Theoretical Investigation of the \( \text{H}_2\text{O}_2 \)-Induced Degradation Mechanism of Hydrated Nafion Membrane via Ether-Linkage Dissociation

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ABSTRACT: A \( \text{H}_2\text{O}_2 \)-induced degradation mechanism is presented for the hydrated Nafion membrane proceeding through the dissociation of the ether linkages of the side chains. Although the durability of proton-exchange membrane fuel cells clearly depends on the degradation rate of the membrane, typically Nafion, the degradation mechanism still has not been resolved. It has often been assumed that the principal mode of degradation involves \( \text{OH}^+ \) radicals; in contrast, we show here that a \( \text{H}_2\text{O}_2 \)-induced degradation mechanism is more likely. On the basis of state-of-the-art theoretical calculations and detailed comparison with experimental results, we present such a mechanism for the hydrated Nafion membrane, proceeding through the dissociation of the ether linkage of the side chains, with a relatively low activation energy. In this mechanism, \( (\text{H}_2\text{O})_{\lambda}\text{HO}_2\text{S} = \text{CF}_2=\text{CF}_2-\text{O} = \text{O} = \text{H} \) (\( \lambda \) is the hydration number) is obtained as a key degradation fragment. Possible subsequent decomposition-reaction mechanisms are also elucidated for this fragment. The calculated vibrational spectra for the intermediates and products proposed in these mechanisms were found to be consistent with the experimental IR spectra. Further consideration of this \( \text{H}_2\text{O}_2 \)-mediated degradation mechanism could greatly facilitate the search for ways to combat membrane degradation.

INTRODUCTION

Degradation of proton-exchange electrolyte membranes is the most serious problem in fuel-cell operations, determining the durability of proton-exchange membrane fuel cells (PEMFCs).\(^1,2\) Proton-exchange membranes in PEMFCs conduct protons produced from the oxidation of hydrogen gas on the anode to a catalyst composed of, for example, Pt alloy on the cathode for oxygen-reduction reactions (ORR) to proceed. Under PEMFC operating conditions, hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) is produced to some extent and degrades the proton-exchange membrane, deteriorating the proton conductivity of the membrane.\(^3\) Experiments have shown that the \( \text{H}_2\text{O}_2 \) production of PEMFC results from \( \text{O}_2 \) crossover in proton-exchange membranes.\(^4-6\) That is, oxygen (\( \text{O}_2 \)) gas injected at the cathode permeates to the anode and then reacts with hydrogen radicals on the anode to produce \( \text{H}_2\text{O}_2 \). A rotating ring-disk measurement study clearly shows that \( \text{H}_2\text{O}_2 \) is formed by the reaction of \( \text{O}_2 \) and \( \text{H}_2 \) adsorbing on Pt surface at low potentials; especially on Pt(111), 100% \( \text{H}_2\text{O}_2 \) formation is observed.\(^7\) This reaction is so facile that it is useful even as a \( \text{H}_2\text{O}_2 \) synthesis method.\(^8\) Nevertheless, the OH radical has usually been assumed to be the reactive species in the degradation of proton-exchange membranes. Fenton test studies, however, have raised questions concerning this assumption.\(^9,10\) In the Fenton test, the reaction of \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) ions has been interpreted to provide OH radicals as the active intermediate:\(^11,12\) 

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^+ + \text{OH}^- + \text{Fe}^{3+} \]

although several theoretical studies support another hypothesi:\(^13\) that FeO\(^{2+}\) ion is the most likely active intermediate: 

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{H}_2\text{O} + \text{FeO}^{2+} \] \(^14,15\) On the basis of a Fenton test of a Nafion membrane, which is the most widely used proton-exchange membrane, Kinumoto et al. found that the degradation proceeded in 30% \( \text{H}_2\text{O}_2 \) solution at 80 °C and the decomposition ratios of \( \text{SO}_4^{2-} \) groups and C–F bonds were inconsistent with those obtained in the absence of the Fenton reagent in the PEMFC.\(^8\) The ratios were 33 and 68% for \( \text{SO}_4^{2-} \) groups and C–F bonds after 9 days in the Fenton test, and 7 and 1% after 5.5 days under the PEMFC operating conditions, respectively. Using gas-phase \( \text{H}_2\text{O}_2 \) exposure, Hommura et al. found that the rate of COOH formation does not approach zero as \( \text{Fe}^{2+} \) concentration decreases and confirmed, on the basis of the chemical kinetics, that Nafion is decomposed by \( \text{H}_2\text{O}_2 \) alone, that is, without metal ions.\(^10\) IR spectral analyses also showed that after the Fenton test, Nafion exhibited peaks around 900 and 1600 cm\(^{-1}\), which were not found in the IR spectra of the decomposed Nafion under PEMFC operating conditions.\(^16\) The instability of the OH radical in aquo has also been hardly taken into account in conventional studies. The lifetime of OH radicals is 100 ns in aquo, which is too short to cause degradation over a wide region in the proton-conducting channels, where water clusters are present predominantly near the sulfonic acid groups. The large dissociation energy of the

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OH radical on the Pt surface is also an obstacle for the OH-radical-induced degradation: Under a H₂-rich H₂/O₂/H₂O mixed gas, the dissociation of the OH radical from the Pt surface requires more than 40 kcal/mol even at very high temperature (around 1000 K). We note, however, that the degradation can indeed be caused by radicals such as OH⁺ when metal ions are supplied from the end plate of the PEMFC and can be inhibited by adding radical scavengers like cerium dioxide (CeO₂) nanoparticles. It is, therefore, reasonable to consider that the degradation of proton-exchange membranes proceeds through two reactions, H₂O₂-induced and OH-radical-induced reactions, depending on the surrounding environment, such as humidity conditions, the distance from the catalyst layer, and the presence of metal ions.

