

Durability of perfluorinated ionomer membrane against hydrogen peroxide

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Abstract

The durability of perfluorinated ionomer membrane, Nafion[®] 117, with various counter ions against hydrogen peroxide was investigated as a degradation factor of polymer electrolyte fuel cells (PEFC). After protonated Nafion membrane was tested in 30% H₂O₂ solution at 80 °C, small amounts of fluoride ion and sulfate ion, which are derived from the C–F bonds and the sulfonic acid groups, respectively, of the membrane, were detected in the solution. This fact indicated a potential vulnerability of the electrolyte membrane to H₂O₂ formed in the cell. The durability of Nafion with alkali and alkaline earth metal ions as counter ions were similar to that of protonated Nafion, and hence these cations do not have any specific effects on membrane degradation. In contrast, the presence of ferrous and cupric ions as counter ions significantly enhanced the decomposition rate of Nafion. This is due to the formation of strongly nucleophilic radicals such as hydroxy and hydroperoxy radicals upon decomposition of H₂O₂ at these catalyst ions. The results of FT-IR and ¹⁹F NMR measurements of deteriorated Fe²⁺-Nafion membrane revealed that both the main and side chains are decomposed at similar rates by radical attack, most probably because the decomposition proceeds through radical de-polymerization (so-called un-zipping mechanism).

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been developed intensively for use as the power sources of electric vehicles and for use in household co-generation systems [1–5]. However, many problems remain to be solved before commercialization of PEFCs. For example, a long life over 40,000 h (=10 years in the daily start and stop mode, or 5 years in continuous operation) is required for PEFC stacks to be used in the household co-generation systems. Unfortunately, sufficient durability to meet this demand has not been established so far.

Several reports have suggested that the performance of PEFC cell stacks degrades gradually owing to the deterioration of cell components (membrane electrode assemblies, MEAs) [6–14]. One of the serious problems is the deterioration of the perfluorinated ionomer membrane used as the electrolyte [10–13].

Especially, the degradation of the electrolyte membrane is accelerated under operation at low humidification and under open circuit conditions [12,13]. The decomposition of the electrolyte membrane decreases the ionic conductivity and also the mechanical stability of MEAs, resulting in a significant drop of PEFC performance.

In fuel cell reactions, it is believed that water is the only product, which is a great advantage of PEFCs. However, it is also known that a small amount of hydrogen peroxide is formed as a by-product [14], which is a potential factor for membrane degradation. In spite of its importance, a surprisingly limited numbers of reports on the chemical stability of perfluorinated ionomer membranes have been published so far. LaConti et al. [15–17] extensively investigated the stability of various kinds of electrolyte membranes including perfluorinated ones in 1970s, but unfortunately most of their valuable data have been unpublished and are not available today. In the present study, we re-investigated the stability of a perfluorinated ion-exchange

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membrane, Nafion[®], against H₂O₂ as a degradation factor of PEFCs. Nafion membranes with various counter ions were used for durability tests to understand the effects of impurity cations in the cell. Deteriorated samples were analyzed by FT-IR and solid-state ¹⁹F NMR to discuss the mechanism for membrane degradation.

2. Experimental

2.1. Pretreatment of Nafion membranes

Commercially available Nafion[®] 117 membranes (E. I. DuPont de Nemours and Co.; thickness: 175 μm; ion exchange capacity: 0.91 meq g⁻¹; purchased in 2002) were used for durability tests. The formal chemical structure of Nafion is shown in Fig. 1. The membrane was cut into 1.0 cm × 1.0 cm pieces (ca. 35 mg) with a ceramics knife, and they were boiled successively in 3% hydrogen peroxide solution, distilled water, 1.0 mol dm⁻³ sulfuric acid solution, and distilled water for 1 h each. As a consequence of this pretreatment, the protonated membrane, which was originally pale yellow, became transparent and swelled well with water. These samples were stored in highly pure water obtained from a water purification system (Sartorius, Arium 611UV), and hereafter are denoted as H⁺-Nafion.

