



# Effect of H<sub>2</sub>O<sub>2</sub> on Nafion<sup>®</sup> properties and conductivity at fuel cell conditions

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## ABSTRACT

During PEM fuel cell operation, formation of H<sub>2</sub>O<sub>2</sub> and material corrosion occurs, generating trace amounts of metal cations (i.e., Fe<sup>2+</sup>, Pt<sup>2+</sup>) and subsequently initiating the deterioration of cell components and, in particular, PFSA membranes (e.g., Nafion). However, most previous studies of this have been performed using conditions not relevant to fuel cell environments, and very few investigations have studied the effect of Nafion decomposition on conductivity, one of the most crucial factors governing PEMFC performance. In this study, a quantitative examination of properties and conductivities of degraded Nafion membranes at conditions relevant to fuel cell environments (30–100%RH and 80 °C) was performed. Nafion membranes were pre-ion-exchanged with small amounts of Fe<sup>2+</sup> ions prior to H<sub>2</sub>O<sub>2</sub> exposure. The degradation degree (defined as loss of ion-exchange capacity, weight, and fluoride content), water uptake, and conductivity of H<sub>2</sub>O<sub>2</sub>-exposed membranes were found to strongly depend on Fe content and H<sub>2</sub>O<sub>2</sub> treatment time. SEM cross-sections showed that the degradation initially took place in the center of the membrane, while FTIR analysis revealed that Nafion degradation preferentially proceeds at the sulfonic end group and at the ether linkage located in the pendant side chain and that the H-bond of water is weakened after prolonged H<sub>2</sub>O<sub>2</sub> exposure.

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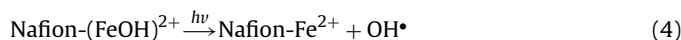
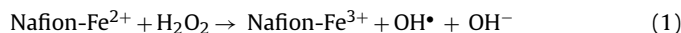
## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) could be potentially exploited in the future as major power generation devices because of their high power density, low temperature of operation, fast start-up, and lack of noxious gas emissions. Up to the present, Pt-based catalysts and perfluorinated sulfonic acid (PFSA) membranes, especially Nafion<sup>®</sup>, have been popularly and extensively used in typical PEM fuel cells. This is because Pt catalysts have low overpotential and high catalytic activity for the electrochemical reactions at both the cathode and the anode [1]. Nafion has demonstrated high proton conductivity, high chemical/mechanical/thermal stabilities, and stable performance in fuel cell applications [2–4]. However, the reliability and durability of hydrogen fuel cell technology need to be improved before it can be implemented on a large commercial scale.

Previous studies have shown that, even if a fuel cell is operated in neat H<sub>2</sub> fuel and oxidant streams, degradation of PEMFC performance can occur [5]. It is well-accepted that the performance is permanently decreased by loss of electrochemically active surface area of the Pt catalyst due to corrosion of the carbon support, by dissolution/migration/precipitation of the Pt catalyst [1,6–11]

and by degradation of the PFSA materials (e.g., Nafion) due to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) formation at the anode or cathode (depending on the operating conditions) [4,12–14]. The decomposition of H<sub>2</sub>O<sub>2</sub>, catalyzed by contaminating metal cations (i.e., Fe<sup>2+</sup>, Pt<sup>2+</sup>), generates highly active oxygen radicals (OH•, OOH•) that initiate the degradation of the ionomer [14–16]. It is known that all PFSA membranes, not only Nafion, are not chemically stable in the presence of both H<sub>2</sub>O<sub>2</sub> and metal cationic contamination under fuel cell conditions [17]. However, most studies have focused on the degradation of Nafion more than other types of PFSA materials due to its popularity.

It has been previously reported that the H<sub>2</sub>O<sub>2</sub> decomposition mechanism in Fenton's reagent {a solution of H<sub>2</sub>O<sub>2</sub> with ppm level of metal contaminants (i.e., Fe<sup>2+</sup>, Cu<sup>2+</sup>, Pt<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>2+</sup>, Ni<sup>2+</sup>, etc.) [3,4,18,19]} is similar to that in typical fuel cell environments [20–22]. The reactive species for Nafion decomposition appear to form as follows [23–27]:



where Nafion-Fe<sup>2+</sup> and Nafion-Fe<sup>3+</sup> represent the membrane having Fe<sup>2+</sup> and Fe<sup>3+</sup> ions neutralizing 2 and 3 sulfonate acid groups,

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respectively. In addition to enhancing degradation of the Nafion, the replacement of protons on the sulfonic groups by non-proton cations by themselves decreases Nafion conductivity [28–34].

The mechanism of  $\text{H}_2\text{O}_2$  formation and chemical degradation of Nafion membranes has already been extensively investigated by various researchers [3,4,10,14,15,35,36]. Some studies have suggested that the ionomer degradation preferentially happens at the cathode, where the oxygen reduction reaction (ORR) occurs [12,13,37–40]. On the contrary, other studies have suggested that greater membrane degradation takes place at the anode, where crossover  $\text{O}_2$  from the cathode exists and the formation of  $\text{H}_2\text{O}_2$  is electrochemically favored [12,23,41]. Previous results found that the degradation process of the ionomer in the membrane is faster than that in the catalyst layer and takes place in the proximity of the membrane-electrode interface [3,42]. Consequently, characterization of the degraded membrane can potentially be a diagnostic approach to evaluate the impact of oxidation on the performance and to predict the lifetime of a PEMFC. However, up to the present, there is no detailed quantitative study reporting the effect of Nafion oxidation on conductivity (one of the most crucial factors for fuel cell performance) or the properties of degraded membranes at conditions relevant to practical PEMFC usage. Several studies have investigated the conductivity of degraded membranes at room temperature in liquid electrolyte (i.e., deionized water) [13,35], while a few studies have reported the conductivity of decomposed membranes in a gas phase at room to elevated temperatures (25–80 °C), but only at 100%RH [4,10], which is not always practical for portable, automotive, and/or stationary fuel cell applications.