The degradation mechanism of the Nafion membrane has also been vigorously investigated. Aoki et al. and other groups revealed that the degradation mainly proceeds near the anode as a result of O₂ crossover. Endo et al. and other groups reported that the degradation rate increased as the relative humidity decreased. Ghassemzadeh et al. revealed that the degradation proceeds only in the presence of a Pt catalyst in addition to H₂ and O₂ and that it is hardly affected by the morphology of the Nafion membrane. Various studies have also been reported on the degradation fragment species. Deng et al. showed that hydrogen fluoride (HF)- and CF₂-containing fragments were produced. LaConti et al. also reported that the degradation produces F⁻ ion, CO₂, and low-molecular-weight perfluorocarbon sulfonic acids. As another possible degradation product, several studies have suggested the perfluoro(3-oxa-5-methyl)pentane-1-sulfonic-5-carboxylic diacid (HOOC−CF(CF₂)=O−CF₂CF₂−SO₂H), implying the degradation through the ether-linkage dissociation of the side chains, although the identification of this compound is not completely certain, as discussed later. Akiyama et al. also supported the formation of a carboxylic acid by showing that the most remarkable difference in the IR spectra of Nafion before and after the degradation was the appearance of the peaks assigned to the vibrational modes of carboxylic acid groups.

There have also been several theoretical studies focusing on the degradation of the Nafion membrane. Assuming that the degradation takes place at the weakest bonds, Okamoto suggested that the C−S bond of the side chain is the most reactive part. Coms calculated decomposition-reaction enthalpies and suggested that only the OH radical is able to abstract a H atom from a carboxylic acid to unzip the main chain of Nafion. Yu et al. have recently explored various radical-induced degradation processes for the end groups of both the main and side chains, assuming that the reactive species are radicals coming from the ORR, such as the OH radical. It is important to note, however, that hydration water clusters attached to the sulfonic acid groups have not been included in their calculation models, although they must certainly be present for protons to be conducted within the membranes. Despite many experimental and theoretical studies on this topic, the degradation mechanism of the Nafion membrane has never been confirmed, as far as we know. It is, therefore, meaningful to theoretically reveal the degradation mechanism of the Nafion membrane using realistic calculation models, considering, for example, the hydration structures of the membrane and H₂O₂.

Proton conduction and hydration structures of Nafion membrane have been investigated from various aspects, both experimentally and theoretically. It has been accepted that the proton conduction in aquo proceeds through the de Grotthuss and vehicle mechanisms. In the de Grotthuss mechanism, protons transfer at high speed using hydrogen-bond networks through the Zundel cation H₂O⁺ complex, that is, the [H₂O−H−OH₂⁺] complex. Because of the very low reaction barrier height of about 2 kcal/mol, the de Grotthuss mechanism has been assumed in past theoretical studies on proton conduction and proton dissociation in the Nafion membrane. Experiments, however, have shown that Nafion contains a number of unconnected hydrogen-bond networks under low-humidity conditions despite its high proton conductivity. Protons in low-humidity Nafion are, therefore, considered to transfer not only by the de Grotthuss mechanism but also by the vehicle mechanism. In the vehicle mechanism, protonated water molecules diffuse to deliver protons. This implies that proton conduction requires the dissociation of protonated water molecules at low humidity. Theoretical calculations, however, show that protonated water clusters require very large energies to dissociate from the sulfonic acid groups of Nafion at low humidity (about 100 kcal/mol). As an alternative mechanism, we have suggested a relay mechanism to explain the proton conduction between the unconnected hydrogen-bond networks in the low-humidity Nafion membrane.

In the relay mechanism, proton conduction proceeds through the relay of protonated water clusters from one sulfonic acid group to another using the long side chains of Nafion. As this mechanism requires only about 30 kcal/mol to dissociate protonated water clusters, it is considered to proceed even at room temperature. We note that this relay mechanism involves doubly hydrated structures of the Nafion membrane. Through a detailed comparison of experimental and theoretical results, we have recently revealed that the sulfonic acid groups of Nafion are doubly hydrated, regardless of humidity conditions. Comparing the experimental humidity dependence of the IR spectrum of the Nafion membrane under PEMFC operating conditions and the theoretical hydration number dependence of the vibrational spectrum of the hydrated Nafion membrane model, we found that the theoretical spectral dependence is consistent with the experimental one only for a doubly hydrated Nafion model optimized using an initial structure, in which protons are detached from the sulfonic acid groups. This result strongly supports the proton conduction through the relay mechanism under the low-humidity condition and the doubly hydrated Nafion membrane structure, regardless of the humidity.