Nafion membrane samples with various metal ions as counter ions (Li⁺, Na⁺, K⁺, Ca²⁺, Cr³⁺, Fe²⁺, Co²⁺, and Cu²⁺) were obtained by the ion-exchange method. The H⁺-Nafion membrane was soaked in 0.1 mol dm⁻³ solution of LiCl, NaCl, KCl, CaCl₂, Cr(NO₃)₃·9H₂O, FeCl₂·6H₂O, Co(NO₃)₂·6H₂O, or CuCl₂·2H₂O for more than 1 day for equilibration, which are hereafter denoted as Mⁿ⁺-Nafion (M: metal cation). All the chemicals used for ion exchange were of reagent grade (Wako Pure Chemical Industries). Each sample was rinsed ultrasonically with highly pure water for at least 1 h before durability tests.

2.2. Durability tests of Nafion membranes in hydrogen peroxide solution

Hydrogen peroxide solution (30 wt.% without stabilizers, Wako Pure Chemical) was used as purchased for durability tests unless otherwise noted. The Nafion sample was immersed in 10 ml of the hydrogen peroxide solution and the durability test was carried out at 80 °C for 12 h. After immersed for 12 h, the sample was removed from the solution, and the solution was analyzed with an ion chromatograph (Dionex, DX-120) equipped with an anion separation column (Dionex, AS-14) and an eluent suppressor column. The column temperature

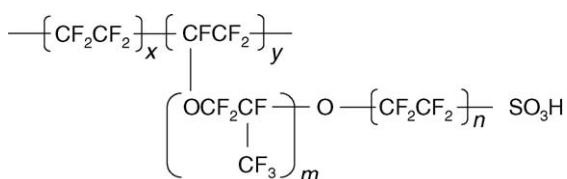


Fig. 1. Chemical structure of Nafion[®].

was set at 30 °C. A mixture of 1.0 × 10⁻³ mol dm⁻³ NaHCO₃ and 3.5 × 10⁻³ mol dm⁻³ Na₂CO₃ was flowed as an eluent at 1.2 ml min⁻¹. Prior to analysis, the analyte solution was diluted tenfold with highly pure water, and Pt mesh was immersed in the solution to decompose residual hydrogen peroxide. Hydrogen peroxide must be completely decomposed to obtain accurate and reproducible results by ion chromatography. Furthermore, highly pure water was injected into the chromatograph as a blank test before each analysis. Anions in the analyte solution were identified and their concentrations were determined using a commercially available standard solution (Kanto Kagaku, F⁻: 5 ppm, Cl⁻: 10 ppm, NO₂⁻: 15 ppm, Br⁻: 10 ppm, NO₃⁻: 30 ppm, PO₄³⁻: 30 ppm, SO₄²⁻: 40 ppm). The 12-h durability test was repeated using fresh hydrogen peroxide solution.

2.3. Analysis of deteriorated membrane

Fe²⁺-Nafion membranes after durability tests were analyzed by FT-IR and solid-state ¹⁹F NMR. FT-IR measurements were performed with an IR-Prestige-21 (Shimadzu Corp.) in the range of 750–2000 cm⁻¹. The spectra were measured using an ATR device (SensIR, DuraSamplIR II) equipped with 3 mm diamond window and ZnSe support element. Solid-state ¹⁹F NMR measurements were performed with a Chemagnetics CMX-300 spectrometer (281.3 MHz) at Toray Research Center, Japan. Membrane samples were cut in small pieces and filled into sample rotors with water or alcohol in order to improve spectral resolution.

3. Results and discussion

3.1. Ion chromatography analysis

Ion chromatograms of the standard solution and the test solution after a typical durability test are shown in Fig. 2. On the chromatogram of the standard solution (Fig. 2a), six peaks assigned to F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻ are clearly separated. A negative peak at around 2 min is assigned to water in the injected solution.

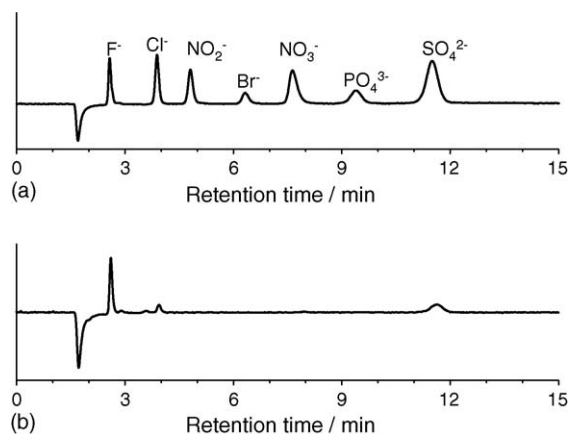


Fig. 2. Ion-chromatograms of (a) a standard sample solution and (b) the solution after a durability of Fe²⁺-Nafion in 30% H₂O₂ at 80 °C for 12 h.