Most studies have pretreated fuel cell components in Fenton's reagent because it provides a very well-controlled environment and requires only a very simple experimental set-up [5]. The reagent is usually refreshed periodically to maintain  $\text{H}_2\text{O}_2$  concentration. However, it is known that multivalent ionic cations (i.e.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) interact with sulfonic sites ( $\text{SO}_3^-$ ) more strongly than protons ( $\text{H}^+$ ) [29,33,43] and the uptake of these non-proton cations severely affects Nafion properties and performance [29]. Accordingly, the accumulation of Nafion- $\text{Fe}^{2+}$  in the membrane and the increase in degradation level concurrently proceed as the solution is changed, potentially leading to a misinterpretation of the experimental results. To date, there are discrepancies in the literature about the influence of treatment in Fenton's reagent on ion-exchange capacity (IEC) loss and on fluorine emission rate (FER). Some authors found significant lost in IEC of Nafion membranes after exposure to Fenton's solution [10,35,44], while others did not observe any change [4,24]. The FER values reported vary significantly from 0.016 to 0.260  $\text{mmol g}^{-1} \text{h}^{-1}$  [3,35,45].

The purpose of this work was to provide more insight into the effect of oxidation on Nafion membranes under normal fuel cell conditions. The procedure for  $\text{H}_2\text{O}_2$  treatment was slightly modified from that of other studies to provide more realistic results relative to a PEMFC. The membranes were first pre-ion exchanged with  $\text{Fe}^{2+}$  ions and then introduced to a freshly-prepared  $\text{H}_2\text{O}_2$  solution to keep Fe content in the pretreated membranes (Nafion- $\text{Fe}^{2+}$ ) constant over all  $\text{H}_2\text{O}_2$  exposure times. Since metal cations on the sulfonic sites ( $\text{SO}_3^-$ ) in the Nafion polymer arise during preparation or from very low concentrations of impurities in the gas streams,  $\text{H}_2\text{O}_2$  decomposition during fuel cell operation proceeds primarily due to the presence of these metal cations in the Nafion instead of ions in solution. Therefore, this modification of the  $\text{H}_2\text{O}_2$  pretreatment procedure yields a better replication of the degradation process in a typical fuel cell environment. Consequently, the quantitative evaluation test (conductivity) and physical and chemical characterizations (loss of ion exchange capacity, weight, and fluorine, water uptake, FTIR and EDX analysis) of  $\text{H}_2\text{O}_2$ -treated membranes pretreated by this modified procedure, reported in this study, provide results that should be more pertinent than previous

investigations using Fenton's reagent. The disagreements in the literature concerning the effect of Nafion degradation on properties (IEC and FER) are also discussed.

## 2. Experimental

### 2.1. Membrane pretreatment

Commercial Nafion 211 membranes (NRE-211, 25  $\mu\text{m}$  nominal thickness, 1100 EW) were purchased from DuPont Inc. Nafion membranes (5.5 cm  $\times$  1 cm) were pretreated by a standard procedure. They were heated at 90 °C for 1 h each in aqueous solutions of 3 vol.%  $\text{H}_2\text{O}_2$  (Fisher Scientific) to remove organic impurities, in 0.5 M  $\text{H}_2\text{SO}_4$  (Fisher Scientific) to remove metallic impurities and to acidify the sulfonic sites, and in deionized (DI) water to remove residual acid solution. The subsequent acidified membranes were washed several times and kept in DI water prior to use.

### 2.2. Pre-ion exchange with Fe and $\text{H}_2\text{O}_2$ treatment of the Nafion- $\text{Fe}^{2+}$ membranes

Reagent grade solutions of 1 M  $\text{FeSO}_4$ , 1 M  $\text{H}_2\text{SO}_4$ , and 50 vol.%  $\text{H}_2\text{O}_2$  were purchased from Fisher Scientific. Instead of following the general procedure for Fenton's reagent pretreatment by immersing acidified membranes in a freshly-prepared Fenton's reagent (ppm level of  $\text{Fe}^{2+}$  ions in  $\text{H}_2\text{O}_2$  aqueous solution) [3,35,24,46], the procedure was modified for this study. The membrane samples were first ion-exchanged using a solution containing 20, 100, or 1000 ppm of  $\text{Fe}^{2+}$  in 0.1 M  $\text{H}_2\text{SO}_4$  at ambient temperature for 7 days under constant shaking to ensure exchange equilibration. The equilibrium isotherm for the bi-valent cation composition between the exchange solution and a Nafion membrane is shown in references [29,32,43]. The equilibrium compositions for protons in Nafion membranes in  $\text{Fe}^{2+}$  exchange solutions are given in Table 1. It can be observed that even trace amounts of  $\text{Fe}^{2+}$  ions in solutions results in a significant uptake of Fe in membranes, indicating that  $\text{Fe}^{2+}$  ions more preferentially adsorb on sulfonic sites than protons. The initial proton composition ( $y_{\text{H}^+-\text{Fe}}^0$ ; where  $y_{\text{H}^+-\text{Fe}}^0$  is the initial fraction after equilibration in a solution of sulfonic sites in a Nafion- $\text{Fe}^{2+}$  membrane still neutralized by protons) is obtained as follows:

$$y_{\text{H}^+-\text{Fe}}^0 = \frac{\text{IEC}_0}{\text{IEC}_{\text{original}}} \quad (5)$$

where  $\text{IEC}_{\text{original}}$  and  $\text{IEC}_0$  are the ion-exchange capacities of Nafion membranes in the original  $\text{H}^+$ -form [928 ( $\mu\text{mol H}^+$ ) $\text{g}^{-1}$ ] and of the Fe-containing membranes before  $\text{H}_2\text{O}_2$  treatment (time = 0 h), respectively. The equation for IEC calculation is given in section 2.3.

In Table 1, the Fe composition in the membrane before exposure to  $\text{H}_2\text{O}_2$  (related to the fraction of protons removed upon ion exchange with  $\text{Fe}^{2+}$ ,  $1 - y_{\text{H}^+-\text{Fe}}^0$ ) increases with an increase in  $\text{Fe}^{2+}$  ion concentration in the exchange solution. The membrane samples are labeled corresponding to the proton composition in the membrane before  $\text{H}_2\text{O}_2$  exposure (time = 0 h, M90 means 90% of  $-\text{SO}_3^-$  groups neutralized with  $\text{H}^+$  and 10% with Fe ions), since this parameter is one of the most crucial factors governing fuel cell performance.

After Fe exchange, the ion-exchanged membranes were rinsed several times with DI water, dried at 80 °C for 8 h, and weighted ( $W_0$ ). Then, these  $\text{Fe}^{2+}$ -containing membranes were individually immersed in a freshly-prepared aqueous solution of 30 vol.%  $\text{H}_2\text{O}_2$  at 80 °C under constant shaking in amber glassware for a specific period of time. The  $\text{H}_2\text{O}_2$  solution was changed every 4 h during the first 24 h and every 8 h afterwards to ensure essentially constant  $\text{H}_2\text{O}_2$  concentration since the degradation tends to be almost stabilized after 24 h. The used solutions and treated membranes were separately allowed to cool to room tem-

**Table 1**  
Equilibrium compositions and physical and chemical properties of Nafion membranes with different Fe contents before and after 24 h H<sub>2</sub>O<sub>2</sub> solution exposure.

Mem.	[Fe] <sup>2+</sup> in exch. sol. (ppm) <sup>a</sup>	[Fe] <sup>2+</sup> in mem. after equil. with exch. sol. (ppm)	y <sub>H<sup>+</sup>-Fe</sub> <sup>0</sup> <sup>b</sup>	Treatment sol.	y <sub>H<sup>+</sup>-Fe</sub> <sup>24</sup> <sup>c</sup>	X <sub>IEC</sub> <sup>24</sup> <sup>d</sup>	X <sub>W</sub> <sup>24</sup> <sup>e</sup>	X <sub>F</sub> <sup>24</sup> <sup>f</sup>	Initial FER <sup>g</sup> [(mmol F <sup>-</sup> )g <sup>-1</sup> h <sup>-1</sup> ]
M100	0	0	1.00	H <sub>2</sub> O	1.00	0.00	0.01	0.0002	0.0005
M90	20	2480	0.90	H <sub>2</sub> O	0.92	0.00	0.01	0.0002	0.0003
M100	0	0	1.00	H <sub>2</sub> O <sub>2</sub>	0.76	0.24	0.02	0.0007	0.0008
M90	20	2480	0.90	H <sub>2</sub> O <sub>2</sub>	0.37	0.59	0.16	0.12	0.179
M61	100	10,172	0.61	H <sub>2</sub> O <sub>2</sub>	0.25	0.59	0.52	0.25	0.833
M22	1000	20,094	0.22	H <sub>2</sub> O <sub>2</sub>	0.08	0.64	0.77	0.29	1.226

<sup>a</sup> The concentration of Fe<sup>2+</sup> ions in a 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous exchange solution.

<sup>b,c</sup> y<sub>H<sup>+</sup>-Fe</sub><sup>0</sup> and y<sub>H<sup>+</sup>-Fe</sub><sup>24</sup> are the fractions of sulfonic sites (-SO<sub>3</sub><sup>-</sup>) neutralized by protons in the Fe-containing membrane before and after 24 h H<sub>2</sub>O<sub>2</sub> treatment at 80 °C, respectively; error ±5%.

<sup>d,e,f</sup> X<sub>IEC</sub><sup>24</sup>, X<sub>W</sub><sup>24</sup>, and X<sub>F</sub><sup>24</sup> are the fractions of ion-exchange capacity (IEC) lost, weight lost, and fluorine lost after 24 h H<sub>2</sub>O<sub>2</sub> treatment at 80 °C, respectively; error ±5%.

<sup>g</sup> FER is the fluorine loss (also called emission) rate obtained from the initial slope of F lost vs. time; error ±2%.

perature and were kept in amber glassware prior to fluorine analysis.