In this study, we theoretically reveal the degradation mechanism of the hydrated Nafion electrolyte membrane in a PEMFC, focusing on the H₂O₂-induced degradation and subsequent reactions of the degradation fragment molecule. After detailing the computational methods, we first elucidate the H₂O₂-induced degradation mechanism of the doubly hydrated Nafion membrane. Then, we verify the decomposed hydrated Nafion membrane and the degradation fragment molecule by comparing the calculated vibrational spectra with the experimental IR spectrum results. We finally investigate the subsequent reaction processes of the degradation fragment molecule.

### COMPUTATIONAL DETAILS

All calculations have been performed for the doubly hydrated structures of Nafion membrane molecular model, in which water molecules are explicitly hydrated, using the long-range correction of Becke exchange plus the Lee–Yang–
Parr correlation\(^\text{47}\) (LC-BLYP) functional (the only parameter \(\mu = 0.4748\)) with the cc-pVDZ basis set.\(^\text{49,50}\) We have adopted the double-unit model of hydrated Na\(^+\)on membrane shown in Figure 1a. Geometry optimizations of the hydrated Na\(^+\)on structures have been carried out for several initial structures maximizing the number of the hydrogen bonds. For the calculated hydrated Na\(^+\)on model, we have used the doubly hydrated structures (Figure 1) following our previous study based on the experimental and theoretical IR spectral analyses of hydrated Na\(^+\).\(^\text{44}\) In Figure 2, the optimum geometries of the doubly hydrated double-unit Na\(^+\)on membrane model with H\(_2\)O\(_2\) molecule are illustrated for the hydration numbers per sulfonic acid group: \(\lambda = 1-4\), which models the low-humidity conditions near the anode.\(^\text{51,52}\) It is important to note that as shown in this figure, protonated water molecules are dissociated only for \(\lambda = 3\) and 4, whereas they attach the sulfonic acid group for \(\lambda = 1\) and 2. This is consistent with conventional theoretical results.\(^\text{43}\) Using these optimum geometries as the initial structures, we have optimized the geometries of the hydrated Na\(^+\)on + H\(_2\)O\(_2\) models by extending the C–O ether-linkage distance (Figure 1) from 1.2 to 4.0 Å. Protons are assumed to be dissociated to model proton transfers in the relay mechanism.\(^\text{43,44}\) The Gaussian 09 suite of program\(^\text{53}\) has been used to perform all of the LC-BLYP calculations. All of the optimized structures have been checked to ensure that they yield positive, real frequencies. Transition-state calculations have been performed by the quadratic synchronous transit method.\(^\text{54,55}\) The predictor−corrector integrator method\(^\text{56,57}\) was used to calculate the intrinsic reaction coordinates of the reactions. The vibrational modes contributing to IR spectra and their assignments were analyzed using GaussView 5.0.8.\(^\text{58}\)

**CALCULATED RESULTS AND DISCUSSIONS**

\textbf{H}_2\text{O}_2\text{-Induced Degradation Mechanism of Na\(^+\)on Membrane.} Following the experimental studies on the degradation mechanism of hydrated Na\(^+\)on membrane mentioned above, we imposed the following assumptions to the calculation model:

1. The degradation of Na\(^+\)on membrane takes place in the vicinity of the anode. This is because the anode side of the membrane undergoes severer degradation than the cathode side.\(^\text{1,24}\) The hydration numbers of the sulfonic acid groups, therefore, should be relatively small to model the hydration conditions near the anode.\(^\text{51,52}\)
2. The sulfonic acid groups are doubly hydrated in the hydrated Na\(^+\). As mentioned above, our previous IR spectroscopy study proves that Na\(^+\)on has a doubly hydrated structure, regardless of the humidity conditions.\(^\text{44}\)
3. The degradation initially proceeds with the ether-linkage dissociation of the side chains. Several experimental studies have suggested a carboxylic acid in the degradation fragment species, which is considered to originate from the ether-linkage dissociation.\(^{26-29}\)

4. The morphology of the hydrated Na\(_{\text{fi}}\)on membrane has negligible effect on the degradation mechanism, although the morphology depends on the hydration number.\(^{59}\) This is because an \(^{19}\)F NMR experiment showed that the morphology of the Na\(_{\text{fi}}\)on membrane hardly affects the degradation ratio.\(^{24}\)

On the basis of these assumptions, we have explored the degradation mechanism of the hydrated Na\(_{\text{fi}}\)on membrane.

