



Study on degradation process of polymer electrolyte by solution analysis

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ABSTRACT

Degradation process of Nafion which is one of the polymer electrolyte generally used for polymer electrolyte membrane fuel cell was investigated by solution analysis and structural analysis of eluted species. Nafion degraded by gamma-ray irradiation and heat treatment was immersed in distilled water and the solutions were analyzed using ion chromatograph, total organic carbon (TOC) analyzer, and inductively coupled plasma atomic emission spectrometer (ICP-AES). The solutions after the Fenton reaction were also analyzed with the same methods. Proton, sulfide ion, fluorine ion and organic carbon were eliminated into the solution, and their ratio was changed depending on the degradation method. To determine the eliminated species to the solution, structural analysis of concentrated dissolved species was performed using FT-IR. As the results, the initial process of degradation was detected sensitively in solution analysis compared with membrane analysis, and difference of the degradation process under different conditions was clearly observed. It was also found that new functional group COOH was formed in the eliminated species. These results showed that solution analysis are very simple yet powerful methods to elucidate the degradation process, which can also be applied to actual fuel cell operation to track minute changes in the polymer electrolyte.

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1. Introduction

High proton conductivity, chemical and physical stability as well as low cost are required for polymer electrolyte membrane used for fuel cell. Perfluorosulfonic acid membrane such as Nafion meets many of these requirements. The membrane consists of PTFE backbone and side chains having ether linkages terminating with sulfonic acid groups. Even though it has high chemical stability due to the high C–F bond energy, degradation takes place under high temperature (>363 K) and low humidity, and this triggers physical damage to the membrane and deterioration in power generation efficiency. In general, degradation of polymer electrolyte is mainly divided into two types: mechanical degradation including repetitive swelling and shrinkage by change in humidity, and chemical degradation including degradation by radical reaction. However, it is considered that chemical degradation has larger impact on total degradation process [1]. The main chemical factors responsible for chemical degradation are hydroxyl and peroxy radicals generated from hydrogen peroxide. Hydrogen peroxide was formed by

reaction between hydrogen and oxygen on the platinum catalyst caused by gas crossover. The hydroxyl radical attacks a polymer, which leads to decomposition of polymer [2–4]. The degradation of polymer electrolyte causes further gas crossover, which accelerates degradation process and may finally lead to pinhole formation in the membrane. It has also been thought that impurities in the membrane brought from Pt catalyst or electrodes are the main factor of radical formation [5–7]. To prevent the degradation of polymer electrolyte membrane, it is required to elucidate the degradation mechanism caused by radicals.

Degradation mechanism has been studied mainly by structural analysis of the membrane itself using X-ray scattering (SAXS), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and thermal analysis [1,8–12], however, detection of the initial stage of the degradation process caused by local scission or crosslinking adjacent to electrodes or catalyst where radical species tends to be generated is difficult to measure by these methods. Decomposition of polymer electrolyte causes scission or crosslinking of polymer chain. In case scission takes place, it is expected that the components of membrane are released out of a system with water generated at cathode. If the factors responsible for degradation can be identified in the initial stages by analyzing eluted chemical components in the water, the degree of degradation can thus be estimated. Solution analysis is one of the convenient methods to track the initial stage of degradation process or local structure change during the

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fuel cell operation which was difficult with the existing methods. In addition, by combining the solution and the membrane analysis, it will be also possible to estimate the respective degree of scission and crosslinking.

In this study, degradation process of Nafion was investigated by analysis of dissolved species eluted from polymer electrolyte. The degradation of Nafion was accelerated by three different methods; heat treatment, gamma-ray irradiation and the Fenton reaction. To identify the scission site and the chemical structure of dissolved species, the electrolyte was soaked in ultrapure water, and solution analysis was performed by ion chromatography, total organic carbon (TOC) analyzer, and inductively coupled plasma atomic emission spectrometry (ICP-AES). In addition, we tried to identify the chemical structure of the fragment generated as a result of scission of the polymer chain by evaporating the solution to dryness and analyzing the residue using FT-IR.

2. Experimental

2.1. Sample preparation

Nafion NR-50 (Aldrich) was used as a sample for the convenience of handling pellet samples. The samples were pretreated by successive reflux in 3% H₂O₂ solution, ultrapure water, 1 M sulfuric acid solution and ultrapure water for one hour each. The pretreated Nafion pellets were irradiated by gamma-rays using Co-60 facility of the Institute of Scientific and Industrial Research, Osaka University.