### 2.3. Ion-exchange capacity (IEC)

The ion-exchange capacities (IECs) are defined in this paper as the concentration of proton sites available in the membranes and were determined by a standard acid-based titration technique using W<sub>0</sub> (original membrane sample weight) as the basis. This technique is widely considered to be a convenient and accurate method [36]. After conductivity measurement, a membrane was immersed in 0.1 M NaCl (Fisher Scientific) solution at ambient temperature for 2 days. It has been found that multivalent cations (i.e., Fe<sup>2+</sup>, Fe<sup>3+</sup>) interact with sulfonic sites (-SO<sub>3</sub><sup>-</sup>) in Nafion more preferably and strongly than monovalent cations (i.e., Na<sup>+</sup>) and protons (H<sup>+</sup>), respectively [29,32,33], and, therefore, Na<sup>+</sup> ions should replace only the remaining protons (H<sup>+</sup>), not the Fe<sup>2+</sup> and/or Fe<sup>3+</sup> attached to the sulfonic sites (-SO<sub>3</sub><sup>-</sup>). After exchange, the membrane was taken out of the solution and dried at 80 °C for 2 days and the dry weight (W<sub>t</sub>) determined. The exchange solution was subsequently back-titrated with a 0.005 M NaOH (Fisher Scientific) using bromothymol blue indicator. The end point of titration was determined at pH 7. The ion-exchange capacity (IEC) was calculated as follows:

$$\text{IEC} = \frac{[C_{\text{NaOH}}]V_{\text{NaOH}}}{W_0} \quad (6)$$

where [C<sub>NaOH</sub>] and V<sub>NaOH</sub> are the concentration (0.005 M) and volume (cm<sup>3</sup>), respectively, of the NaOH solution used for back-titration and W<sub>0</sub> is the initial weight (mg) of the membrane sample.

In order to rectify the discrepancies in the literature about the change in ion-exchange capacity (IEC) of H<sub>2</sub>O<sub>2</sub>-treated membranes and to determine whether or not the reported negligible effect on IEC was due to a post-degradation acid treatment, an IEC investigation and FTIR analysis of membranes was carried out in this work both before and after exposure to an acid solution. In order to minimize the variation between membrane samples, the Fe-containing membrane with y<sub>H<sup>+</sup>-Fe</sub><sup>0</sup> = 0.22 was cut in half. The first half was treated in 1 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 8 h, rinsed with DI water, and kept in the dark. The other half was exposed to 30 vol.% H<sub>2</sub>O<sub>2</sub> at 80 °C under constant shaking in amber glassware for 4 h and rinsed with DI water. Then, it was acid-treated at the same conditions as those for the first half. After that, IEC measurements and FTIR examination of these two halves were performed.

### 2.4. Fluorine analysis

The F<sup>-</sup> concentrations in the collected H<sub>2</sub>O<sub>2</sub> solutions before and after Nafion degradation were determined using a fluoride ion selective electrode 9609BNWP (Thermo Scientific Orion).

### 2.5. Conductivity, swelling, and weight change measurements

The procedures have already been described in more detail elsewhere [28]. The membrane sample was pretreated at 30% relative humidity (RH) and 80 °C for 4 h before it was placed into a custom-made polyetheretherketone (PEEK) holder to prevent stresses developing in the membrane during humidification. Then, the conductivity measurement of the membrane in the lateral or in-plane direction at 30%RH and 80 °C was performed by a two-probe impedance analyzer (Gamry Potentiostat Reference 600) with an amplitude of 50 mV until constant conductivity was obtained. After that, the relative humidity was raised in steps from 30%RH to 100%RH and the conductivity was measured after equilibration at each step in %RH. The membrane dimensions and weight (W<sub>100%RH</sub>) were obtained immediately after the conductivity measurements. The conductivity was calculated from the following expression:

$$\sigma = \frac{l}{RA} \quad (7)$$

where  $\sigma$  is the conductivity (S cm<sup>-1</sup>);  $l$  is the distance between the two Pt electrodes (cm);  $R$  is the membrane resistance ( $\Omega$ ), obtained from the intercept of the real component axis in a Nyquist plot;  $A$  is the cross sectional area of the membrane (cm<sup>2</sup>).

### 2.6. Water uptake measurement

After the conductivity measurement at 100%RH and 80 °C, the water content of a Nafion membrane was obtained as follows:

$$\lambda_{\text{H}_2\text{O}} = \frac{1100(W_{100\%RH} - W_t)}{18W_t} \quad (8)$$

where  $\lambda_{\text{H}_2\text{O}}$  is the water uptake of the Nafion membrane at 100%RH and 80 °C (defined as adsorbed water molecules per sulfonic acid functionality [(mol H<sub>2</sub>O)/(mol-SO<sub>3</sub><sup>-</sup>)]), W<sub>100%RH</sub> is the weight of the membrane equilibrated at 100%RH and 80 °C, and W<sub>t</sub> is the dry weight of the membrane after treatment in H<sub>2</sub>O<sub>2</sub> solution for a period of time  $t$ .

### 2.7. Fourier transform infrared (FTIR) analysis

FTIR spectroscopy was performed to examine the change in chemical structure of the Nafion samples. After the Fe<sup>2+</sup>-membranes were soaked in 30% H<sub>2</sub>O<sub>2</sub> aqueous solution at 80 °C for various immersion times, the degraded membranes were rinsed

several times with DI water, dried, and kept in the dark prior to analysis. FTIR measurements were conducted with a Nicolet Magna-IR spectrometer equipped with an ATR device. The spectrum was collected at ambient temperature with a wave number resolution of  $4\text{ cm}^{-1}$  in the range of  $500\text{--}4000\text{ cm}^{-1}$ . For comparison purposes, each FTIR spectrum was normalized by the absorbance intensity of the vibration at  $1145\text{ cm}^{-1}$ . This peak can be attributed to the C–F bond, which is a characteristic bond in the polytetrafluoroethylene (PTFE) backbone. Therefore, this peak was used as an internal standard in this study.