As a result, we succeeded in elucidating a H\(_2\)O\(_2\)-induced degradation mechanism of the hydrated Na\(_{\text{fi}}\)on membrane. Figure 3 displays the hydrated Na\(_{\text{fi}}\)on model before and after the H\(_2\)O\(_2\)-induced decomposition for the hydration number of \(\lambda = 4\). As shown in the figure, H\(_2\)O\(_2\), which participates in a hydrogen-bond network with the hydration water cluster of the sulfonic acid groups, decomposes the ether linkages, forming an alcohol group and an \(-\text{O}OH\) group. That is, the H\(_2\)O\(_2\)-induced decomposition is expressed in the following scheme:

\[
\text{R}_p\text{O}-\text{CF}_2\text{CF}_2\text{SO}_4^- + \text{H}_2\text{O}_2 \rightarrow \text{R}_p\text{O}^-\text{OH} + \text{HO-O-CF}_2\text{CF}_2\text{SO}_4^- (\text{H}_2\text{O})
\]

We should emphasize that this reaction path is obtained by simply extending the ether C–O bond of the hydrated Na\(_{\text{fi}}\)on membrane with the H\(_2\)O\(_2\) molecule. This indicates that the ether linkage is directly cleaved by H\(_2\)O\(_2\) without producing OH radicals. Although this scheme has the appearance of being unlikely because of the unfamiliar \(-\text{O}OH\) group produced, it is interesting to note that this scheme is analogous to the double-bond cleavage mechanism by ozone:

\[
\text{R}_1\text{H} + \text{O}_3 \rightarrow \text{R}_1\text{O}^{-} + \text{R}_3\text{H}
\]

Similar mechanisms are also suggested for decompositions after TiO\(_2\) photocatalytic reactions.\(^{60}\) It is, therefore, reasonable to suppose that the \(-\text{O}OH\) bond is not uncommon in the process of bond cleavages in gas phase.

Figure 4 illustrates the potential energy curves of the H\(_2\)O\(_2\)-induced ether-linkage dissociation of the doubly hydrated Na\(_{\text{fi}}\)on membrane for \(\lambda = 1–4\) in terms of the C–O bond distance of the ether linkage. The figure shows that the reaction
barrier heights are moderate, 32−40 kcal/mol, nearly independent of hydration number. This indicates that the ether-linkage dissociation reaction proceeds irrespective of the humidity of the membrane, without any other reactive species, such as radicals. On the other hand, the reaction energies decrease from \( \lambda = 1 \) to 2 but then gradually increase from \( \lambda = 2 \) to 4: 20.4, 15.1, 19.4, and 25.7 kcal/mol for \( \lambda = 1−4 \), respectively. This result seems inconsistent with the experimental results showing that the degradation ratio increases with decreasing humidity.\textsuperscript{21−23} This inconsistency is explained by the decrease of \( \text{O}_2 \) crossover and \( \text{O}_2 \) adsorption as well as the instability of OH radicals in aquo. The increase of humidity leads to the obstruction of the membrane channels by water, decreasing the \( \text{O}_2 \) crossover, which causes the degradation.\textsuperscript{3−6} It is also known that water molecules prevent \( \text{O}_2 \) adsorption on the electrode surface. Therefore, the increase of humidity suppresses \( \text{H}_2\text{O}_2 \) production and consequently slows the degradation. The increasing humidity also destabilizes OH radicals, which are reactive species in other degradation mechanisms; therefore, it may reduce the infiltration of OH radicals into the internal region of the membrane. The calculated potential energy curves suggest that the \( \text{H}_2\text{O}_2 \)-induced degradation reaction of the ether linkages naturally proceeds irrespective of the water volume of the Na\textsuperscript{+} membrane channels. Because \( \text{H}_2\text{O}_2 \) is incorporated in the hydrogen-bond networks of water clusters, this result is

Figure 5. Vibrational spectra of decomposed hydrated Na\textsuperscript{+} membrane model before and after degradation in the wavenumber region of 0−4000 cm\textsuperscript{-1} for \( \lambda = 1−4 \), which are calculated by LC-BLYP/cc-pVDZ method.
Table 1. Peak Energies and the Corresponding Peak Assignments of IR Spectra of Predecomposed and Decomposed Doubly Hydrated Nafion Membrane Model for $\lambda = 4$
(Eight Hydration Water Molecules in Total)$^a$

| Peak Energy (cm$^{-1}$) | Assignments |
|------------------------|-------------|
| predecomposed Na$^+$ and hydrated H$_2$O$_2$ | | decomposed Nafion |
| O$^-$H stretching of H$_2$O | 3153, 3700 |
| O$^-$H stretching of H$_2$O$_2$ | 1522, 1606, 1801, 2178, 2532, 2855, 3020, 3173, 3174, 3345, 3433, 3491, 3589, 3597, 3672, 3693, 3721, 3900, 3913 |
| C$^-$C stretching | 1420 |
| O$^-$H swinging of H$_2$O$_2$ | 3553, 3700 |
| SO$_3^-$ asymmetric stretching + C$^-$F stretching | 1234, 1261, 1265, 1268, 1275, 1284, 1286, 1289, 1297, 1299, 1304, 1306, 1310, 1315, 1322, 1328, 1335, 1336, 1339, 1367, 1379 |
| C$^-$F stretching | 1209, 1212, 1232 |
| SO$_3^-$ asymmetric stretching + H$_3$O$^+$ scissoring | 593, 614, 676, 835, 859, 908 |
| O$^-$C$^-$C scissoring | 507 |
| SO$_3^-$ asymmetric stretching + H$_2$O$^+$ rocking | 546, 693, 717, 726, 761, 777, 887, 925, 1045, 1063, 1131 |
| H$_2$O$^+$ rocking | 507 |
| C$^-$C$^-$C symmetric stretching + H$_2$O rocking |