As the radical species formed by gamma-ray depends on the ambient conditions such as in water and in different kinds of gases, several irradiation conditions were adopted. To evaluate the influence of water included intrinsically in the samples, the samples dried in vacuum for 24 h were also prepared in addition to non-dried samples prior to irradiation. The irradiation was carried out using NR-50 Nafion resin in ultrapure water (2 g/30 ml), and in air, nitrogen or oxygen atmosphere for 3 h. The absorbed doses were varied from 0.05 to 1000 kGy, where dose rate ranged from 1.7 to 333 kGy h⁻¹. The absorbed dose was measured by Fricke dosimetry.

Heat treatment was done at the temperature within the range from 313 to 473 K for 12 h in an air draft oven, and the samples were cooled at room temperature after heat treatment.

As chemical degradation method, the Fenton reaction was carried out according to the following procedure. Nafion pellets were soaked in 0.1 mol dm⁻³ solution of FeCl₂·6H₂O (the solution pH was adjusted to 3 by HCl) for more than 1 day for equilibration, and then the pellets were rinsed ultrasonically with ultrapure water for at least 1 h. Nafion sample was immersed in 10 ml of the hydrogen peroxide solution (30 wt.% without stabilizers, Wako Pure Chemical Industries, Japan) and the test was carried out at 353 K for 24–144 h. Prior to analysis, the analyte solution was diluted ten-fold with ultrapure water, and Pt mesh (20 mm × 20 mm 100 mesh) was immersed in the solution to decompose residual hydrogen peroxide [13]. Hydrogen peroxide must be completely decomposed to obtain accurate and reproducible results by ion chromatography, and the presence of residual hydrogen peroxide was checked by redox titration using 0.02 M potassium permanganate (Kishida Reagent Chemicals, Japan).

Gamma-ray irradiation and heat treatment were also carried out for PTFE film (1 mm thickness, Nippon Valqua Industries Ltd., Japan) as reference.

2.2. Measurement of water content

Water content of Nafion was measured by TG-DTA. The samples were exposed to air atmosphere at room temperature over 24 h, heated to 473 K at a speed of 5 K min⁻¹, kept at 473 K for 30 min, and

then cooled down. Water content was estimated from the weight loss after heating.

2.3. Chemical analysis of eluted species

About 1 g of Nafion from each irradiated samples was soaked in 30 mL of ultrapure water. pH was monitored every day, and after reaching stable pH (4 days), the pellets were removed. Proton concentration in the solution was calculated from change in pH. Only the pellets irradiated in water were removed immediately after irradiation for chemical analysis. The eluted chemical components were analyzed by the following methods; sulfate ion and fluorine ion by ion chromatograph (DX-120, Dionex) equipped with an anion separation column (IC-PAC A25G), Organic Carbon by total organic carbon (TOC) analyzer (TOC-V CSH, SHIMADZU) and sulfur by inductively coupled plasma atomic emission spectrometry (ICP-AES) (ICPS-7500, Shimadzu). ICP and TOC were measured three times and ion chromatograph was measured twice for a sample, and average value and standard deviation was calculated.

2.4. FT-IR measurement

The solutions obtained in the process shown in Section 2.3 were evaporated to dryness in vacuum at 333 K for 12 h. The residue was measured with FT-IR (FT-IR 470 Plus, JASCO Corporation) in the KBr pellet method. The Fenton reacted solution was used after removing hydrogen peroxide by Pt mesh to prevent further fragmentation. On the other hand, Nafion-117 (10 mm × 30 mm, 3 pieces) was degraded by the method referred in Section 2.1, taken out from the solution, dried at room temperature and FT-IR was measured with the ATR (Attenuated total reflection) method.

3. Results and discussion

3.1. Eluted species by gamma-ray irradiation

Nafion was degraded by gamma-ray irradiation, which is able to generate radicals quantitatively and uniformly proportional to absorbed dose. The irradiation was performed in air, water, oxygen and in nitrogen after vacuum drying, because it is expected that kinds of generated radicals or contribution of direct/indirect effect strongly depend on water content and atmosphere. It was shown by thermogravimetry that the water content of Nafion irradiated in air and oxygen atmosphere was ca. 8 wt.%, and that irradiated in water was ca. 21 wt.%. Most of water was considered to be removed (less than 1%) by vacuum drying.