### 2.8. Scanning electron microscope (SEM)

The physical changes at the surfaces and over the cross-sections of Nafion membranes before and after treatment were investigated by SEM analysis (SEM-Hitachi S-3400N). Membrane cross-sections were prepared by a freeze-fracture technique. The membrane sample was allowed to freeze in liquid nitrogen and was then fractured while still immersed in liquid nitrogen.

### 2.9. Elemental analysis

Elemental analyses (oxygen, fluorine, sulfur, and iron) of the membranes before and after  $\text{H}_2\text{O}_2$  treatment were performed to confirm EDX results. Measurements were carried out by Galbraith Laboratories in Knoxville, TN.

## 3. Results and discussion

### 3.1. Effect of $\text{H}_2\text{O}_2$ treatment and Fe content on Nafion decomposition

The degree of degradation of Fe ion-exchanged Nafion membranes by  $\text{H}_2\text{O}_2$  was investigated by changes in ion-exchange capacity (IEC), weight, and fluorine content. These properties have been demonstrated to be important ones for evaluating degradation level and membrane stability. This is because degradation occurs at the polymer side chains via a side chain cleavage mechanism causing the cleavage of  $\text{SO}_3\text{-H}$ ,  $\text{CF}_3$ ,  $\text{OCF}_2$ , and  $\text{CF}$  groups [47] and also occurs via an unzipping mechanism at the main chain where there are reactive end groups (e.g.,  $\text{COOH}$ ) [15,17,20,47]. Since ion-exchange capacity (IEC) is one of the most important parameters regulating the properties of PFSA membranes (e.g., water uptake, proton conductivity), this property is popularly used to investigate the characteristics of Nafion membranes. In addition, the losses of weight and fluorine content are believed to be accurate and direct measurements of Nafion stability [26]. In this study, the level of Nafion degradation is defined by fractional loss of IEC, weight, and fluorine content as follows:

$$\text{Ion exchange capacity fraction loss : } X_{\text{IEC}} = \frac{y_{\text{H}^+-\text{Fe}}^0 - y_{\text{H}^+-\text{Fe}}^t}{y_{\text{H}^+-\text{Fe}}^0} \quad (9)$$

$$\text{with } y_{\text{H}^+-\text{Fe}}^0 = \frac{\text{IEC}_{t=0}}{\text{IEC}_{\text{original}}}, y_{\text{H}^+-\text{Fe}}^t = \frac{\text{IEC}_t}{\text{IEC}_{\text{original}}}$$

where  $X_{\text{IEC}}$  is the fraction of original proton composition lost by a degraded Nafion sample;  $y_{\text{H}^+-\text{Fe}}^t$  is the fraction of original sulfonic sites in the membrane remaining after treatment time  $t$ ;  $\text{IEC}_{\text{original}}$  is the ion-exchange capacity of a Nafion membrane in the original proton form of the membrane [ $928\text{ }(\mu\text{mol H}^+)\text{g}^{-1}$ ]; and  $\text{IEC}_{t=0}$  and  $\text{IEC}_t$  are the ion-exchange capacities [ $(\mu\text{mol H}^+)\text{g}^{-1}$ ] of Fe-containing membranes before and after treatment in  $\text{H}_2\text{O}_2$  solutions for a period of time  $t$ , respectively.

$$\text{Weight loss fraction : } X_W = \frac{W_0 - W_t}{W_0} \quad (10)$$

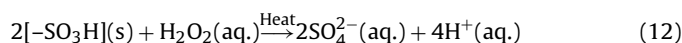
$$\text{Fluorine loss fraction : } X_F = \frac{[C_F]_t V_{\text{H}_2\text{O}_2}}{W_0 F_0} \quad (11)$$

where  $X_W$  and  $X_F$  are the fractions of weight lost and of fluorine lost of a degraded Nafion sample, respectively;  $[C_F]_t$  is the concentration of fluorine in the  $\text{H}_2\text{O}_2$  solution at treatment time  $t$  [ $(\text{mg F}^-)\text{cm}^{-3}$ ];  $V_{\text{H}_2\text{O}_2}$  is the volume of  $\text{H}_2\text{O}_2$  solution ( $\text{cm}^3$ );  $W_0$  and  $W_t$  are the dry weights (mg) of the Fe-contaminating membranes before and after  $\text{H}_2\text{O}_2$  treatment for a period of time  $t$ ; and  $F_0$  is the initial weight fraction of fluorine in the  $\text{Fe}^{2+}$ -containing membranes at treatment time 0 with a value of 0.68 (results from elemental analysis).

It was previously found that the average Fe release rate from components in a normal fuel cell without protective coating on metallic bipolar plates is  $6.5\text{ }\mu\text{g cm}^{-2}$  [48]. If the typical daily operating time for an MEA (using an NE-1135 membrane,  $190\text{ g m}^{-2}$ ) is considered to be 6.5 h and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ion contaminants are assumed to be completely taken up by the membrane, the proton fraction remaining ( $y_{\text{H}^+-\text{Fe}}$ ) of the MEA after 108 days of operation should be ca. 0.86–0.91. Thus, the investigation of M90 membranes ( $y_{\text{H}^+-\text{Fe}}^0 = 0.90$ ) was a particular focus of this study, since these Fe contamination levels are relevant to practical fuel cell usage. However, to gain better insight into the degradation mechanism during fuel cell operation, the properties and conductivities of membranes containing various higher Fe compositions were also examined. Higher Fe compositions enabled a more complete analysis of the influence of Fe concentration on degradation. Table 1 illustrates the degree of Nafion decomposition (fractions of IEC, weight, and F lost) during 24 h exposure to a solution of  $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ , and fluorine loss (emission) rate (FER) for the 4 levels of Fe content in the Nafion membranes studied.