| Peak Energy (cm$^{-1}$) | Assignments |
|------------------------|-------------|
| O$^-$H stretching of H$_2$O | 2401, 2517, 3032, 3105, 3144, 3168, 3320, 3353, 3431 |
| O$^-$H stretching of H$_2$O$_2$ | 3640, 3646, 3660, 3664, 3703, 3763, 3834 |
| O$^-$H stretching of $-$O$^-$OH | 3206 |
| O$^-$H stretching of $-$OH and H$_2$O | 1598, 1777, 2000, 2035 |
| C$^-$C stretching | 1345, 1416, 1427, 1443, 1464 |
| H$_2$O stretching, wagging and rocking | 1502, 1667, 1820 |
| SO$_3^-$ asymmetric stretching + H$_2$O scissoring | 350, 1359 |
| C$^-$F stretching | 1261, 1264, 1268, 1273, 1289, 1295, 1304, 1307, 1311, 1315, 1316, 1321, 1326, 1328, 1333, 1336, 1339, 1345, 1361, 1374 |
| SO$_3^-$ asymmetric stretching + C$^-$F stretching | 1192, 1215, 1220, 1222, 1238 |
| O$^-$C$^-$C scissoring | 1035, 1064 |
| SO$_3^-$ asymmetric stretching + $-$O$^-$OH stretching + H$_3$O$^+$ rocking | 1015, 1060 |
| SO$_3^-$ C$^-$C$^-$C symmetric stretching + H$_2$O$^+$ rocking | 831 |
| $-$O$^-$H swinging of $-$O$^-$OH | 507 |

$^a$For comparison, H$_2$O$_2$ molecule is hydrated in the hydration water molecules attached to the predecomposed Nafion membrane. Only the peaks with strength higher than $10^{-38}$ esu$^2$ cm$^2$ are listed. The peak assignments corresponding to the vibrations of H$_2$O$_2$ in the predecomposed Nafion and $-$OH and $-$O$^-$OH groups in the decomposed Nafion are underlined.
consistent with the experimental results showing that the degradation progresses deeply into the interior of the membrane.\(^1\)

In Figure 4, the dependence of the barrier heights on the hydration number, that is, \(\lambda = 2 > 1 > 4 > 3\), seems unreasonable. However, this dependence can be interpreted by considering the proton-dissociation nature of the Nafion membrane. As shown in Figure 2, the proton is dissociated from the sulfonic acid group at \(\lambda = 3\). On the basis of this barrier height dependence, we, therefore, suppose that the presence of the dissociated proton may support the ether-linkage dissociation by decreasing the barrier heights. This support may be attenuated by increasing the hydration number. This hydration number dependence of the barrier heights suggests that this ether-bond dissociation proceeds under low-humidity condition around \(\lambda = 3\).

How likely is the \(\text{H}_2\text{O}_2\)-induced degradation compared to the OH-induced degradation? In the OH-induced degradation mechanism, the formation of OH radicals on the electrode catalyst surface has been taken as the rate-determining step. Yu et al. theoretically found the following reaction path for the OH-radical formation on the Pt(111) surface: \(^{31}\)

\[
\text{HOOH}_{\text{ad}} \rightarrow \text{OH}_{\text{ad}} + \text{OH}^* \quad (1)
\]

Because of the lower reaction barrier (18 kcal/mol), this reaction seems to proceed in preference to the \(\text{H}_2\text{O}_2\)-induced degradation because of its higher reaction barrier (30–40 kcal/mol). We note, however, that reaction 1 is endothermic, with a reaction energy of \(-17\) kcal/mol, and has another similar low-barrier exothermic reaction path (reaction barrier is 10 kcal/mol and reaction energy is 30 kcal/mol)

\[
\text{HOOH}_{\text{ad}} \rightarrow 2\text{OH}_{\text{ad}} \quad (2)
\]

In this reaction, OH radicals need to desorb to become reactive species. The adsorption energy of the OH radical is evaluated as 48 kcal/mol,\(^{31}\) which is much higher than the reaction barrier of the \(\text{H}_2\text{O}_2\)-induced degradation. This process is supposed to be the rate-determining step of the OH-radical-induced mechanism. It is important to note, also, that in the vicinity of the electrode surface, there are hydration water clusters, to which adsorbed molecules, such as \(\text{H}_2\text{O}_{\text{v}}\), are hydrated. It is theoretically revealed that OH radicals have no stable structures in water and therefore these radicals react spontaneously with each other, with no reaction barrier, when the surrounding water molecules are explicitly incorporated. That is, when there are vicinal water clusters, OH radicals are converted back to \(\text{H}_2\text{O}_2\) in reactions 1 and 2. This indicates that OH radicals need to avoid vicinal water clusters to be reactive species. However, we would emphasize that this does not disprove the OH-radical-induced degradation. In the presence of metal ions, such as \(\text{Fe}^{2+}\) ions, experimental studies have observed that OH radicals are formed with a very low activation energy, as mentioned above. We, therefore, conclude that the \(\text{H}_2\text{O}_2\)-induced degradation proceeds together with the OH-induced degradation.