The results of solution analysis are shown in Fig. 1(a) and (b), where the samples were irradiated in oxygen and nitrogen. The standard deviation of concentration calculated from the triplicate measurement of carbon measured by TOC and sulfur measured by ICP-AES was 4×10^4 and 2×10^{-5} mmol g⁻¹, respectively. The difference between two measurements of ion chromatograph was as small as ca. 5×10^{-5} mmol g⁻¹ for both sulfate and fluorine ion. This indicates the accuracy of these analysis methods and is sufficient for quantitative discussion.

The limits of sensitivity of these analysis methods in this study which was converted from ppm to the amount per 1 g of Nafion were 0.02–0.2 μmol g⁻¹. The dissolved amount of F⁻, for example, in actual fuel cell is reported as ca. 0.3–2.0 μmol g⁻¹ [15,16], which is higher than the sensitivity shown by our method. Therefore this method can possibly applied for detection of degradation in actual fuel cells as well. The eluted amount of chemical components and their ratio depended on absorbed dose and those were different in each irradiation condition, indicating that the degradation process was changed depending on the existence of water and oxygen. In oxygen atmosphere, eluted amount of F⁻ was large, whereas elu-

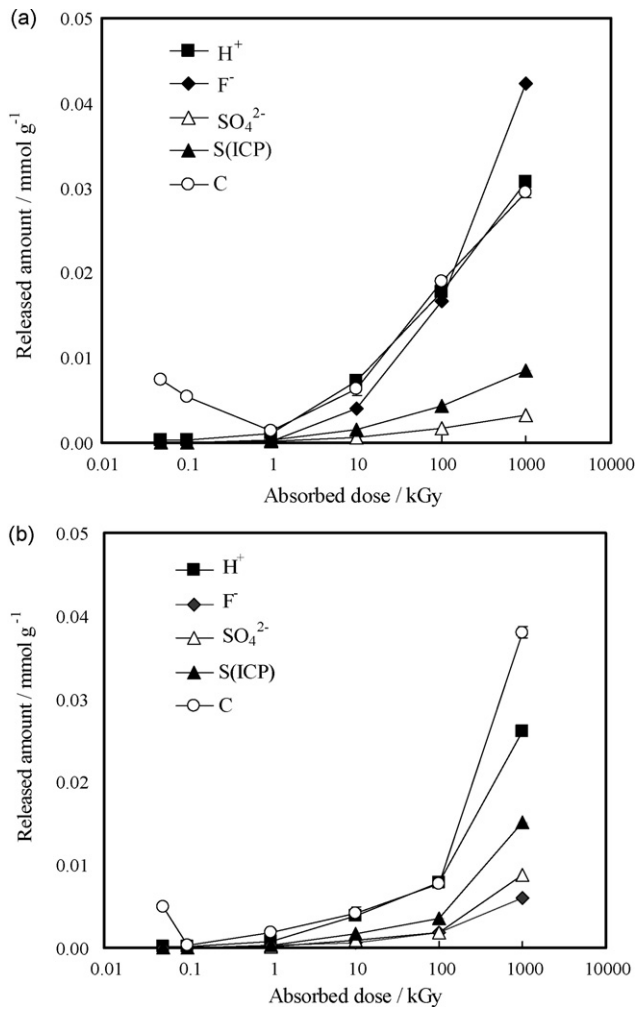


Fig. 1. The amount of eluted chemical components from gamma-ray irradiated Nafion under air atmosphere: (a) in oxygen and (b) in nitrogen after vacuum drying.

tion of S was less in amount, however, the tendency was opposite in nitrogen. This shows that the scission site differs depending on the irradiation condition. In addition, the amounts of the eluted ions and atoms were notably increased from 10 kGy for the sample irradiated in oxygen (Fig. 1(a)), whereas the amounts increased from 100 kGy for the sample irradiated in nitrogen after vacuum drying (Fig. 1(b)). This shows that the irradiation effect in oxygen atmosphere is possibly an indirect effect, whereas is direct effect in nitrogen atmosphere after vacuum drying. The reason being in the presence of water indirect scission associated with water radiolysis is easier to take place compared with direct scission of polymer chain. This is because the bond-breaking reaction energy of side chain [17] is higher than formation energy of hydroxyl radical [18]. The ratio and the dose-dependence of the eluted chemical components for the samples irradiated in air and water were almost the same as those in oxygen, indicating that the same reaction takes place in oxygen, air and water.