Fig. 2b shows the chromatogram for the solution after a durability test of Fe²⁺-Nafion at 80 °C for 12 h, in which two large positive peaks appeared. The peak at around 2.5 min is assigned to F⁻ and the other peak at around 12 min to SO₄²⁻. The former is derived from the C–F bonds of the side chain and/or the main-chain of Nafion, while the latter is from the sulfonic acid groups of Nafion. The concentrations of the anions were determined from the peak areas, and the decomposition ratios of the C–F bonds and the sulfonic acid groups of Nafion were calculated. Here we used the values $x = 6.5$, $y = 1$, $m = 1.1$, and $n = 2.3$, which was determined by ¹⁹F NMR measurements described in a later section, in the chemical structure of Nafion shown in Fig. 1. In addition to these two peaks, a few minor peaks were observed in the range of 2.8–4 min. These peaks are not assigned to Cl⁻ because they appeared when the solution and Nafion was completely free from Cl⁻. It is known that monovalent carboxylate ions such as formate, acetate, and propionate ion appear between the F⁻ peak and Cl⁻ peak [18]. On the basis of this fact, the minor peaks in the range of 2.8–4 min are probably assigned to perfluorinated short-chain carboxylate fragments that are derived from the side chain and the main chain of Nafion upon decomposition.

3.2. Durability of H⁺-Nafion membranes

When H⁺-Nafion was immersed in 30 wt.% H₂O₂ solution at 80 °C, remarkable changes, such as evolution of bubbles, were not observed. Besides, the transparency and the geometric area of the membrane did not change after 12 h. However, small amounts of F⁻ and SO₄²⁻ were detected in the solution by ion chromatography. Decomposition ratios of the C–F bonds and the sulfonic acid groups of H⁺-Nafion are plotted against immersion time in Fig. 3. It is believed that Nafion is chemically stable, but the results in Fig. 3 show vulnerability of Nafion to hydrogen peroxide. The decomposition ratio of the C–F bonds was very low and was only 1% even after 5.5 days. In contrast, the decomposition ratio of the sulfonic acid groups was higher than that of the C–F bond, and reached 7% after 5.5 days. These facts revealed that the ion-exchange sites are more vulnerable to H₂O₂ than the C–F bonds. In these durability tests, no catalyst for decomposition of H₂O₂ or radical formation was added [19–21], and hence it is considered that H⁺-Nafion is

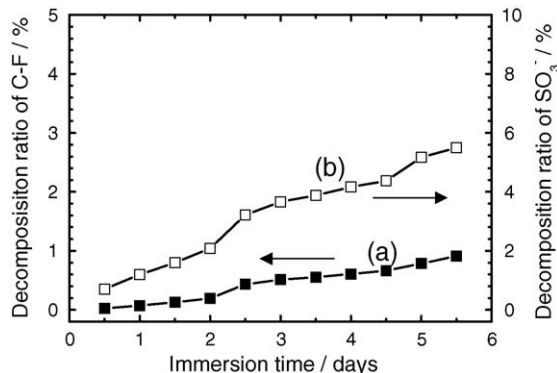


Fig. 3. Decomposition ratios of (a) the C–F bonds and (b) the sulfonic acid groups of H⁺-Nafion in 30% H₂O₂ at 80 °C.

decomposed by the strong oxidation ability of H₂O₂:



It should be noted that the conditions of durability tests in the present study are extremely hazardous, and conventional hydrocarbon-based ion-exchange membranes would be decomposed at a much faster rate. The data of H⁺-Nafion in Fig. 3 therefore prove a splendid chemical stability of Nafion.