**Vibrational Spectra of Decomposed Hydrated Nafion Membrane.** Next, let us compare the vibrational spectra of the decomposed hydrated Nafion membrane and degradation fragment molecule, that is, \((\text{H}_2\text{O})_4\text{HOS}^–\text{CF}_2–\text{CF}_2–\text{O}=\text{O}–\text{H}\), with the experimental IR spectra of decomposed hydrated Nafion membrane and its degradation fragment species to discuss the reliability of the \(\text{H}_2\text{O}_2\)-induced degradation mechanism. Akiyama et al. observed the IR spectra of the fragment species and decomposed Nafion membrane in aqueo.\(^{16}\) The experimental IR spectra show that the degradation generates sharp peaks around 1700 cm\(^{-1}\) and wide peaks around 2300 and 3300 cm\(^{-1}\) and that the Fenton test, producing OH radicals, results in various IR peaks around 900 and 1600 cm\(^{-1}\) compared to those of decomposed hydrated Nafion membrane. Comparing the calculated vibrational spectra of the hydrated Nafion before and after degradation, we can, therefore, test the decomposed Nafion membrane and degradation fragment molecule.

Figure 5 displays the calculated IR spectra of hydrated Nafion before and after degradation for \(\lambda = 1–4\). As shown in the figure, strong peaks appear around 2000, 2400, and 3300 cm\(^{-1}\) after the degradation. On the other hand, the degradation slightly changes the peaks in the wavelength region below 1700 cm\(^{-1}\). We note that the experimental IR spectra of the degradation fragment species also show strong peaks in the wavelength regions of 1700–2000, 2200–2400, and 3000–3700 cm\(^{-1}\), slightly affecting the peak strengths for the wavelength region below 1700 cm\(^{-1}\).\(^{16}\) This consistency strongly supports the \(\text{H}_2\text{O}_2\)-induced ether-linkage dissociation mechanism. This also suggests that the main degradation fragment molecule is \((\text{H}_2\text{O})_4\text{HOS}^–\text{CF}_2–\text{CF}_2–\text{O}=\text{O}–\text{H}\), not containing a carboxylic acid group \(\text{–COOH}\) but a hydroperoxyl group \(\text{–O}=\text{OH}\). Although this degradation fragment molecule is considered to be converted to the carbonylic acid, it seems chemically stable due to its poor reactivity, as shown above. On the basis of the vibrational spectra, we propose that \((\text{H}_2\text{O})_4\text{HOS}^–\text{CF}_2–\text{CF}_2–\text{O}=\text{O}–\text{H}\) is one of the main degradation fragment molecules and that several byproducts are derived from the subsequent reactions of this molecule.

**Figure 6.** Vibrational spectra of main degradation fragment molecule, \((\text{H}_2\text{O})_4\text{HOS}^–\text{CF}_2–\text{CF}_2–\text{O}=\text{O}–\text{H}\), in the wavenumber region of 0–4000 cm\(^{-1}\) for \(\lambda = 1–4\), which are calculated by LC-BLYP/cc-pVDZ method.
What types of vibrational modes do the peaks appearing after the degradation of hydrated Nafton membrane correspond to? Table 1 displays the theoretical peak assignments of the IR spectra of hydrated Nafton membrane before and after the H2O2-induced ether-linkage dissociation for \( \lambda = 4 \). The table clearly indicates that the strong peaks appearing around 2000, 2400, and 3000-3700 cm\(^{-1}\) after the degradation correspond to the OH stretching modes of the hydroperoxy and alcohol groups formed after the ether-linkage dissociation and the accompanying OH stretching modes of water molecules around these groups. We note that the peaks corresponding to the vibrations of the hydroperoxy group appear at 831, 1015, and 1060 cm\(^{-1}\). As shown in Figure 5, these peaks are hidden behind other peaks in the calculated IR spectra. Interestingly, these peaks are, however, visible in the experimental IR spectra of the decomposed Nafton membrane.\(^{16}\) It is also interesting to note that the high peaks assigned to the OH-bond stretching of H2O2 appear at 3553 and 3700 cm\(^{-1}\) for the predecomposed Nafton. The IR absorption of these peaks supports the H2O2-induced dissociation because the OH stretching of H2O2 determines the reactivity of this dissociation. The assignment of the vibrational spectral peaks, therefore, also supports the H2O2-induced ether-linkage dissociation.