In addition, only the elution of organic carbon increased at lower absorbed dose below 0.1 kGy. This tendency was also observed in the results for the samples irradiated in air and in water, suggesting that different reactions were induced at lower absorbed dose of 0.1 kGy. In our previous study, the proton conductivity and the ion-exchange capacity considerably dropped at absorbed dose below 0.1 kGy and then returned to the value of unirradiated sample [19]. In low absorbed dose, elution of organic carbon was observed, while elution of F⁻ and S was hardly observed, indi-

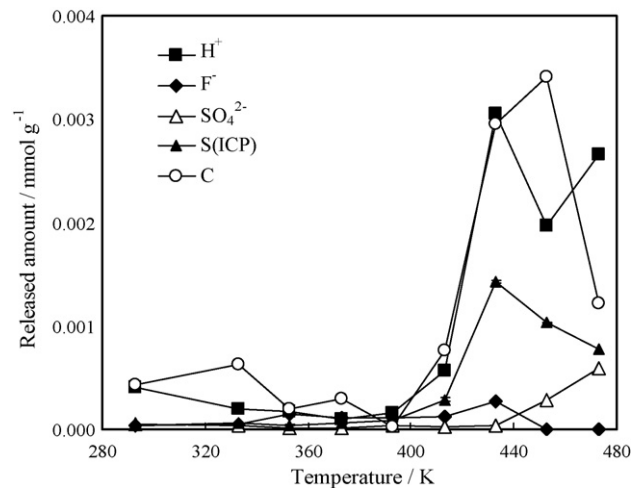


Fig. 2. The amount of eluted chemical components from gamma-ray irradiated Nafion by heat treatment.

cating that a part of the PTFE backbone was dissolved by scission of C–C bond.

3.2. Degradation by heat treatment

Though the previous section was devoted to the radical reaction caused by gamma-ray irradiation, deterioration of cell performance is reported to be caused over the temperature of 373 K in an actual fuel cell, and is accelerated under the low humidifying condition [14]. To examine degradation by heat treatment, Nafion was heated within the range from 313 to 473 K, and the solutions after immersion of heated pellets were analyzed with the same method as gamma-ray irradiation (Fig. 2). The amount of eluted chemical components was as low as 1/10 of that in the gamma-ray irradiation. The elution was hardly seen at 393 K or less, increased with temperature from 393 to 453 K, and then decreased a little over 453 K. The glass transition temperature of Nafion is reported as 385 K for α transition and 293–300 K for β transition [20], indicating that scission of the polymer chain takes place in the temperature higher than α transition temperature.

A large amount of organic carbon and S atom shows the side chain scission including the sulfonic group. This tendency is different from that for any of gamma-ray irradiated samples, which shows that the degradation process by heat treatment differs from that by the gamma irradiation.

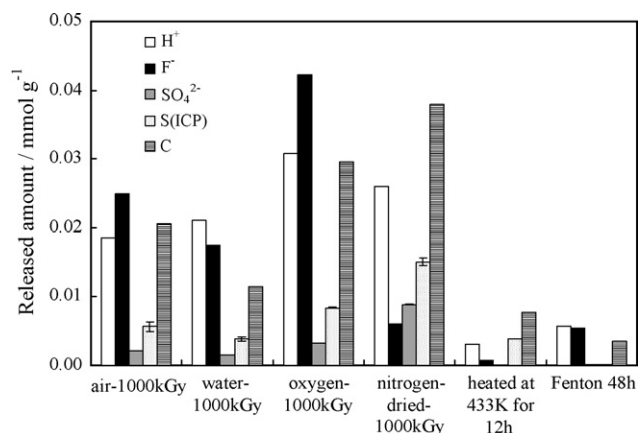
3.3. Difference of eluted chemical components through degradation process

It was supposed that polyelectrolyte was dissolved as a result of scission of polymer chain by gamma-ray irradiation and heat treatment, and the scission site was changed depending on the degradation conditions. To estimate the structure of the eluted fragments, the ratio of each chemical component obtained by the solution analysis was calculated for the samples experienced degradation process, including the Fenton reaction. The amounts of dissolved species under various degradative conditions are summarized in Fig. 3, and the molar ratios among the chemical components are shown in Table 1. These figure and table correspond to the maximum dissolution condition (1000 kGy in gamma-ray irradiation and 433 K in heat treatment). As described in Section 3.1, it was considered that the irradiation effect was mainly direct effect in nitrogen atmosphere, whereas was mainly indirect effect in other irradiation conditions at 1000 kGy.