The influence of exposure to just pure  $\text{H}_2\text{O}$ , as opposed to exposure to the  $\text{H}_2\text{O}_2$  solution, at  $80\text{ }^\circ\text{C}$  for both M100 and M90 membranes was also studied to be able to account for any changes simply due to exposure to  $\text{H}_2\text{O}$  in the  $\text{H}_2\text{O}_2$  solution. In Table 1, no significant decrease in IEC, weight, or fluorine content was observed for the membranes subjected only to water treatment, indicating that Nafion is chemically stable in the presence of hot water and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions in the membrane.

The effect of  $\text{H}_2\text{O}_2$  treatment on degradation of the non-Fe containing membrane (M100) was also studied. It can be seen in Table 1 that the fractional losses of weight and fluorine content of M100 membranes exposed to  $\text{H}_2\text{O}_2$  solution for 24 h were negligible, consistent with the results of Kinumoto et al. [49]. Unexpectedly, since no Fe ions were present, but also consistent with the results of Kinumoto et al. [49], IEC loss for M100 appeared to be significant. This could be because  $\text{H}_2\text{O}_2$  treatment causes the evolution of cross-linking S–O–S [3,13] and/or decomposes the sulfonic groups ( $-\text{SO}_3\text{H}$ ) located at the pendant side chain, proposed to occur as follows [49]:



On the other hand, for Fe-containing membranes, significant degradation in  $\text{H}^+$  and fluorine content occurred after 24 h  $\text{H}_2\text{O}_2$  treatment. The treated membranes lost considerable  $y_{\text{H}^+-\text{Fe}}$ , weight, and fluorine content. The level of degradation, except for  $y_{\text{H}^+-\text{Fe}}$ , increased significantly with the concentration of  $\text{Fe}^{2+}$  ions in the membrane. The Fe-containing membranes had a somewhat greater loss of  $y_{\text{H}^+-\text{Fe}}$  ( $X_{\text{IEC}}$ ) than M100, but proportionally the

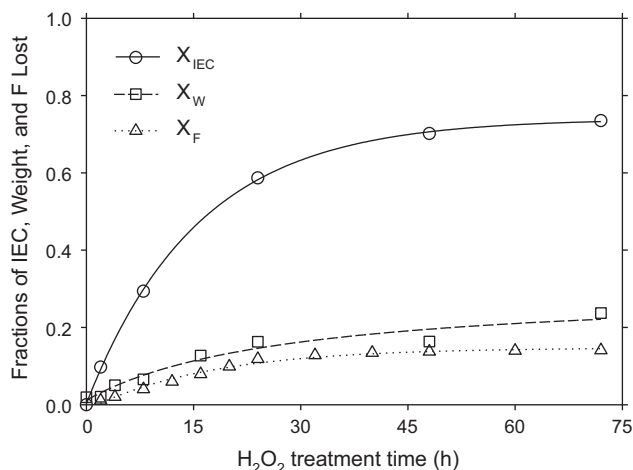


Fig. 1. Fractions of ion-exchange capacity (IEC), weight, and fluorine lost from M90 membranes as a result of H<sub>2</sub>O<sub>2</sub> treatment.

losses were approximately identical for all loadings of Fe studied (M90, M61, and M22).

Fig. 1 presents the fractions of  $y_{\text{H}^+-\text{Fe}}$ , weight, and fluorine lost for Nafion membranes (M90) with  $y_{\text{H}^+-\text{Fe}}^0 = 0.90$  (10% of sulfonate sites neutralized with Fe<sup>2+</sup> ions rather than H<sup>+</sup> ions) pretreated in a 30% H<sub>2</sub>O<sub>2</sub> solution at 80 °C for various periods of time. It can be seen that the fractional losses of IEC, weight, and fluorine followed the same trend, but the decomposition fractions of weight and fluorine lost were lower at all treatment times than that of IEC lost. Based on these results, it can be suggested that the reactive radicals not only cause the cleavage of Nafion's matrix, but may also cause the formation of cross-linking S–O–S, SO<sub>2</sub>–O–SO<sub>2</sub>, and/or SO<sub>2</sub>–F bonds in the degraded Nafion ionomer since the evolution of these crosslinks decrease only IEC and does not affect the weight or fluorine lost. This suggestion is consistent with those in the literature [3,49]. As seen in Fig. 1, an apparent stabilization after initial loss occurred after ca. 24 h. The results imply that as reactions of H<sub>2</sub>O<sub>2</sub> decomposition {Eqs. (1) and (2)} proceed, Nafion–Fe<sup>2+</sup> is oxidized to Nafion–Fe<sup>3+</sup>, as shown in Eq. (1), resulting in the loss of the active catalytic species. In this study, since the membranes were individually submerged in H<sub>2</sub>O<sub>2</sub> reagent in amber glassware and in a dark room, the reconversion of Nafion–Fe<sup>3+</sup> back to Nafion–Fe<sup>2+</sup>, catalyzed by light as shown in Eq. (4), was inhibited and minimized. Thus, it would appear that the extent of the degradation of the Nafion membranes by H<sub>2</sub>O<sub>2</sub> was probably governed by the availability of Fe with a lower oxidation state [46,49].