The degradation fragment molecule can be explored in further detail on the basis of the vibrational spectra. Akiyama et al. also observed the IR spectrum of the degradation fragment species dried in vacuum. In the experimental IR spectrum, strong peaks appeared around 1700, 2500, and 3500 cm\(^{-1}\) after the degradation. Figure 6 illustrates the calculated vibrational spectra of the hydrated degradation fragment molecule, \((\text{H}_2\text{O})_\lambda \text{H}_3\text{O}_2\text{S}−\text{CF}_2−\text{CF}_2−\text{O}−\text{O}−\text{H}\) for various \( \lambda \) values. As shown in the figure, the peaks corresponding to the strong peaks of the experimental IR spectrum are assigned to the vibrational modes of the degradation fragment molecule for different hydration numbers. This result suggests that the degradation fragment molecule can exist simultaneously with different numbers of hydration water molecules. Because the experimental IR spectrum is given for the dried species in vacuum, this also indicates that hydration water molecules strongly bind to the sulfonic acid groups of the Nafton membrane. This result also supports the conclusion of our previous study that the proton conduction proceeds through the relay mechanism in Nafton under low-humidity conditions due to the very high hydration energy of the sulfonic acid groups.\(^{31}\) We, therefore, propose that the degradation fragment molecule is strongly hydrated, even under dry conditions.

Subsequent Decomposition Reactions of the Degradation Fragment Molecule. For comparative verification with the experimental results, it is meaningful to consider the subsequent decomposition reactions of the presumed main degradation fragment molecule, \((\text{H}_2\text{O})_\lambda \text{H}_3\text{O}_2\text{S}−\text{CF}_2−\text{CF}_2−\text{O}−\text{O}−\text{H}\). Several past studies have suggested that \(\text{H}_3\text{O}−\text{CF}_2−\text{O}−\text{CF}−\text{(CF}_2−\text{COOH, called "molecule A", is the main degradation product.}^{10,29,61}\) Molecule A is similar to the present degradation fragment molecule in that both of them are derived from the ether-linkage dissociation of the side chain of Nafton membrane. Actually, a similar molecule, \(\text{HO}_2\text{S}−\text{CF}_2−\text{CF}_2−\text{O}−\text{CF}−\text{(CF}_2−\text{CF}_2−\text{O}−\text{OH}, is considered to be formed by the present decomposition mechanism, although it is different from molecule A, including the end \(−\text{CF}_2−\text{O}−\text{OH} \) group instead of the \(-\text{COOH \) group. Although molecule A was assigned on the basis of \(^{19}\text{F} \) NMR and IR spectral analyses,\(^{16,61}\) this assignment prompts several questions: The \(^{19}\text{F} \) NMR spectrum was not observed after a PEMFC degradation but after a Fenton test, and the IR spectrum also supports the present degradation fragment molecule, as mentioned above. What we need to confirm the presumed main degradation fragment molecule is, however, not to rule out the existence of molecule A but to elucidate how experimentally found decomposition byproducts are formed from this molecule. It is, therefore, meaningful to explore the subsequent decomposition-reaction mechanisms of the presumed main degradation fragment molecule.

As a result, we found two probable monomolecular degradation fragment molecule, \(\lambda\text{HO}_2\text{S}−\text{CF}_2−\text{CF}_2−\text{O}−\text{OH}\)
\[
\begin{align*}
\text{(H}_2\text{O})_\lambda \text{HO}_2\text{S}−\text{CF}_2−\text{CF}_2−\text{O}−\text{OH} & \rightarrow \text{CF}_2\text{CFO}−\text{O}−\text{OH} + \text{SO}_2 + \text{H}^+(\text{H}_2\text{O})_\lambda
\end{align*}
\]

(3)

\[
\begin{align*}
\text{(H}_2\text{O})_\lambda \text{HO}_2\text{S}−\text{CF}_2−\text{CF}_2−\text{O}−\text{OH} & \rightarrow \text{(H}_2\text{O})_\lambda \text{HO}_2\text{S}−\text{CF}_2−\text{CF}_2−\text{CF}_2−\text{O}−\text{OH} + \text{FC−OH}
\end{align*}
\]

(4)

The potential energy curves of these reactions on the intrinsic reaction coordinates are drawn in Figure 7. We note that...
Figure 8. Decomposition-reaction potential energy curve of FC−O−OH to HF + CO₂, on the intrinsic reaction coordinate, which is calculated by LC-BLYP/cc-pVDZ method. The intrinsic reaction coordinates are normalized for each reaction step. The optimized structures of local minimum (MIN) and TS points are also shown.

despite both these reactions are exothermic as mentioned later, they are considered not to proceed without a catalyst, for example, Pt surface and metal ions, under fuel-cell operating conditions, due to the very high barrier heights.

As shown in Figure 7(a), reaction 1 exothermically produces sulfur dioxide (SO₂), which is experimentally found as a degradation product, for any hydration number. Although SO₂ is a gas at room temperature, it is hydrated to produce sulfuric acid (H₂SO₄), which is also experimentally found. The degradation fragment molecule of reaction 1, CF₃−CFO−O−OH, appears to be unstable and therefore seems to convert to a carboxylic acid. In many trial calculations, we, however, found that no monomolecular decomposition reaction takes place without artificial bond cleavage for this molecule. We, therefore, presume that this molecule is also included in the residual species of the degradation. The vibrational spectrum of this molecule provides intense peaks for 1000−1700 and 3023 cm⁻¹. By reference to the experimental IR spectrum of dried dissolved species, such peaks were found to appear in these wavenumber regions after the degradation. However, these intense peaks are hidden in the vibrational spectrum of the main degradation fragment molecule in Figure 6. This fragment molecule is expected to be found in the ¹⁹F NMR spectrum because it simply exhibits two peaks with 3:1 peak strengths. However, we consider that this reaction requires a catalyst to proceed due to the high barrier heights, which exceed 60 kcal/mol at least (λ = 1).