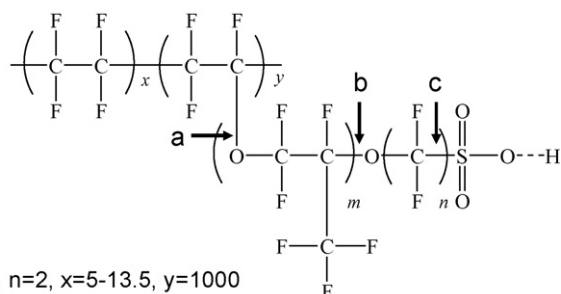
Table 1

The mole ratio of released chemicals from gamma-ray irradiated Nafion under different conditions (absorbed dose; 1000 kGy).

| | Irradiated in air ¹⁸⁾ | Irradiated in water ¹⁸⁾ | Irradiated in oxygen ¹⁸⁾ | Irradiated in nitrogen after drying ¹⁸⁾ | Heated at 433 K for 12 h | Fenton treated for 48 h |
|---|----------------------------------|------------------------------------|-------------------------------------|--|--------------------------|-------------------------|
| F ⁻ /S(ICP) | 4.5 | 4.4 | 5.0 | 0.4 | 0.2 | 7.8 |
| SO ₄ ²⁻ /S(ICP) | 0.4 | 0.4 | 0.4 | 0.6 | 0.0 | 0.3 |
| C/S(ICP) | 2.9 | 3.6 | 3.5 | 2.5 | 2.3 | 5.1 |
| C/(S(ICP)-SO ₄ ²⁻) | 5.0 | 5.8 | 5.7 | 6.1 | 2.3 | 6.9 |

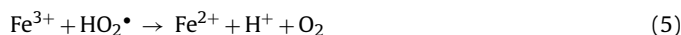
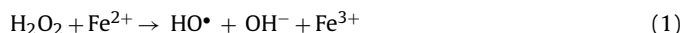
**Fig. 3.** The amount of eluted chemical components from gamma-ray irradiated Nafion degraded by different methods.

The ratio between total organic carbon measured by TOC analyzer and sulfur measured by ICP-AES, C/S (ICP), was ranged from 2 to 3. As scission possibly takes place at ether linkage, two kinds of fragments would come out from Nafion, since it has two ether linkages in a side chain. As shown in Fig. 4, in case the scission of terminal ether linkage (b) occurs, C/S=2, and in case the scission of ether linkage near main chain (a), C/S>=5. Based on this and assuming $m=1$ in Fig. 4, the scission site would be estimated by taking the ratio (Table 1). Scission at two ether linkages were taken place comparably in the samples irradiated in water and oxygen atmosphere, however, the scission at terminal ether linkage was dominant rather than that of another ether linkage in other irradiation conditions. In addition, F⁻ eliminated as much as total organic carbon, indicating the scission at C–F bond was taken place comparably in the samples without vacuum drying. In contrast, for the vacuum dried samples, elimination of SO₄²⁻ was enhanced instead of F⁻ as shown in Fig. 3. It shows that scission site was changed by vacuum drying, i.e. removal of water inhibits C–F bond scission and accelerated elimination of sulfonic groups, indicating that generated radical species by gamma-ray irradiation depend on existence of water.

**Fig. 4.** Chemical structure of perfluorosulfonic acid; in Nafion, $m > 1$, $n = 2$, $x = 5-13.5$, $y = 1000$.

The value of C/S ratio was 2.3 for the heated sample, which is similar to the irradiated sample under nitrogen after vacuum drying, showing the scission of terminal ether linkage. This suggests that the polymer radicals are generated in the same position in side chain in both cases of irradiating in the nitrogen and heat treatment. However, it is supposed that scission of C–S bond ((c) in Fig. 4) hardly take place in heat treatment, because the elution of SO₄²⁻ was hardly detected unlike the case of the irradiation in nitrogen.

Chemical degradation by the Fenton reaction of Nafion was also investigated to compare the effect of radicals generated by gamma-ray irradiation and the chemical reaction. It is reported that the hydroxyl radical and the peroxy radical are generated by the Fenton reaction as the following reactions [13]:



As shown in Fig. 3 and Table 1, the ratios among dissolved components were approximately similar to those of irradiated samples in air, oxygen and water, and C/S ratio of 5.1 shows scission of ether linkage near main chain. Elution of F⁻ was also significant for the irradiated samples in air, oxygen and water. It was shown that the hydroxyl radical and the peroxy radical generated by water radiolysis and the Fenton reaction mainly cut the ether linkage near main chain and the C–F bond.