Fig. 2 presents the kinetics of fluorine removal from the degraded membranes. It shows that the level of Fe<sup>2+</sup> ions in the membrane significantly affects the degree and rate of Nafion decomposition. Given in Tables 1 and 2, the slopes of F loss (emission) vs. time in the initial linear region and over the ca. 24 h period to reach a stable state represent the initial and average fluorine loss (emission) rates (FERs), respectively. It is clear that the presence of Nafion–Fe<sup>2+</sup> in the structure considerably enhances the membrane deterioration rate. Fig. 3 shows the effect of Fe composition on average FER. The squares in Fig. 3 represent the average FERs reported by Chen et al. [3] assuming that all of the 3–300 ppm of Fe<sup>2+</sup> ions in 100 mL of Fenton's reagent were taken up by the 0.25 g Nafion membranes (N-112) in that study (used to calculate  $y_{\text{H}^+-\text{Fe}}$ ). Considering the differences in experimental procedure and conditions (see Table 2), the data from this study and that of Chen et al. [3] are reasonably similar. Surprisingly, however, it can be seen for the results of Chen et al. [3] that the highest Fe content in their study yielded lower FER values, which contradicts logic and results in the literature [21]. However, regardless of the data for the highest Fe concentration,

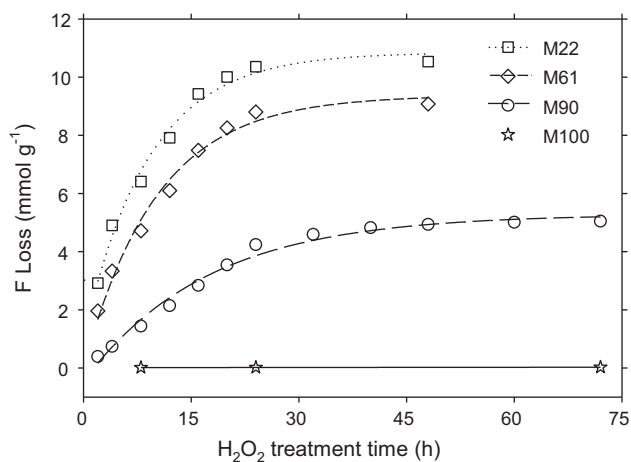


Fig. 2. Fluorine loss (emission) of Nafion membranes with various levels of Fe content as a function of H<sub>2</sub>O<sub>2</sub> exposure time.

which is questionable, it can be seen in Fig. 3 that the average FERs obtained in this study are similar and in the same range with results in Ref. [3]. The reasons for the slight differences are discussed in section 3.2. Unfortunately, other related papers in the literature do not provide sufficient detail or vary Fe content in a way to permit a comparison of average FER vs. Fe content.

### 3.2. Comparison of the fluorine loss (emission) rate (FER) reported in this work and in the literature

A comprehensive comparison of FER values obtained in this study with reported values in the literature is given in Table 2. It can be seen that the average FERs found in this work are in the same order of magnitude as those reported by other researchers. The initial FERs for degraded membranes M90, M61, and M22 are shown in Table 1. Unfortunately, these values cannot be compared as they are not given for the other studies in the literature. The discrepancies in the average values of FER are probably due to differences in properties of commercial Nafion membranes, differences in experimental procedures (e.g., frequency of solution change, method of introducing Fe<sup>2+</sup> ions, etc.), and differences in accelerated treatment conditions (i.e., temperature, H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> ion concentration, etc.).

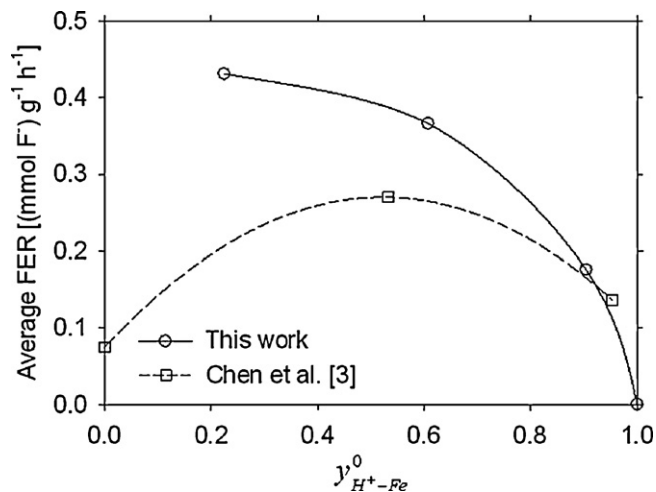


Fig. 3. Influence of Fe content in the membrane on the average rate of fluorine loss (emission) (FER) of H<sub>2</sub>O<sub>2</sub>-treated Nafion membranes.