The potential energy curves of reaction 2 appear to indicate that it does not proceed due to the very high reaction barrier heights, 137.34, 139.52, 140.14, 140.83, 141.03, and 141.25 kcal/mol for λ = 0−5, respectively, and the endothermic nature, with high, positive reaction energies, 50.74, 52.06, 51.24, 51.27, 48.31, and 46.27 kcal/mol. Following the endothermic nature, we should note that FC−O−OH would be too unstable to be present as a residual species. Figure 8 plots the potential energy curve of the decomposition reaction of FC−O−OH. As shown in the figure, FC−O−OH transforms into the carboxylic acid FCOOH with a very large reaction energy (155.15 kcal/mol) and then it is decomposed to HF and CO₂, which are both experimentally found in the degradation species, with relatively low activation energies (30.68 kcal/mol at the maximum). Overall, therefore, reaction 2 is considered very exothermic, with a large reaction energy, which totals more than 100 kcal/mol. We should, however, be reminded that this reaction requires a catalyst to proceed due to the very high barrier heights. Let us then assume that a catalyst supports this reaction. The degradation fragment molecule of this reaction is (H₂O)₃HO₃S−CF₃, although this molecule has not yet been experimentally assigned, as far as we know. However, it may be included in the low-molecular-weight perfluorocarbon sulfonic acid in the degradation species because the terminal products of this reaction, HF and CO₂, are experimentally detected. The experimental IR spectrum of this molecule depend on the hydration number for the maximum peak wavenumbers: 616, 2768, 2038, and 2526 cm⁻¹ for λ = 0−3, respectively. As shown in Figure 6, peaks are also seen in the vibrational spectrum of the main degradation fragment molecule except for the peak at 2038 cm⁻¹ (λ = 2). Because the experimental IR spectrum of dried dissolved species exhibits no peak around 2038 cm⁻¹, this may suggest that the λ value for (H₂O)₃HO₃S−CF₃ is very small (λ = 0 or 1) under dry conditions.

In summary, we propose that CF₃−CFO−O−OH and (H₂O)₃HO₃S−CF₃ molecules are formed as stable byproducts in addition to the experimentally observed SO₂, HF, and CO₂ molecules in the thermal decomposition of the main degradation fragment molecule, (H₂O)₃HO₃S−CF₃−CF₂−O−O−H. We expect that these degradation fragment molecules will be experimentally found, for example, in the ¹⁹F NMR spectrum analysis.

### CONCLUSIONS

In this study, we have theoretically investigated the H₂O₂-induced degradation mechanism of doubly hydrated Nafion membrane in the PEMFC and its subsequent decomposition reactions focusing on the ether-linkage dissociation of the side chain and thermodynamic reactions. As a result, we have revealed the ether-linkage decomposition mechanism by the H₂O₂ molecule, which is hydrated in the protonated water cluster around the sulfonic acid group. We have also found the decomposition reactions of the degradation fragment molecule derived from the ether-linkage dissociation and have confirmed that the expected products are consistent with conventional experimental results.

On the basis of reasonable assumptions, we have calculated the potential energy curves of the ether-linkage dissociation of the doubly hydrated Nafion membrane model with H₂O₂
molecule in the hydration-protonated water cluster for various hydration numbers. Consequently, we have found the decomposition-reaction pathways providing relatively low reaction barriers of 32–40 kcal/mol, which are analogous to the C–C double-bond cleavage mechanism by ozone.

We have compared the vibrational spectra of the resulting decomposed Naion membrane and degradation fragment molecule, (H₂O)₅H₂SO₄·CF₃−CF₂−O−O−H. As a result, we have confirmed that the vibrational spectra are consistent with the experimental IR spectra of the decomposed hydrated Naion membrane and degradation fragment species, despite the fragment molecule having an unfamiliar end group, −CF₂−O−OH.

We have also explored the subsequent reactions of the presumed degradation fragment molecule for various hydration numbers. In consequence, we have obtained two possible decomposition-reaction processes giving CF₃−CFO−O−OH and (H₂O)₅H₂SO₄·CF₃ molecules as degradation byproducts in addition to the experimentally observed SO₂, HF, and CO₂. However, we found that these subsequent reactions would require a catalyst, such as Pt surface or metal ions, to proceed, due to the high barrier heights. We have also found that these byproducts are quite stable and would not be expected to undergo subsequent monomolecular reactions and therefore suggested that these byproducts should be contained in the degradation species.

In conclusion, we have proposed a H₂O₂-induced decomposition mechanism of Naion membrane, which is likely to proceed simultaneously with conventional OH-radical-induced mechanisms. The schematic diagram of the decomposition mechanism is illustrated in Figure 9. We expect that elucidating this decomposition mechanism will shed light on ways to develop strategies to combat the degradation of proton-exchange membranes.

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**Notes**

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