We theoretically analyzed the chemical degradation mechanism of Nafion side chain by OH radicals on the basis of density functional theory calculations. We found that the cleavage of the C–O bond in ether groups is a main pathway of the degradation from the Nafion side chain by OH radicals under well-hydrated condition. The ether group, which is located near the sulfo group, is vulnerable to the OH radical attack rather than the other ether group connecting the side chain with the polymer main chain.

Introduction

Polymer electrolyte fuel cell (PEFC) is intensively studied as a promising power source for automobiles and cogeneration systems. For the practical application of fuel cells, the durability of the membrane electrode assembly (MEA) is one of the main issues to be tackled. The majority of membranes used in PEFCs has a perfluorinated backbone and are modified to include sulfonic groups that facilitate the transport of protons. Perfluorosulfonic acid (PFSA) polymers, such as Nafion, are widely used due to their chemical stability, permselectivity, and high proton conductivity. The degradation of PFSA accounts for a large part of the overall performance degradation of MEA (1-7). An understanding of the degradation mechanism of PFSA is thus important in the development of durable MEA. It is generally believed that the degradation of PFSA membrane is caused by the attack of free radicals, such as hydroxyl (OH) radical, which are produced through the formation of hydrogen peroxides (H₂O₂) in MEA (6,8). Such free radicals attack the weak chemical groups in the polymer membrane. The most well-known decomposition mechanism of the PFSA membrane is an unzipping mechanism (9) expressed as,

\[ \text{Rf–CF₂COOH +2OH}^- \rightarrow \text{Rf–COOH} + \text{CO}_2 + 2\text{HF}. \]  

This degradation mechanism is supported by the experimental observation that the existence of carboxylic (COOH) acid groups at the polymer main chain terminal is well correlated with the degradation rate of PFSA membrane. However, recent study reported that a linear relationship with a decidedly persistent intercept is observed when the fluoride ion emission rate (FER) is plotted against the number of carboxylic acid groups in Nafion (10). In the report, it is clarified that over 10% of the total FER remains even when the carboxylic acid group does not exist in Nafion. This result indicates the possibility of degradation by the attack of free radical on Nafion except the COOH group.
at the polymer main chain terminal. Ishihara and co-workers recently indicated that the ether group in the PFSA side chain is vulnerable to OH radical on the basis of experiments using small model compounds (11).

In our previous study, we have theoretically analyzed the degradation mechanisms of CF₃(CF₂)₃O(CF₂)₂OCF₂SO₃H as a model compound representing the PFSA side chain by using density functional theory (DFT) method (12). We have found different chemical degradation mechanisms for the model compound by the OH radical, depending on the protonation and deprotonation states of the sulfo group, which correspond to the low and high humidity conditions, respectively. When the sulfo group is deprotonated, we have identified the degradation mechanism through the cleavage of the C–O bond in the ether group by the OH radical. This result shows reasonable agreement with the experimental observations. On the other hand, we have identified a sulfo-unzipping mechanism when the sulfo group is protonated, i.e. the OH radical attacks and abstracts the undissociated proton of the sulfo group as expressed in the following equation.

\[
\text{Rf–CF₂SO₃H} + \text{OH·} \rightarrow \text{Rf–CF₂SO₃·} + \text{H₂O} \tag{2}
\]

Although we have theoretically obtained important insights on degradation mechanisms of PFSA based on the analysis for the model compound system, it is necessary to analyze the degradation mechanism of the realistic side chain of Nafion in detail. In this study, we analyzed the chemical degradation mechanisms from Nafion side chain by OH radicals using DFT method.

**Computational Details**

Figure 1 shows the structure model of Nafion side chain used in this study. We adopted a deprotonated state of sulfo group, Rf–SO₃⁻, as a structure model representing the Nafion side chain under high humidity condition. All calculations were performed under the generalized gradient approximation (GGA) with Becke-88 exchange and Lee-

![](image)

Figure 1. Structure model of deprotonated Nafion side chain used for the calculation.
Yang-Parr correlation functionals (BLYP) as implemented in the DMol³ package (13,14). Double numerical atomic basis sets augmented with polarization functions (DNP) were used. Full geometry optimization was performed for each system in the gas phase (isolated molecule) and in the solution phase. Normal mode analyses were performed to verify all frequencies are positive for the optimized structures. We checked only one imaginary frequency at the transition state. Solvent effects were estimated using the conductor-like-screening model (COSMO), which provides reasonable free energy of solution (15,16). The value of 78.54 was chosen for the relative dielectric constant \( \varepsilon \) of water. In the potential energy profiles, the enthalpy values of intermediate, transition state structures, and products are calculated relative to the reactants as follows,

\[
E = \text{enthalpy of intermediate or transition state or products) - (enthalpy of reactants).} \quad [3]
\]

