Molecular Modeling of Proton Transport in Partially Hydrated Polymer Electrolyte Membranes

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Abstract

The benefit of Nafion®-type polymer electrolyte membranes (PEMs) comes from their excellent proton conductivity under well-humidified conditions. Hydrated acid groups, fixed on a stable polymer host, dissociate and donate their protons to mobile water in the porous membrane. Once released, the protons exhibit high transfer rates that have been rationalized (1,2) on the basis of a "structural diffusion" mechanism similar to that in bulk-water (3,4). This mechanism, often referred to as the "Grotthuss" mechanism (5), comprises a sequence of forward and backward transformations between an Eigen-ion ($H_9O_4^+$), in which a hydronium ion is hydrogen bonded and stabilized by three water molecules, and a Zundel-ion ($H_5O_2^+$), in which the excess proton is delocalized between two water molecules. The rate-determining cleavage of a hydrogen bond in the second solvation shell stimulates the initial $H_9O_4^+ \longrightarrow H_5O_2^+$ transformation. The back transformation $H_5O_2^+ \longrightarrow H_9O_4^+$ can stabilize the proton on a neighboring water molecule. Random fluctuations in the solvation structure generate the net motion of protonic charge.

In the complex environment of a hydrated PEM, a full molecular treatment of proton transport is for all practical purposes impossible. The generic difficulties involved in the molecular modeling of proton transfer are due to a disparity of time scales: while molecular motion, including proton transfer, occur on a *fs*-time scale, the time interval between consecutive transfer events is usually orders of magnitude larger (> 1 *ps*). In view of the difficulties involved in observing transfer events within the scope of *ab-initio* molecular dynamics calculations, only prototype systems of restricted complexity may be considered. Important insight may be obtained from numerous studies on structure and dynamics of a hydrated excess proton in liquid water, and from electronic structure calculations identifying proton dissociation and stabilization within the first hydration shell of pertinent acidic moieties (6,7).

The triflic acid monohydrate (TAM) crystal, which has a 1:1 composition of triflic acid (CF_3SO_3H) and water, comprises an important reference system for proton transfer in perfluorinated sulfonic acid PEMs, highlighting specific aspects of polymer/water interactions in a regime of minimal water content and high concentration of ionic groups. Our structural and energetic data reveal intriguing dynamical features of this system, which are relevant for various proton transport phenomena.

The TAM crystal has a known crystallographic structure, providing an appropriate basis of controlled molecular dynamics simulations. Initial coordinates of atoms for the bulk crystal calculation were taken from published experimental data at 298K. Thorough analysis of structure and energetics did not reveal any significant events in the native crystal. The transfer of a proton ($H_3O^+ \rightarrow CF_3SO_3^-$) along a hydrogen bond was rarely observed and the back transfer was always observed within a few *fs*. The corresponding counterpart to the stable low-energy crystal configuration in the context of proton transport in bulk water is the $H_9O_4^+$-cluster (Eigen-ion), the structure into which a proton defect relaxes between consecutive transfer events.

A Schottky-type proton defect was introduced into the native crystal structure through the removal of a proton from one of the H_3O^+. Simultaneously, an electron was removed from the compensating background in order to retain electro-neutrality of the crystal. During execution of our standard protocol (steps 1 to 3 with a microcanonical run of 4 *ps*), we observed the formation of an $H_5O_2^+$ -complex in 2 out of the 5 conformations. The outward pointing OH-bonds in $H_5O_2^+$ (0.99 ± 0.02 Å) are slightly shorter with somewhat suppressed fluctuations as compared to H_3O^+ (1.03 ± 0.04 Å). The OO-distance has decreased from 6.0 ± 0.3 Å in the native crystal to 2.45 ± 0.06 Å within the formed $H_5O_2^+$, exhibiting regular oscillations with an O–O-stretching frequency $\approx 450\, cm^{-1}$. The proton between the two oxygens is strongly delocalized, as expected. Overall our results indicate the formation of a stable $H_5O_2^+$ with suppressed fluctuations as a likely event in the distorted crystal, which is correlated with a considerable reorganization of $CF_3SO_3^-$ sites. Evidently, the approach of H_2O and H_3O^+ in the course of $H_5O_2^+$-formation is accompanied by a simultaneous rearrangement of S–S-distances, both processes occurring over a time scale of ≈ 2 *ps*. In particular, one pair of S-atoms approaches each other from an initial distance of ≈ 7 Å to < 5 Å during this period.

In the context of the important technological issue of proton transport in minimally hydrated PEMs, our study advertises a relay-type mechanism with strongly bound, effectively immobilized water. Assuming high concentrations of fixed anionic charges, a viable intermediate state involves the formation of a Zundel-ion and a strong classical reorganization of anionic sites.

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