3.3. Effect of alkali and alkaline earth metal ions as counter ions

The results of durability tests for Nafion membranes with alkali and alkaline earth metal ions as counter ions are shown in Fig. 4. The decomposition ratios of Nafion membranes with these metal ions were similar to those of H⁺-Nafion. These results indicate that alkali and alkaline ions do not have special catalytic activity for H₂O₂ decomposition and deterioration of Nafion, and the membranes are oxidatively decomposed by H₂O₂ as was the case for H⁺-Nafion.

Hydrogen peroxide decomposed to oxygen and water according to Eq. (2), and its reaction rate greatly depends on the catalytic activity of metal ions.

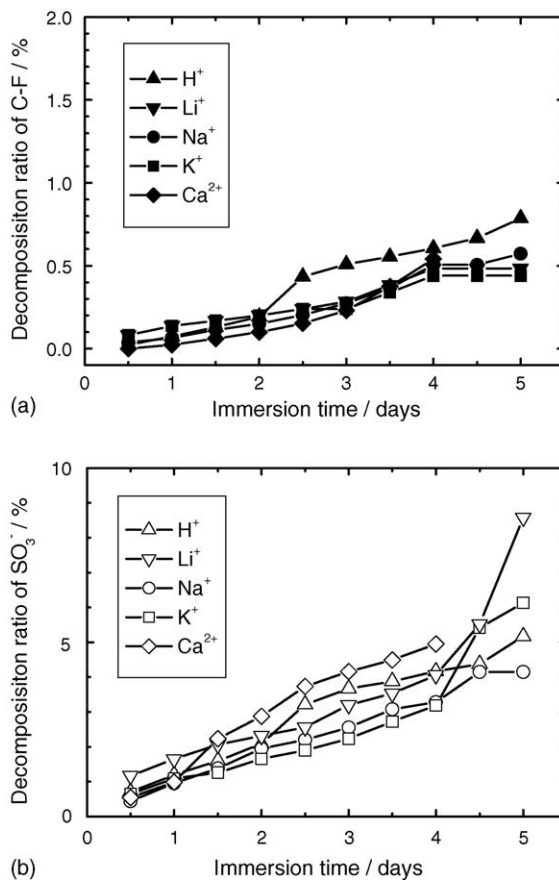
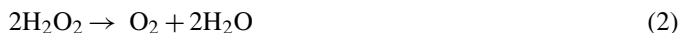


Fig. 4. Decomposition ratios of (a) the C–F bonds and (b) the sulfonic acid groups of Nafion with various alkali and alkaline earth metal as counter ions in 30% H₂O₂ at 80 °C.

The effects of metals and metal ions on the stability of hydrogen peroxide were thoroughly investigated by Schumb et al. [22] and it was reported that alkali metal cation has no catalytic effect on the decomposition of H_2O_2 . In contrast, it has not completely understood whether alkaline earth metal cations have a catalytic effect for the decomposition of H_2O_2 or not [22]. As shown in Fig. 4, the decomposition ratios of Ca^{2+} -Nafion up to 4 days are almost the same as those of the other membranes. This fact shows that Ca^{2+} has no catalytic effect on the decomposition of Nafion membrane. Alkali and alkaline earth metal ions, especially Ca^{2+} and Na^+ , are easily entrapped and accumulated in the MEAs during operation, and may deteriorate the performance [23]. The results of Fig. 4, however, suggest that the contamination of these ions does not affect on the stability of the electrolyte membrane against hydrogen peroxide, though it may deteriorate the other properties of the MEAs such as ionic conductivity and the electrode reaction rate, in particular, of the cathode oxygen reduction.

3.4. Effect of transition metal ions as counter ions

The results of durability tests of Nafion with various transition metal ions in 30% H_2O_2 at 80°C are shown in Fig. 5. The decomposition ratios of the C–F bonds and the sulfonic acid groups for Cr^{3+} - and Co^{2+} -Nafion are nearly equal to those

