RMD algorithm is composed of the following steps:
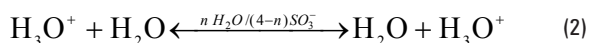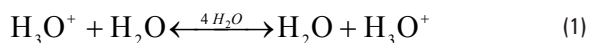
1. Satisfaction of triggers – checks whether the reactants are in a favorable configuration for the reaction to take place by satisfying a set of geometric and energetic triggers based on the transition state obtained from *ab initio* calculations.

2. Instantaneous reaction – coarse grains out the reaction path and the proton gets transported instantaneously from the hydronium ion to a water molecule.

3. Local equilibration – satisfies the target heat of reaction and ensures the products are in correct ending configuration.

The algorithm was validated by modeling structural diffusion of proton in an extensively studied system for which the most reliable data are available, namely bulk water. The determination of the functional form of the triggers were based on the structure of the predominant hydrated models (Zundel and Eigen cations) necessary for the structural diffusion of protons and were parameterized to reproduce the experimental rate constant and activation energy. Using this procedure, 150 replicates of a single hydrated proton in a system of 650 water molecules were studied as a function of temperature from 280 K – 320 K. By fitting the reaction rate the model predicts the transport property of the proton. A detailed study of the two components (structural and vehicular) of the total charge diffusion was conducted. Other systems were also modeled with the new algorithm to study its sensitivity and

the adaptability to different environments. T he RMD algorithm endeavors to have a valid starting and ending configuration for the structural diffusion by mapping the transition state onto a set of triggers without having to dynamically describe the transition state structure. Therefore, the algorithm is generalized by the environmentally sensitive geometric and energetic triggers.

The pH dependence of proton transport was investigated by implementing the algorithm for bulk aqueous HCl solutions with different concentrations (0.22 M – 0.83 M). The presence of the chloride ion disrupts both the structural and energetic environment for the occurrence of the reaction and was effectively captured by the triggers. Proton diffusion in water confined in carbon nanotubes of radii ranging from 5.42 Å – 10.85 Å was studied to analyze the effect of confinement on structural and transport properties of a proton. The model shows that enhanced confinement drastically reduces structural diffusion by disrupting the energetic balance around the Zundel ion.

Having independently examined the effect of acidity (HCl solution) and confinement (carbon nanotubes), we next apply the RMD algorithm to proton transport in a system that contains both confinement and acidity, namely hydrated PFSA PEMs. The structural diffusion of proton in hydrated membrane can take place via three classes of reactions.

$$H_3O^+ + H_2O \xleftrightarrow{4 H_2O} H_2O + H_3O^+ \qquad (1)$$

$$H_3O^+ + H_2O \xleftrightarrow{n H_2O/(4-n)SO_3^-} H_2O + H_3O^+ \qquad (2)$$

$$SO_3H + H_2O \xleftrightarrow{2 H_2O} SO_3^- + H_3O^+ \qquad (3)$$

The prevalence of each reaction is dependent on the degree of hydration of the membrane, which the first reaction being most important at high water contents and the last reaction being least important at high water contents. Equation 1 is similar to proton transport in bulk water and will take place along the center of the aqueous channels and reactions as shown in equations 2 and 3 will occur at the interface of the hydrophobic and hydrophilic regions. RMD algorithm can accommodate all the above reactions and the triggers can register the presence of the sulfonic acid groups and other environmental factors like confinement (as shown in the earlier systems). These reactions are individually implemented in three different stages to better understand the contribution of each reaction to the structural diffusion of proton in the PEM at different hydration levels. Thus the algorithm will allow us to measure the diffusivities in the hydrated membranes and provide a molecular level understanding of how the environment in the nano-aqueous regions impact proton mobility.

Publications (including patents) acknowledging the grant or contract

1. Esai Selvan, M., Keffer, D.J., Cui, S.T., Paddison, S.J., "A reactive molecular dynamics algorithm for proton transport in aqueous systems", **J. Phys. Chem. C**, under review.

2. Esai Selvan, M., Keffer, D.J., Cui, S.T., Paddison, S.J., "Proton transport in water confined in carbon nanotubes: A reactive molecular dynamics study", **Molecular Simulation**, in press.

3. Esai Selvan, M., Keffer, D.J., "Molecular-Level Modeling of the Structure and Proton Transport within the Membrane Electrode Assembly of Hydrogen Proton Exchange Membrane Fuel Cells", **Modern Aspects of Electrochemistry, Number 46**: Advances in Electrocatalysis, in press.