

## The Effects of Nanoconfinement and Hydrophobic Environment on Structural and Dynamical Properties of Water and Triflic Acid: An *Ab Initio* Study

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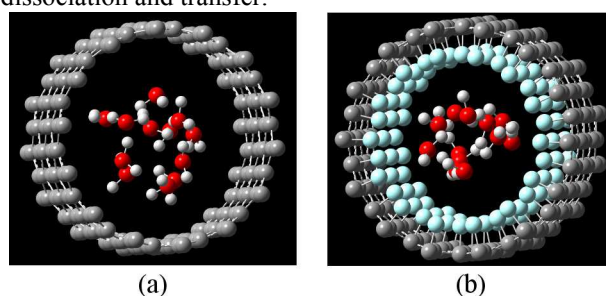
Fuel cells offer potential to replace conventional energy systems based on the combustion of fossil fuels due to their wide range of applicability and minimal environmental impact. Proton exchange membranes (PEMs) are commonly used as the electrolyte in hydrogen fuel cells. PEM fuel cells offer high power density, fast startup time, and are light weight which make them promising candidates for stationary, portable, and automotive use.<sup>1</sup> An ideal PEM must be highly proton conducting, have good mechanical integrity, and exhibit long-time thermal and chemical stability. Currently, perfluorosulfonic acid (PFSA) ionomers are the most widely used PEMs.

A PFSA membrane consists of a hydrophobic poly(tetrafluoroethylene) (PTFE) backbone functionalized with pendant perfluorinated side chains each terminated by a single hydrophilic sulfonic acid group. Hydrophilic domains are formed upon hydration facilitating long-range proton transport through the membrane. However, high proton conductivity in currently available PFSA membranes is only observed at high degrees of hydration which leads to water cross-over due to electro-osmotic drag. This also limits the operating temperature to below 100 °C which leads to adverse effects, such as catalyst poisoning.<sup>2</sup> This has led to immense effort to develop membrane materials that exhibit high proton conductivity at lower hydration levels allowing for higher temperature operation.

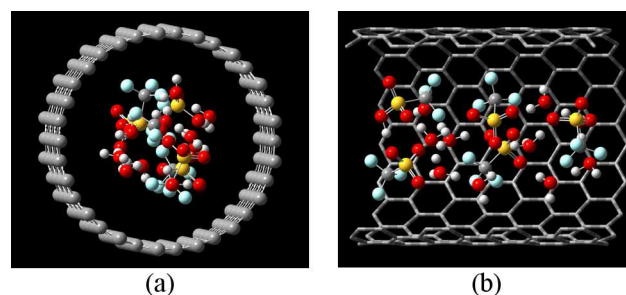
In hydrated PEMs, the hydrophilic domains containing the water molecules, protons, and acidic groups are only a few nanometers in diameter.<sup>3</sup> Due to the confined environment, the structural and dynamical properties of water and protons differ distinctly from that observed in the bulk. These properties are heavily influenced by the density of acidic groups, the hydration level, and the nature of the confined environment.<sup>3</sup> Furthermore, proton transport in these materials is highly dependent on the structure and dynamics of the hydrogen bonding between water molecules, which are considerably impacted by nanoscale confinement. As such, an understanding of how the confined environment affects the nature of confined water is needed. Due to the small scale of the confined dimensions and the complexity of the membrane, model systems are often used to study nanoconfinement effects.

Carbon nanotubes (CNTs) provide simple, well-structured model systems to investigate nanoscale confinement while also allowing for systematic alteration of relevant parameters. Simulations on proton transport in water confined in narrow CNTs have revealed that a 1-D water 'wire' forms which increases proton conductivity by a factor of 40 over bulk water.<sup>4</sup> Simulations have also been performed on CNTs of various diameters with either bare or fluorinated walls and functionalized with  $-\text{CF}_2\text{SO}_3\text{H}$  groups to explore the effects of sulfonic acid group density, nanoscale confinement, and the nature of the confined surface on proton transport properties at low hydration levels.<sup>5-8</sup> We have used CNTs to serve as a confinement vessel in *ab initio* molecular dynamics

(AIMD) simulations with: (1) water molecules at different densities and (2) aqueous triflic acid where the number of  $\text{H}_2\text{O}$  molecules per  $\text{CF}_3\text{SO}_3\text{H}$  was varied from 1 to 3. The use of AIMD allows for probing into molecular level features, including hydrogen bond dynamics and proton dissociation, without any *a priori* assumptions. Periodic boundary conditions were imposed along the length of the CNT, and up to 30 ps trajectories were obtained in the microcanonical ensemble. To explore the effect of the confinement dimension on structural and dynamic properties in these systems, two different diameter CNTs were used, with chirality (14,0) and (17,0). Furthermore, the inner walls of the CNTs were either left bare or functionalized with fluorine atoms to investigate the influence of the hydrophobic environment. Examples of the systems containing only water molecules and one with water molecules and triflic acid are shown in Figures 1 and 2, respectively. The simulations reveal the significant influence the fluorinated CNT walls have on the development and structural features of the hydrogen bond network between water molecules, and the effect of the hydration level and density of mobile sulfonic acid groups on proton dissociation and transfer.



**Figure 1.** Front view of the (14,0) CNTs: (a) bare walls and (b) fluorinated walls with length 12.8 Å each containing 12  $\text{H}_2\text{O}$  molecules.



**Figure 2.** (a) Front view and (b) side view of the (17,0) CNT with bare walls containing triflic acid and water at a hydration of  $\lambda = 2$ .

### References

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