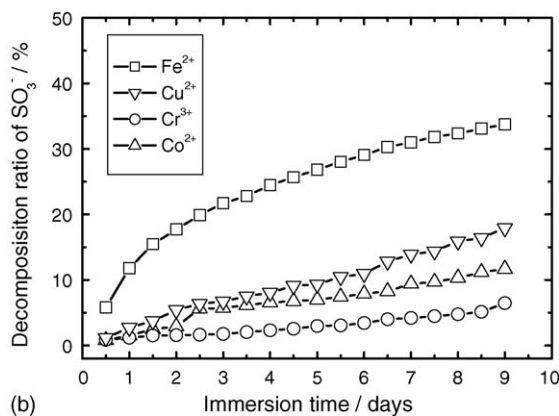
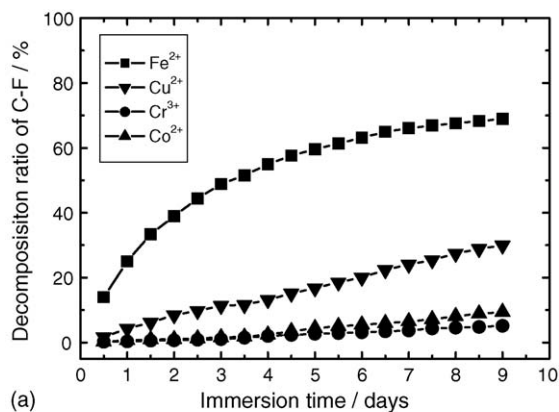


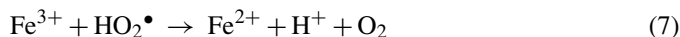
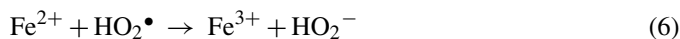
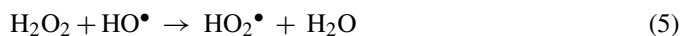
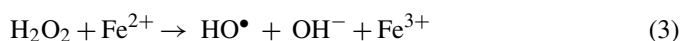
Fig. 5. Decomposition ratios of (a) the C–F bonds and (b) the sulfonic acid groups of Nafion with various transition metal ions as counter ions in 30% H_2O_2 at 80°C .

for H^+ -Nafion, and hence these ions do not have any specific catalytic activity, as alkali and alkaline earth metal ions do not.

In contrast, the presence of Fe^{2+} - and Cu^{2+} ions significantly enhanced the rate of membrane degradation. Especially, the effect of Fe^{2+} ion was significant, and the decomposition ratios of the C–F bond and the sulfonic acid group reached 68 and 33%, respectively, after 9 days. Moreover, the decomposition ratio of the C–F bond was larger than that of sulfonic acid group for Fe^{2+} - and Cu^{2+} -Nafion, which suggests that the decomposition mechanism for Fe^{2+} - and Cu^{2+} -Nafion is totally different from that for the other types of Nafion.

The surface area and the thickness of Fe^{2+} -Nafion were considerably reduced after durability tests, though those of H^+ -Nafion were almost unchanged as mentioned earlier. Fig. 6 shows the variation of the dry weight of Fe^{2+} -Nafion. The weight decreased steeply up to 1.5 days and then they gradually decreased. The weight loss reached 40% after 5 days. Furthermore, the mechanical strength of the membrane was lowered after the durability tests for 5 days.

It is known that Fe^{2+} ion is a good catalyst for decomposition of H_2O_2 (Eq. (2)), which is accompanied by active oxygen radical formation [19,24]. The detailed reaction mechanism for radical formation was reported by Haber and Weiss (called the Haber–Weiss mechanism) as [24]:



Hydroxy and hydroperoxy radicals generated in Eqs. (3) and (5), respectively, have strong nucleophilicity, and therefore H_2O_2 solution containing a small amount of Fe^{2+} ion (usually of the order of ppm) is often called Fenton's reagent and has been used for durability tests of various kinds of polymer materials [20].

When Fe^{2+} - and Cu^{2+} -Nafion membranes were immersed in 30 wt.% H_2O_2 at 80°C , oxygen bubbles evolved intensively.

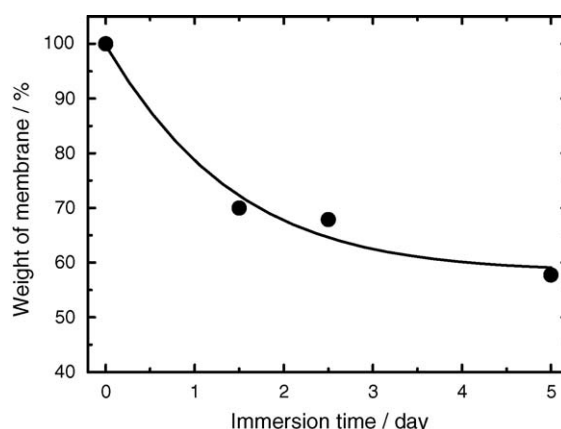


Fig. 6. Variation of the dry weight of Fe^{2+} -Nafion upon durability tests in 30% H_2O_2 at 80°C .