From above-mentioned results, the degradation process of Nafion is mainly divided into two types:

- Scission of terminal ether linkage by formation of polymer radicals.
- Scission of ether linkage near main chain and C–F bond by hydroxyl and peroxy radicals.

It is supposed that Type (i) degradation is mainly caused by direct effect of gamma-ray and heat, whereas Type (ii) degradation by indirect effect through the reaction with hydroxyl and peroxy radicals generated by water radiolysis or the Fenton reaction. The former type mainly causes elimination of sulfate ion and shows C/S around 2, and the latter type mainly causes elimination of fluorine ion and shows C/S over 5. The amount of eluted species differs by absorbed dose, temperature or reaction time, depending on the amount of generated radicals.

As it was uncertain only by taking the ratio of eluted chemical components whether the eluted components originated from the main chain or the side chain, PTFE, which forms main backbone of perfluorosulfonic acid, was treated in the same procedures as Nafion. The results both for PTFE and Nafion are shown in Fig. 5. The contribution of a main chain scission was estimated based on the ratio of eluted organic carbon in PTFE to that in Nafion, since the eluted amount for PTFE was thought to originate from the scission of main chain. It was shown that about 30% and 25% of organic

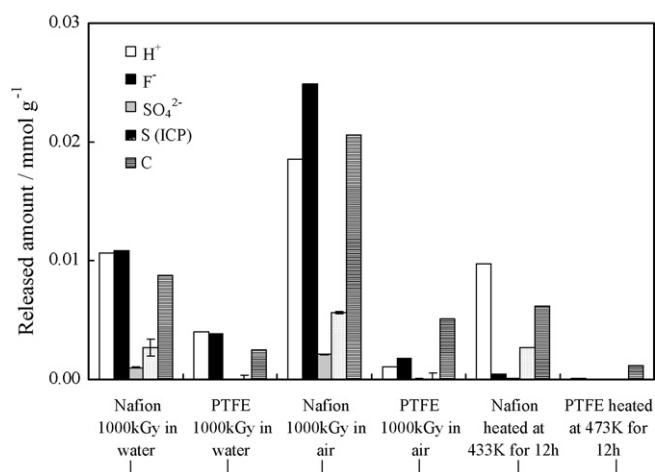


Fig. 5. Comparison of the amount of eluted chemical components from degraded Nafion and PTFE by different methods.

carbons originated from main chain, respectively for gamma-ray irradiation and thermal, degradation. Thus, the C/S ratio in Table 1 must be larger, because it was calculated based on the assumption that all the carbon originate from side chain, but the results of re-calculation showed that it did not effect on the main scission site in two ether linkages.

The elution of the proton was also observed as shown in Fig. 3 along with the elution of the polymer chain, which was due to dissociation of chemical species in the solution. Considering that sulfuric acid is a dihydric acid under dissociation equilibrium, the concentration of proton should be consistent with that of dissociable group shown in the following equation:

$$[\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{F}^-] + [\text{RSO}_3^-]. \quad (6)$$

Based on Eq. (6), the ratio of macromolecular fragments $[\text{RSO}_3^-]$ generated by cleavage of ether linkage against all the eluted chemical species was calculated by the following equation:

$$\alpha = \frac{[\text{RSO}_3^-]}{[\text{H}^+]} = \frac{\{[\text{H}^+] - 2[\text{SO}_4^{2-}] - [\text{F}^-]\}}{[\text{H}^+]} \quad (7)$$

when α is close to 1, it shows that almost the eluted chemical species are macromolecular fragments $[\text{RSO}_3^-]$, and when it is close to 0, it shows that most of eluted species are ions such as F^- and SO_4^{2-} . The value of α was 0.9 and 0.0, respectively for heated sample and the Fenton reacted sample. This shows that the main eluted species by heat treatment was the macromolecular fragments and those by the Fenton reaction were ions. This also suggests the clear difference between indirect scission caused by radicals originating in water or hydrogen peroxide and direct formation of polymer radicals.

The dependence of α on absorbed dose is shown in Table 2. The ratio of macromolecular fragments, α , decreased with increase in the absorbed dose in all irradiation condition showing that the fragments undergo further dissociation with increase in the absorbed dose. It is also notable that α became negative at high absorbed

dose in the samples irradiated in air and in oxygen, which would reflect excess elimination of F^- against H^+ . It is possible that the proton would be captured again into the electrolyte and/or the fragments by forming new functional groups such as COOH with small dissociation degree.

