

# Molecular Modeling of Proton Conduction in Polymer Electrolyte Membranes of Nafion® Type

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## 1 ABSTRACT

Molecular mechanisms of proton conduction in polymer electrolyte membranes are addressed by *ab initio* molecular dynamics calculations, utilizing the VASP program, on the model system trifluoromethane sulfonic acid monohydrate solid. After establishing that the experimental crystal is stably simulated, these computations are used to seek crystal defects that might contribute to proton conduction. The most favorable defect found involves formation of a Zundel ion,  $\text{H}_5\text{O}_2^+$ , and H-bonded, paired sulfonate groups. The energy of this defect is 0.3-0.4eV above the energy of the undefected solid, in suggestive agreement with the observed activation energy for proton transport in minimally hydrated Nafion®.

## 2 INTRODUCTION

The trifluoromethane sulfonic acid solid is a suitable model system for the study of elementary proton transfer events in sulfonate-based polyelectrolyte membranes, relevant particularly to a regime of minimal water content and high concentration of anionic groups. The known crystallographic unit cell[1] contains four each of  $\text{CF}_3\text{SO}_3^-$  and  $\text{H}_3\text{O}^+$  ions and provides an appropriate basis for controlled molecular dynamics simulations. This system melts into a 'room temperature' ionic liquid at 309K at ordinary pressures.

In this work we first verified that this model system is stable with current *ab initio* molecular dynamics simulation tools[2-6]. See Figure 1. With the unit cell parameters fixed, we repeatedly quenched and rethermalized this 48 atom system to 300K, and then further extended *ab initio* molecular dynamics calculations in excess of 10 ps. These structures were dynamic but no suggestion of instability was observed. Significant OH bond extensions toward sulfonate oxygens were fleeting and stably restored on femtosecond time scales.

Then we sought crystal defects that might permit ionic conduction. This was done in two steps: Firstly, we removed arbitrarily chosen single protons, quenched, and rethermalized the system to 300K. In 2 out of the 5 trials,

this procedure lead to the formation of a Zundel cation,  $\text{H}_5\text{O}_2^+$  from combination of the 'proton hole'  $\text{H}_2\text{O}$  and a nearby hydronium ion,  $\text{H}_3\text{O}^+$ . This was invariably accompanied by rearrangement of the rest of the system including the triflate anions. Secondly, for the cases that a Zundel ion was formed, we replaced the removed proton in a bonding position with respect to a sulfonate group. The systems prepared this way were then quenched and rethermalized to 300K.

Fuller reports of this work are in preparation[7].

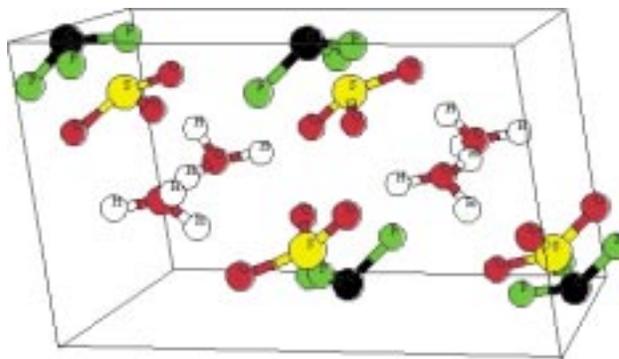


Figure 1: Unit cell of trifluoromethane sulfonic acid monohydrate crystal. Four hydronium cations,  $\text{H}_3\text{O}^+$ , are seen in the middle of this view. The periodic boundary conditions connect the triflate anions,  $\text{CF}_3\text{SO}_3^-$ , through the top and bottom boundaries shown here.

## 3 RESULTS

In one of the trials, after restoration of the manipulated proton considerable relaxation reformed the native crystal. In the other trial, however, rearrangements lead to the defective structure shown in Figure 2. After rethermalization to 300K this system has been observed for 14 ps, so it has that degree of thermal stability. Transfer of the proton shared between triflate oxygen atoms, from one to other of those atoms, was observed 2-3 times in that 14 ps and this leads to a rough estimate of 6 ps for that hopping time. Energies of quenched

structures extracted from this simulation were 0.3-0.4eV higher than energies of the quenched native crystal.

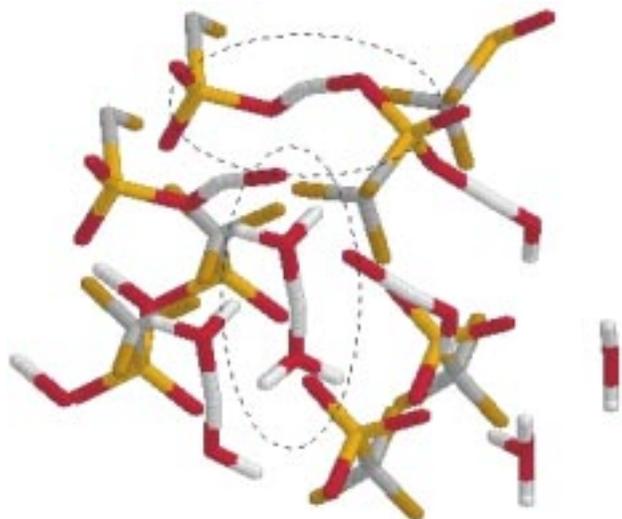


Figure 2: Defective structure found as described in the text. The dashed ellipses locate the formed Zundel ion (middle) and the H-bonded, paired triflate anions (top). A doubled view of the unit cell is shown for clarity.

## 4 DISCUSSION

In less simple systems other possibilities for conductive ionic defects will be available. Compositional defects involving additional water or other ions would be particularly interesting. But, intrinsic proton defects found in the solid can serve to identify pathways for sequential proton transport and re-binding. For example, the Zundel ion formed here can serve as a 'proton hole' that might be transported separately from the organic fraction of this system. Net proton transfer in the solid may involve the approach of  $\text{H}_5\text{O}_2^+$  to another  $\text{H}_3\text{O}^+$ , followed by the breakup of the initial  $\text{H}_5\text{O}_2^+$  and the recreation of  $\text{H}_5\text{O}_2^+$  on a neighboring site. More generally, the  $\text{H}_5\text{O}_2^+$  as well as the sulfonate  $\text{O}\cdots\text{H}\cdots\text{O}$ -complex function as relay-groups, which can mediate the proton transfer.

The trifluoromethane sulfonic acid monohydrate system exhibits conductivities in the range  $1\text{-}10\text{ S m}^{-1}$  for temperatures between 309.15 K and 408.15 K[8]. The conductivity data are reasonably approximated by an Arrhenius-type dependence with an activation energy of 0.3eV. Conductivity studies of Nafion®117 under conditions of minimal humidity exhibited activation

energies of 0.36 eV at high ( $> 220\text{ K}$ ) and 0.67 eV at low ( $< 220\text{ K}$ ) temperatures[9]. This suggests that such defects contribute to the proton conductivity in minimally hydrated Nafion®. More generally, this mechanism is relevant under conditions of high density of anions.

A difference between the system studied here and minimally hydrated Nafion® is the side chains. But it has been shown[9] that folded and extended conformations of those side chains have about the same conformational energy and the minimum energetic barrier between those extreme conformations is smaller than the defect formation energy found here. This supports the idea that side chain conformational energy changes are secondary to these processes.

Direct observation of proton transfer events between stable states such as these is typically prohibitively expensive of computational resources. The present result reveals one of the reorganizational steps. This knowledge, however, provides a foothold for further investigation of the detailed mechanism, utilizing e.g. methods of transition path sampling[11].

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