Fe^{2+} -Nafion was transparent pale green before the test, which is the color of Fe^{2+} ion, but the transparency was lost and the color changed to white brown after a durability test at 80°C for 12 h. The change in color of the Fe^{2+} -Nafion membrane confirms the change in the oxidation state of the Fe^{2+} ion in the decomposition of H_2O_2 (Eq. (2)), which is accompanied by the formation of large amounts of hydroxy and hydroperoxy radicals as by-products. These radicals attack vulnerable part of Nafion, which accelerates its decomposition. For Fe^{2+} -Nafion, the decomposition ratio of the C–F bonds was higher than that of the sulfonic acid groups. This fact suggests that the radicals attacked not only the side chain, but also the main chain of Nafion, the details of which will be discussed later.

In Fig. 5, Cu^{2+} -Nafion was decomposed remarkably in 30% H_2O_2 as well; that is, Cu^{2+} ion also has a specific catalytic effect on membrane degradation. The color of the membrane changed from clear light blue to white brown after the test. Although the detailed reaction mechanism is not clear, the decomposition mechanism for Cu^{2+} -Nafion is similar to that for Fe^{2+} -Nafion, through radical formation described in Eqs. (3)–(7). Because the durability of Fe^{2+} -Nafion was lower than Cu^{2+} -Nafion, the catalytic activity of cupric ion to generate the active oxygen species was lower than that of ferrous ion.

The loss of sulfonic acid groups of Nafion reduces the proton conductivity, and the decomposition of the C–F bonds leads to membrane thinning and the formation of pinholes [15,25]. Consequently, the decomposition of the membrane degrades significantly the performance of the cell. Nafion is not only used as an electrolyte membrane, but also added in the catalyst layer to enhance ionic conductivity. The decomposition of impregnated Nafion inside the catalyst layer leads to a reduction in the effective reaction area and increases the overpotential.

The results obtained in this study revealed that commercially available Nafion is not completely stable against H_2O_2 , especially in the presence of Fe^{2+} and Cu^{2+} ion, and hence H_2O_2 formation is a potential degradation factor of PEFCs. Transition metal ions such as Fe^{2+} and Cu^{2+} are typical contaminants from piping tubes and humidification bubblers of PEFC systems as well as from cell components [10,23]. These ions accumulate in the MEA as counter ions of the electrolyte membrane during operation. Therefore, the contamination of these ions should be suppressed as much as possible to achieve a long life. It is also important to understand the mechanism for H_2O_2 formation in the cell and to suppress the formation of H_2O_2 on the catalyst.

3.5. Analysis of deteriorated Nafion membranes

Fig. 7 shows FT-IR spectra of fresh H^+ -Nafion (a) and deteriorated Fe^{2+} -Nafion (b and c) after durability tests in 30% H_2O_2 at 80°C for 4 and 8 days. A weak peak at around 1640 cm^{-1} in each spectrum is assigned to water in the membranes [26]. The strongest peak at 1148 cm^{-1} is assigned to the antisymmetric vibration of the C–F bonds of Nafion [27]. Each spectrum is normalized using the absorbance of this peak. Another strong peak at 1204 cm^{-1} is also assigned to the antisymmetric vibration of the C–F bonds [27]. The doublet peaks at 978 and 983 cm^{-1} , and the peak at 1058 cm^{-1} are characteristic peaks of the side