3.4. Structural identification of eluted species and films with FT-IR

The FT-IR spectra of the fragments eluted into the solution are shown in Fig. 6. The IR spectra of eluted fragments in all the degradation methods showed common peaks corresponding to C–F bond, ether linkage and sulfonic group regardless of degradation methods. These peaks were commonly observed for Nafion membrane [21–31], which were also observed in untreated membrane in this study (ATR method). Additional peak appeared for all the dissolved fragments around $1600\text{--}1700\text{ cm}^{-1}$ and around 3500 cm^{-1} , which was hardly observed in Nafion membrane. It corresponds to the absorption band of stretching vibration of ketonic group C=O [32] and hydroxyl group O–H, respectively, showing formation of new functional group COOH. It is possible that the degradation treatments not only cause the polymer chain scission but also form the new functional group. This supports the above-mentioned possibility of capture of the proton in the electrolyte or fragment.

Moreover, the peaks appeared sharply in heated sample, whereas broad peak was observed in gamma-ray irradiated or Fenton reacted samples, indicating that a specific site cleavage took place by heat treatment while many different bondings were cut by gamma-ray and the Fenton reaction to form mixture of various kind of fragments. Particularly, the Fenton treated sample showed weak peaks indicating further fragmentation of the products. The difference between the samples irradiated in oxygen and nitrogen after drying was never observed in IR spectra of dissolved fragments, whereas there were obvious differences between eluted chemical components. It indicates that the main difference between oxygen and nitrogen is the eluted amount of low-molecular ions such as F^- and SO_4^{2-} , which will be investigated in near future by HPLC (high-speed liquid chromatography) and the mass spectrometry.

On the other hand, in order to examine change in structure of the membrane by elution of the fragments, Nafion-117 membrane was degraded under the same condition as the pellet mentioned in Section 2.1, namely, it was immersed into ultrapure water for 4 days at room temperature and then taken out after drying to measure FT-IR with ATR. The IR spectra were shown in Fig. 7. It was preliminarily confirmed for Nafion-117 that the ratio among eluted chemical components was the same as that for the Nafion NR-50 pellets. Neither decrease in the peaks nor formation of new functional groups was observed for the gamma-ray irradiated and heated samples, besides the decrease in all the peak intensities for Fenton reacted sample. The ion-exchange capacity of Nafion is about 0.9 meq g^{-1} , indicating that the 0.9 mmol of side chains exist per 1 g of Nafion. The maximum amount of eliminated sulfur of gamma-ray irradiation (1000 kGy in nitrogen) was about 0.015 mmol g^{-1} . Because all the eluted sulfur is considered to originate from the side chain, it can be said that at most 1.7% of the side chains underwent scission. It is difficult to detect such local

Table 2
The ratio of $[\text{RSO}_3^-]$ to total proton elution under different conditions.

| Absorbed dose (kGy) | Irradiated in air | Irradiated in water | Irradiated in oxygen | Irradiated in nitrogen after drying |
|---------------------|-------------------|---------------------|----------------------|-------------------------------------|
| 0.05 | 0.5 | 0.4 | 1.0 | 0.9 |
| 0.1 | 0.7 | 0.4 | 1.0 | 0.8 |
| 1 | 0.1 | 0.4 | 0.7 | 0.5 |
| 10 | −0.3 | 0.2 | 0.3 | 0.3 |
| 100 | −0.4 | −0.2 | −0.1 | 0.2 |
| 1000 | −0.6 | 0.0 | −0.6 | −0.1 |

