A Computational Study on the Correlations between Water Content and Degradation of Polymer Electrolyte Membrane

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In the past several years, the chemical reaction is one of the reasons for the degradation of perfluorosulfonic acid (PFSA) polymer membrane in PEFCs. Moreover, many studies are suggested that the reaction of PFSA with hydroxyl radical which is generated by the operating PEFCs are depended on its humidity conditions (water content λ). For example, under low humidity conditions, it is important to considered not only the unzipping mechanism of polymer end group (such as -COOH) which was discussed by Curtin et al.[1] but also the mechanism is started from the abstraction reaction of hydrogen at the sulfonic acid group in the side chain which was proposed by Endoh[2]. In order to clarify the details of this degradation mechanism, many studies have been carried out by theoretical approaches [3-5].

In our previous studies, we focused on the degradation reactions of PFSA side chain with hydroxyl radical. We investigated two reactions as followings, the C-O bond (ether bond) cleavage reaction, such as equation (1), and the C-S bond cleavage, such as equation (2). As a result, we found that the barrier height of the C-S bond cleavage reaction (about 12 kcal/mol) is lower than the reaction barrier of C-O bond cleavage (about 34 kcal / mol).

$$R\text{-}OCF_2CF(CF_3)O(CF_2)_2SO_3H + OH \rightarrow R\text{-}OCF_2CF(CF_3) + HO(CF_2)_2SO_3H \ldots (1)$$

$$R\text{-}OCF_2CF(CF_3)O(CF_2)_2SO_3H + OH \rightarrow R\text{-}OCF_2CF(CF_3)O(CF_2)_2 + H_2SO_4 \ldots (2)$$

In this study, we investigated that the correlations between water content λ and the barrier height of degradation reaction using *ab initio* calculations. To estimate the correlations, we analyze the barrier height of the reactions between hydroxyl radical and clusters consist of the modeled PFSA and water molecules, such as Fig. 1. The water content λ is defined as equation (3).

$$\lambda = \frac{(H_2O)_n}{(\text{-}SO_3H)_m} \ldots (3)$$

Note that, the parameter *m* in equation (3) is fixed to 1 in this calculation.

As future prospects, we will discuss about a macro simulation using this correlation data to calculate the distribution of membrane degradation in the PEM fuel cell under various operating conditions.

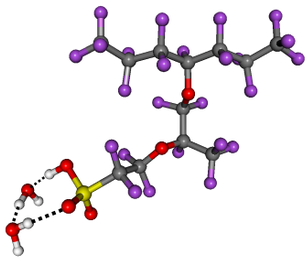

Fig.1 Optimized structure of PFSA model molecule and H2O cluster ($\lambda = 2$) calculated by BLYP/cc-pVDZ+diff. level of theory

References

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