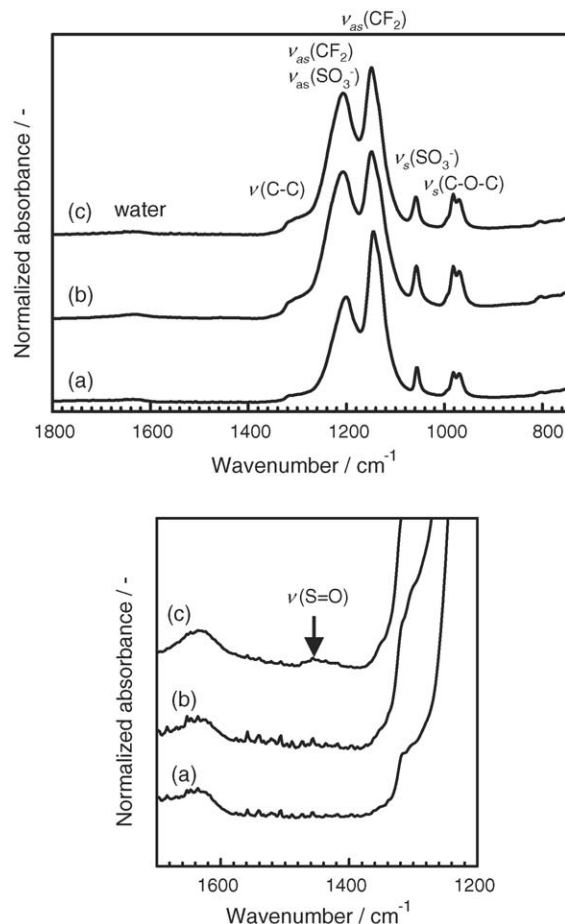


Fig. 7. FT-IR spectra of (a) fresh H^+ -Nafion and (b and c) Fe^{2+} -Nafion after durability tests in 30% H_2O_2 at 80°C for (b) 4 and (c) 8 days. Lower figure shows magnified spectra in the range of 1200 – 1700 cm^{-1} .

chain of Nafion, and are assigned to the symmetric vibrations of the C–O–C bonds and SO_3^- , respectively [27,28]. The shoulder peak at around 1300 cm^{-1} is from the C–C bonds [27]. The normalized absorbances of these peaks did not change appreciably after durability tests, which clearly shows that both the main chain and side chain of Fe^{2+} -Nafion were decomposed by the attack of the radicals.

A close look at magnified spectra in Fig. 7 revealed that a small peak appeared at 1460 cm^{-1} after the durability test for 8 days. Iwato et al. [29] reported that a peak assigned to the S=O stretching vibration of SO_2F or $\text{SO}_2\text{O-SO}_2$ appeared at 1460 cm^{-1} when Nafion membrane was heated at temperatures above 240°C for 8 h in air. The appearance of the 1460 cm^{-1} peak for deteriorated Nafion indicates that a small amount of the sulfonic acid group was transformed to SO_2F or $\text{SO}_2\text{O-SO}_2$ by the attack of the HO^\bullet and HOO^\bullet radicals. However, the intensity of this peak was very small, and therefore most of the sulfonic acid group decomposed to SO_4^{2-} that is soluble in water.

Fig. 8 shows ^{19}F NMR spectra of fresh H^+ -Nafion (a) and deteriorated Fe^{2+} -Nafion (b and c) after durability tests in 30% H_2O_2 at 80°C for 0.5, 1.5, and 2.5 days. Each sample showed five peaks at ca. -78 [CF_3 (e in the chemical structure of Nafion), OCF_2 (d and g)], -117 [CF_2 (b and g)], -120 [CF_2 (a and b)],

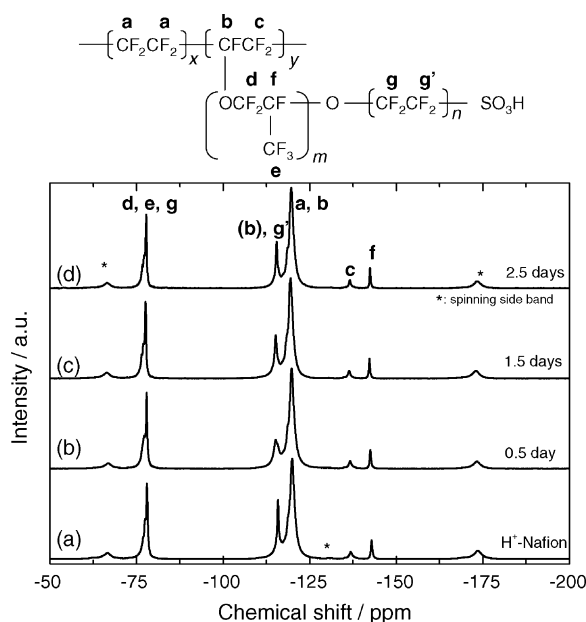


Fig. 8. ^{19}F NMR spectra of (a) fresh H^+ -Nafion and (b–d) Fe^{2+} -Nafion after durability test in 30% H_2O_2 at 80°C for (b) 0.5, (c) 1.5, and (d) 2.5 days. Symbols a–g (and g') show the positions of corresponding fluorine atoms in the chemical structure of Nafion.