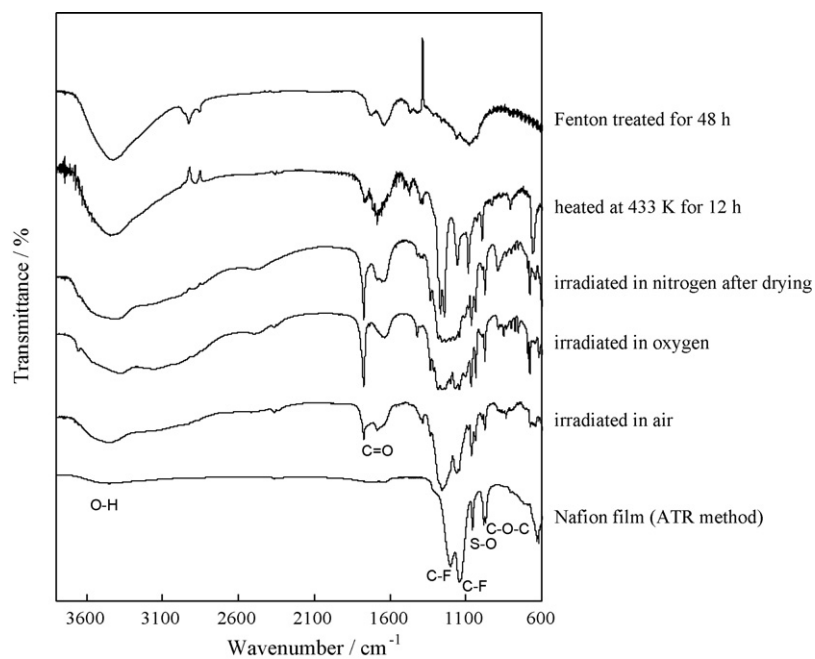


Fig. 6. IR spectra of dissolved species dried in vacuum from degraded Nafion.

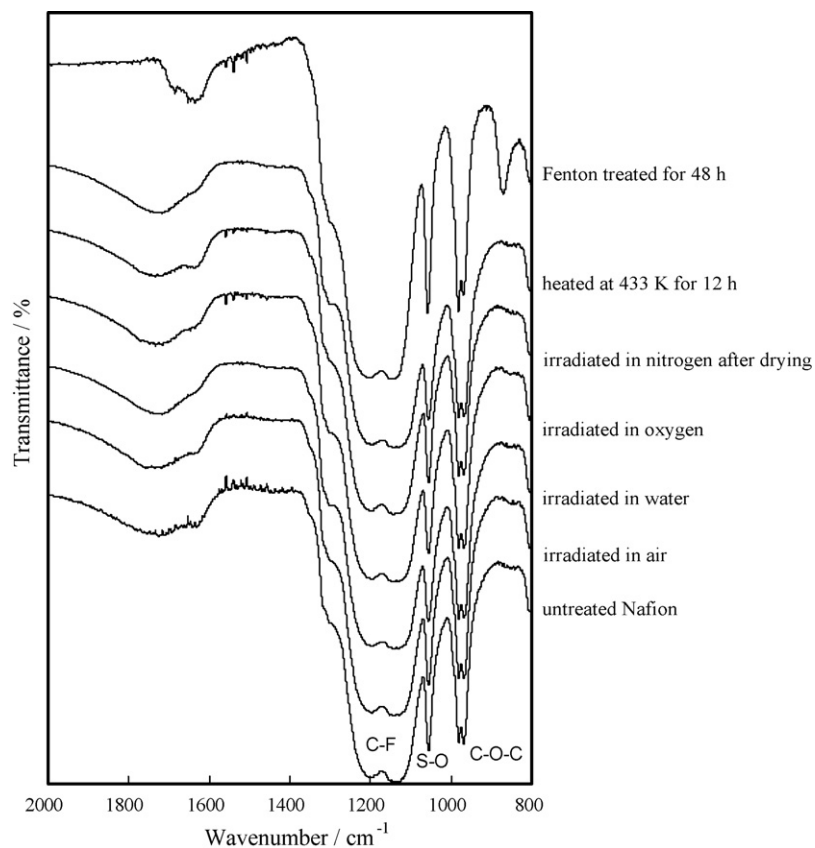


Fig. 7. IR spectra of Nafion membrane after immersion to ultrapure water for 4 days.

changes in usual IR spectra of membrane, in spite of large effects on the proton conductivity and the ion-exchange capacity. It can be said that the analysis of the eluted species is a useful technique which can observe the minute degradation sensitively related to the performance of the polymer electrolyte.

4. Conclusion

The degradation process of perfluorosulfonic acid caused by gamma-ray irradiation, heat treatment and Fenton reaction was investigated by solution analysis. The chemical structures of dis-

solved species were estimated by taking the ratio between eluted ions and atoms, and the functional groups in the fragments were identified by FT-IR. With this method, it was found that the scission site of Nafion clearly differs in different degradation process, i.e. the scission site was strongly influenced by whether the damage on the chain was caused by indirect effect due to hydroxyl and/or peroxy radicals, or direct effect due to radicals produced on the polymer chain. These results showed that solution analysis and structure analysis of dissolved species is very simple and yet a powerful and helpful methods not only to detect degradation of polymer electrolyte sensitively but also to elucidate the degradation process from a viewpoint of decomposition product. This method can also be applied to the analysis of the water generated during actual fuel cell operation to track minute changes in the polymer electrolyte in order to clarify the deterioration mechanism.

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