

Quantum chemical analysis about deprotonation reaction of sulfonic group of perfluorosulfonic acid species in the low hydration level

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A perfluorosulfonic acid (PFSA) membrane such as Nafion is usually adopted as a polymer electrolyte membrane (PEM) in a polymer electrolyte fuel cell (PEFC). The great asset of PFSA is high proton diffusivity independent on hydration level. This feature would be caused by easiness of deprotonation as well as membrane flexibility¹. However, deprotonation mechanism of PFSA by water molecule(s) was not clarified yet. Paddison and his coworkers studied about stable state of PFSA in low hydration levels by quantum chemical investigation. According to their study, in hydration levels of one and two, the most stable state was a sulfonic group which was not deprotonated state. On the other hand, in hydration level of three, the most stable state was a deprotonated state which consisted of sulfonate (SO_3^-) group, H_3O^+ and two water molecules². Thus, sulfonic group of PFSA would be deprotonated at least hydration level of three. However, activation energy (ΔE_a) and energy difference between reactant and product (ΔH) for deprotonation reaction were not reported. Thus, no one can explain the reaction rate or the stability of produced SO_3^- with H_3O^+ in this deprotonation reaction quantitatively.

Then, we attempted to clarify the deprotonation reaction about PFSA species by some water molecules. As mentioned above, deprotonation of PFSA would be occurred at hydration level of three. We mainly focused on low hydration level, especially from one to three.

The most stable conformations, which were reported by Wang et al. were assumed as the product state in each hydration levels. Reactants in hydration level of one and two were presumed as different protonated conformations inside of the sulfonic group on the assumption that only proton exchange transition state would be formed. Reactant in hydration level of three was presumed as sulfonic group and three water molecules. Transition states were determined along the reaction from reactant to product. Energies of each geometries, reactant, transition state and product were calculated by B3LYP/6-311+G(d,p) level of theory. The basis set super position error was corrected by counterpoise method. All of calculations were performed by Gaussian09³, installed on super computer systems of Institute of Fluid Science, Tohoku University.

Energy changes along the reaction in hydration level from one to three were depicted in Fig. 1. All of energies were treated as relative energy. The predicted ΔE_a s for hydration level of one, two and three were 10.94, 5.24 and 0.70 kcal/mol, respectively. ΔE_a s were obviously decreased with increasing hydration level. In hydration levels of one and two, predicted proton exchange transition states inside of the sulfonic group via water molecule(s) were certainly obtained. However, ΔE_a s in these hydration levels were much higher than the heat energy around the 350K (0.7kcal/mol), which was the operation temperature of PEFC. Thus, these proton exchange reactions will not occur in real PEM. In hydration level of three, as shown in Fig. 1, calculated ΔE_a was very low and ΔH was large. The product geometry which consisted of SO_3^- group, H_3O^+ and two

water molecules was much more stable than reactant. Considering the computational error of B3LYP, it is hard to evaluate this low ΔE_a . However, at least, this reaction can almost be regarded as a barrierless reaction. Thus, in hydration level of three, sulfonic group must be deprotonated by three water molecules smoothly.

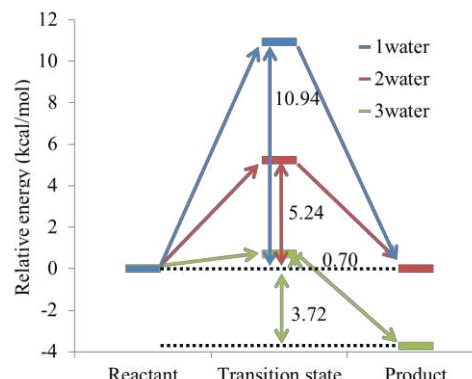


Fig. 1. Energy changes along the reaction in each hydration levels.

We also analyzed the bond order to determine the strength of hydrogen bond between SO_3^- group and H_3O^+ . The result of natural bond analysis suggests that hydrogen bond strength between SO_3^- group and H_3O^+ (Fig. 2(a)) was the same level of hydrogen bond strength in the Eigen cation (Fig. 2(b)). This result indicates that produced H_3O^+ would be attracted by SO_3^- group strongly. For this reason, the mobility of H_3O^+ in hydration level of three would be low. To achieve the efficient power generation of PEFC, thus, required hydration level might be over three.

In conclusion, our study revealed five interesting features about PFSA species; i) ΔE_a was obviously decreased with increasing hydration level, ii) proton exchange reaction in hydration level of one and two should not occur by its high ΔE_a , iii) deprotonation reaction in hydration level of three would proceed smoothly, iv) produced SO_3^- and H_3O^+ by the result of deprotonation reaction was much more stable than sulfonic group with three water molecules and v) the strength of hydrogen bond between H_3O^+ and SO_3^- group in hydration level of three was the same level of hydrogen bond of Eigen cation.

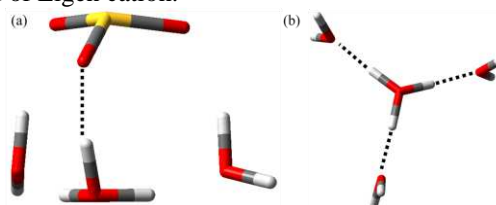


Fig. 2. (a) Molecular conformations for SO_3^- group, H_3O^+ and two water molecules in hydration level of three and (b) Eigen cation. The black dotted line indicates the hydrogen bond.

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References

- (1) Kopitzke, R. W.; Linkous, C. A.; Anderson, H. R.; Nelson, G. L. J. *Electrochem. Soc.* **2000**, 147, 1677.
- (2) Wang, C.; Clark, J. K.; Kumar, M.; Paddison, S. J. *Solid State Ion.* **2011**, 199, 6.
- (3) M. J. Frisch et al. Revision C.01 ed.; Gaussian, Inc.: 2010.