Results and Discussion

To study the chemical degradation pathways of Nafion side chain by the OH radical, we investigated the reactivity of the OH radical with two ether groups in Nafion side chain. As shown in Fig. 1, we investigated the degradation of deprotonated Nafion side chain, representing the structure under well-hydrated high humidity condition. We assumed this structure referring the previous literatures, which indicates that the proton will be fully dissociated when the number of water molecules around the sulfo group is sufficient (17–20). The potential energy profile of the reaction is shown in Fig. 2. The degradation reaction pathways via O1 and O2 in Nafion side chain are denoted as the pathways 1 and 2, respectively. The optimized structures of intermediate, transition state, and products for pathways 1 and 2 are shown in Figs. 3 and 4, respectively. Two reaction intermediate structures, Int1-1 and Int1-2, were obtained by the weak attractive interactions between OH radical and O atoms in ether groups. The stabilization energies of Int1-1 and Int1-2 were –34.6 and –14.1 kJ/mol, respectively. These intermediate compounds have led to different products through the transition states. In the transition state, the C–O bond cleavage is induced by the OH radical in both cases. The energy of

Figure 2. Potential energy profile for the ether bond cleavage of Nafion side chain. The energy values (kJ/mol) are relative to reactants.
the C–O2 bond cleavage at TS2 was about 30 kJ/mol lower than that of C–O1 at TS1. We did not observe difference in the strength of ether bonds from the bond overlap population analyses. The atomic charges of O1 and O2 in Nafion side chain were −0.473 and −0.478, respectively. Large stabilization was observed in Int1-1 because the O1...H distance in Int1-1 is about 0.2 Å shorter than O2...H distance in Int1-2. At the transition state, C–O1 and C–O2 bond distances in pathways 1 and 2 were 2.067 and 2.530 Å, respectively. This result indicates that the C–O2 bond cleavage via TS2 is easier to occur compared to the C–O1 bond cleavage via TS1.

Figure 3. Optimized structures of intermediate, transition state, and products for Rf–OCF2CF(CF3)O(CF2)2SO3– + OH → Rf–OH + OCF2CF(CF3)O(CF2)2SO3–. The ether group including O1 is reaction point with OH radical. Selected interatomic distances are shown in Å unit.

Figure 4. Optimized structures of intermediate, transition state, and products for Rf–OCF2CF(CF3)O(CF2)2SO3– + OH → Rf–OCF2CF(CF3)O + HO(CF2)2SO3–. The ether group including O2 is reaction point with OH radical. Selected interatomic distances are shown in Å unit.

To discuss the reactivity of two ether groups with OH radical quantitatively, we analyzed the ratio of rate constants for the corresponding reactions,

\[
\text{Rf–OCF2CF(CF3)O(CF2)2SO3}^- + \text{OH} \xrightarrow{k_1} \text{Rf–OH} + \text{OCF2CF(CF3)O(CF2)2SO3}^-, \quad [4] \\
\text{Rf–OCF2CF(CF3)O(CF2)2SO3}^- + \text{OH} \xrightarrow{k_2} \text{Rf–OCF2CF(CF3)O} + \text{HO(CF2)2SO3}^-. \quad [5]
\]
We evaluated the $k_2/k_1$ at 350 K using the following equation,

$$
\frac{k_2}{k_1} = \exp\left(-\frac{(E_a^2 - E_a^1)}{RT}\right),
$$

where the $R$ and $T$ are gas constant and temperature, respectively. The $E_a^1$ and $E_a^2$ are activation energies of reactions [4] and [5], respectively. Because the $k_2/k_1$ is estimated to be $4.0 \times 10^3$, the reaction [5] will be a major pathway accounting for the degradation from the Nafion side chain.

Comparing the structures in Figs. 3 and 4 with those in our previous study for the model compound system (12), we noticed the difference in the interacting structures of OH radical with ether bond near the sulfo-group. In the model compound system, H of OH radical is oriented to the O of sulfo-group while this is not the case in the Nafion side chain model. This is simply because the model compound has only one -CF$_2$- group in between sulfo-group and the ether bond while the Nafion has two -CF$_2$- groups there. However, the overall tendency of the degradation pathway is not influenced by this different interacting structure, indicating that the degradation of the Nafion side chain will proceed with the same mechanism as the results by Ishihara and coworkers (11) reported for the model compound system.

Conclusions

In this study, we theoretically analyzed the chemical degradation mechanism of Nafion side chain by OH radical using a structure model under high humidity condition on the basis of DFT calculations. We found the cleavage of C–O bond in the ether group by the OH radical induces the degradation. The ether group, which is located near sulfo group, is more vulnerable to OH radical attack than the other ether group connecting the side chain with the main chain. Comparing the rate constants of degradation reaction of two ether groups in Nafion side chain, it was confirmed that the ether group near sulfo group will account for the overall degradation from the Nafion side chain. The obtained results are almost same with those obtained in our preceding research, indicating that the degradation of Nafion side chain proceeds with the same mechanism observed in the model compound system.

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