–137 [OCF (c)], and –143 ppm [OCF (e)] [30–32], all of which originate from the perfluorinated ionomer. Again at a glance, the deteriorated membranes did not show appreciable changes in ^{19}F NMR spectra. The values x , y , m , and n in the chemical structure of Nafion (Fig. 1) were calculated using the assignments (a–g) and the peak areas in Fig. 8, and are summarized in Table 1, where the values of x , m , and n were normalized by y , that is $y = 1$. Fresh H^+ -Nafion has a composition of $x = 6.5$, $y = 1$, $m = 1.1$, and $n = 2.3$. The equivalent weight (EW) of dry polymer is calculated to be 1126 using these values, which is very close to the nominal EW (1100) of Nafion[®] 117.

The values of m and n did not change noticeably, which indicated that partially decomposed fragments of the side chain were not present in deteriorated membranes. In contrast, the value of x increased with increasing test time; that is, the fraction of the main chain slightly increased after durability tests. This fact indicates that the side chain is decomposed more easily than the main chain. It should be noted that the weight loss after the durability test for 2.5 days was larger than 30% as shown in Fig. 6. However, the observed increase in x was not so large and such a large weight loss (>30%) cannot be explained solely by the decomposition of the side chains because the mass of the side chains is only 35% of the molecular weight of Nafion[®] 117.

Table 1
Compositional changes of Fe^{2+} -Nafion after durability tests in 30% H_2O_2 at 80°C for different times

Counter ion and test times	x	y	m	n
H^+ -Nafion, fresh	6.5	1.0	1.1	2.3
Fe^{2+} -Nafion, 0.5 day	6.4	1.0	1.0	2.3
Fe^{2+} -Nafion, 1.5 days	7.3	1.0	1.1	2.1
Fe^{2+} -Nafion, 2.5 days	7.1	1.0	1.1	2.3

Probably the side chain and main chain were decomposed at similar rates. It seems that once decomposition begins at weak part of Nafion by radical attack, the whole molecule decomposes and disappears. This is not unlikely if we assume that the decomposition proceeds through radical de-polymerization (so-called un-zipping mechanism) as was suggested for thermal decomposition of Nafion [33]. For the improvement of the durability of perfluorinated ionomer membranes, it is therefore important to understand the decomposition mechanism of Nafion by the radical attack in more detail and to identify the weak part to radical attack. Curtin et al. [13] reported that radical attack to residual H-containing terminal bonds of the main chain of Nafion is the principal degradation mechanism.

4. Conclusions

To clarify the degradation mechanism of perfluorinated ionomer membranes during the operation of PEFCs, durability tests of Nafion[®] 117 membrane were carried out in 30% H_2O_2 solution at 80°C . The results of the durability tests indicated that Nafion is not completely stable against H_2O_2 . The effects of impurity cations were investigated, and it was found that the presence of Fe^{2+} and Cu^{2+} greatly enhances the decomposition rate of Nafion. This is due to the formation of strongly nucleophilic radicals such as hydroxy and hydroperoxy radicals upon decomposition of H_2O_2 at these catalyst ions.

The results of FT-IR and ^{19}F NMR measurements of deteriorated Fe^{2+} -Nafion membrane revealed that both the main and side chains are decomposed at similar rates by radical attack, most probably because the decomposition proceeds through radical de-polymerization (so-called un-zipping mechanism).

The results obtained in the present study indicated that hydrogen peroxide formation is a potential factor for the degradation of the electrolyte membrane. For the improvement of the stability of the electrolyte membrane, it is very essential to understand its decomposition mechanism in more detail. It is also important to understand the mechanism for H_2O_2 formation in the PEFC cell.

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