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Theoretical Investigation of Proton Conductivity in Proton Exchange Membranes for Fuel Cells

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Introduction: Nafion (DuPont) is the most used proton exchange membrane in polymeric electrolyte membrane fuel cells (PEMFCs) because of its highly proton conductive properties and excellent chemical and physical stabilities. However, some potential drawbacks such as high production cost, high methanol permeability and poor mechanical stability at high temperatures of these polymers have prompted for development of novel membranes.[1] In quest of alternatives to perfluorinated polymers membranes for automotive applications, multiblock sulfonated poly (arylene ether sulfone)s (SPE) (Fig. 1) containing highly sulfonated hydrophilic component seem to be very promising.[1] The multiblock SPE membranes have shown more developed phase separation between hydrophobic and hydrophilic blocks than that of the random copolymer equivalents. It has been observed that the proton conductivity of SPE-bl-2 membrane is higher than Nafion (NRE212) over a wide range of humidity and at high temperature (>100 ^{o}C) but fails at low humidity. The reasons behind the poor proton conductivities of these SPE membranes at low humidity are still unknown and unexplored either experimentally or theoretically, and deserve utmost attention for the future membrane development. This study intends to figure out why Nafion shows higher proton conductivity than those of other hydrocarbon membranes at low humidity.

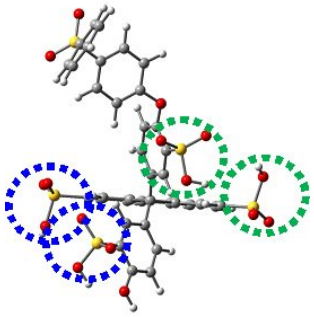

Figure 1: The optimized structure of SPE membrane, in which green and blue dotted circles indicate the separated and paired sulfonic acid groups.

Computational Details: Geometry optimizations and frequency calculations have been carried out by the generalized Kohn-Sham method using long-range corrected Becke 1988 exchange+ Lee-Yang-Parr correlation (LC-BLYP) functional in conjunction with cc-pVDZ basis set without imposing any symmetry restriction and all structures have positive real frequencies. The computations have been performed using GAUSSIAN 09 program.

Results and Discussion: To discuss the state of protons in the hydrated sulfonic acid groups (–SO_3H), we firstly optimized the geometries of Nafion and SPE models with various number of water molecules, i.e. –SO_3H-$(H_2O)_n$ for n = 0, 1, 2, …, 10. It was found that the optimized distance between the sulfonic acid group and proton increases sharply from 1.032 to 3.084 Å and 1.037 to 2.084 Å for one to three hydration water molecules in Nafion and SPE, respectively, while the distance between the sulfonic acid group and the closest water

molecule are nearly constant up to eight hydration water molecules for both the membranes. This clearly indicates that minimum three water molecules are needed to detach proton from the sulfonic acid of both the membranes. For SPE, however, we found that the sulfonic acid groups hydrated in pairs ("paired" in Fig. 1) detach no proton even with 12 hydration water molecules (i.e. 6 molecules per group). The presence of such inactive sulfonic acid groups is supported by an IR spectrum study. In addition, we also found that the proton is always located at the edge of the hydration water cluster after the dissociation as supported by a study on *ab initio* molecular dynamics simulations and isotopic-exchange spectroscopy.[2] Furthermore, we analysed the molecular orbitals of hydrated Nafion and SPE membranes to discuss the proton detachments from the viewpoint of electronic structure. As results, it was noticed that the electron distribution of HOMO drastically changes from the backbone of the chain to the sulfonic acid groups in Nafion as the hydration level increases. This seems to make it easy to dissociate protons and protonated water clusters from the sulfonic acid groups. On the other hand, the HOMO and LUMO of SPE are hardly affected by the hydration.

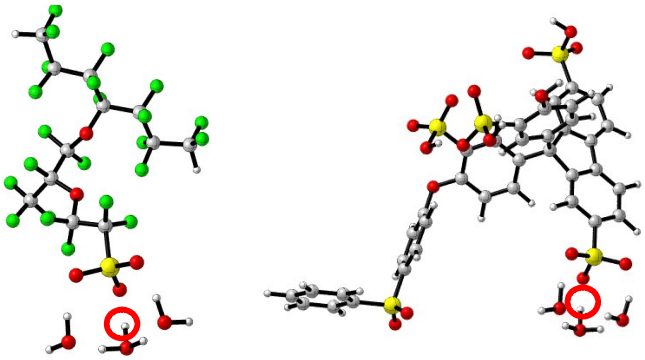

Figure 2: The optimized hydrated structures of Nafion (left) and SPE (right) membrane models, for which the detachment of proton (red circle) requires three hydration water molecules in vacuo.

To investigate the proton conductivity of Nafion and SPE at low humidity in further detail, we calculated the dissociation energies of protonated water clusters from the sulfonic acid groups. As a result, we found that these require more than 100 kcal mol^{-1} in vacua. This indicates that protonated water clusters hardly detach from the sulfonic acid groups at low humidity. We, therefore, considered that the proton conductance proceeds through the relay. It was found that the dissociation energies drastically decrease to around 40 kcal mol^{-1} through the relay. We are now exploring the feasibility of this relay.

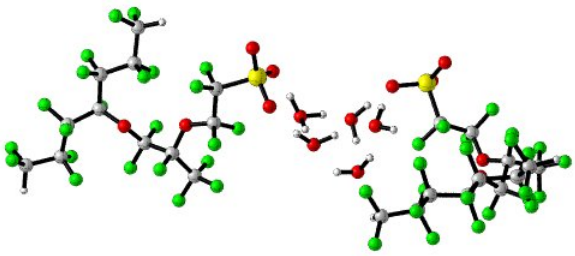

Figure 3: The optimized structure of double Nafion models hydrated in pairs with 5 hydration water molecules. The distance of the sulphur atoms is fixed at the averaged distance given in a previous MD calculation.

References:

1. Miyatake, K.; Bae, B.; Watanabe, M. *Polym. Chem.* **2011**, *2*, 1919-1929.
2. Buch, V. et al., *Proc.. Nat. Acad. Sci.* **2007**, *104*, 7342-7347.