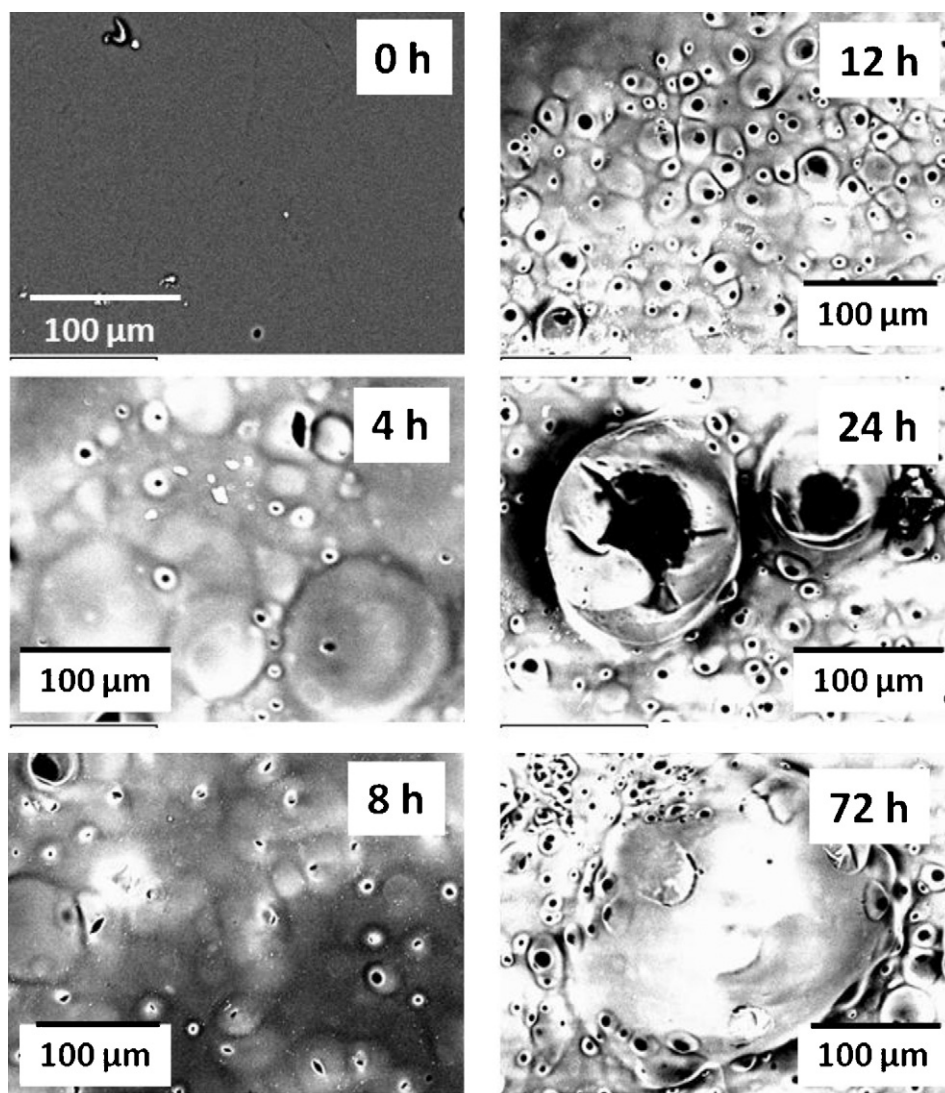
**Table 2**

Comparison of fluorine loss (emission) rates (FERs) for Nafion membranes (NRE and Nafion EW 1100 series) pretreated in different ways.

Ref.	Treatment	Temp. (°C)	Frequency of solution change	Average FER [(mmol F <sup>-</sup> ) g <sup>-1</sup> h <sup>-1</sup> ]	Δt (h)
This work	Fe <sup>2+</sup> -containing membranes were pretreated in 30% H <sub>2</sub> O <sub>2</sub> solution for 4–72 h in amber glassware (NRE-211: M100–M22).	80	Every 4 h	0.176–0.432	0–24
Sethuraman et al. [45]	The Fe <sup>2+</sup> -form of the membranes were degraded in 3% H <sub>2</sub> O <sub>2</sub> for 24–96 h (N-112: M00).	80	Every 24 h	0.018–0.050	0–24, 0–96
Chen et al. [3]	The H <sup>+</sup> -form of the membranes were soaked in 10% H <sub>2</sub> O <sub>2</sub> solution with 3–300 ppm Fe <sup>2+</sup> for 24 h (N-112: M100).	80	Every 24 h	0.070–0.260	0–24
Wang et al. [35]	The H <sup>+</sup> -form of the membranes were immersed in 30% H <sub>2</sub> O <sub>2</sub> solution containing 20 ppm Fe <sup>2+</sup> for 48–96 h and the replaced solution was concentrated prior to the fluorine analysis (N-1110: M100).	100	Every 30 min	0.016	0–48, 0–96

In this study, NRE-211 Nafion membranes (EW 1100) were used, while the other studies used Nafion membranes N-112 or N-117 (EW 1100). Although these two kinds of membranes have the same equivalent weight and similar properties, it has been reported that N-112 and N-117 membranes are more robust in H<sub>2</sub>O<sub>2</sub> solution than NRE-211 membranes [38].

As indicated in Table 2, the variation in experimental procedures for the study of Nafion decomposition for the studies in the literature and this work can be noted, for example, the difference in frequency of solution change. Fenton's reagent or the H<sub>2</sub>O<sub>2</sub> solution was renewed once every 24 h in most studies except that of Wang et al. (30 min) [35] and this study (4 h). Therefore, the reported FER



**Fig. 4.** SEM images of the surface of a M90 membrane ( $y_{\text{H}^+-\text{Fe}}^0 = 0.90$ ) after various times of H<sub>2</sub>O<sub>2</sub> treatment.

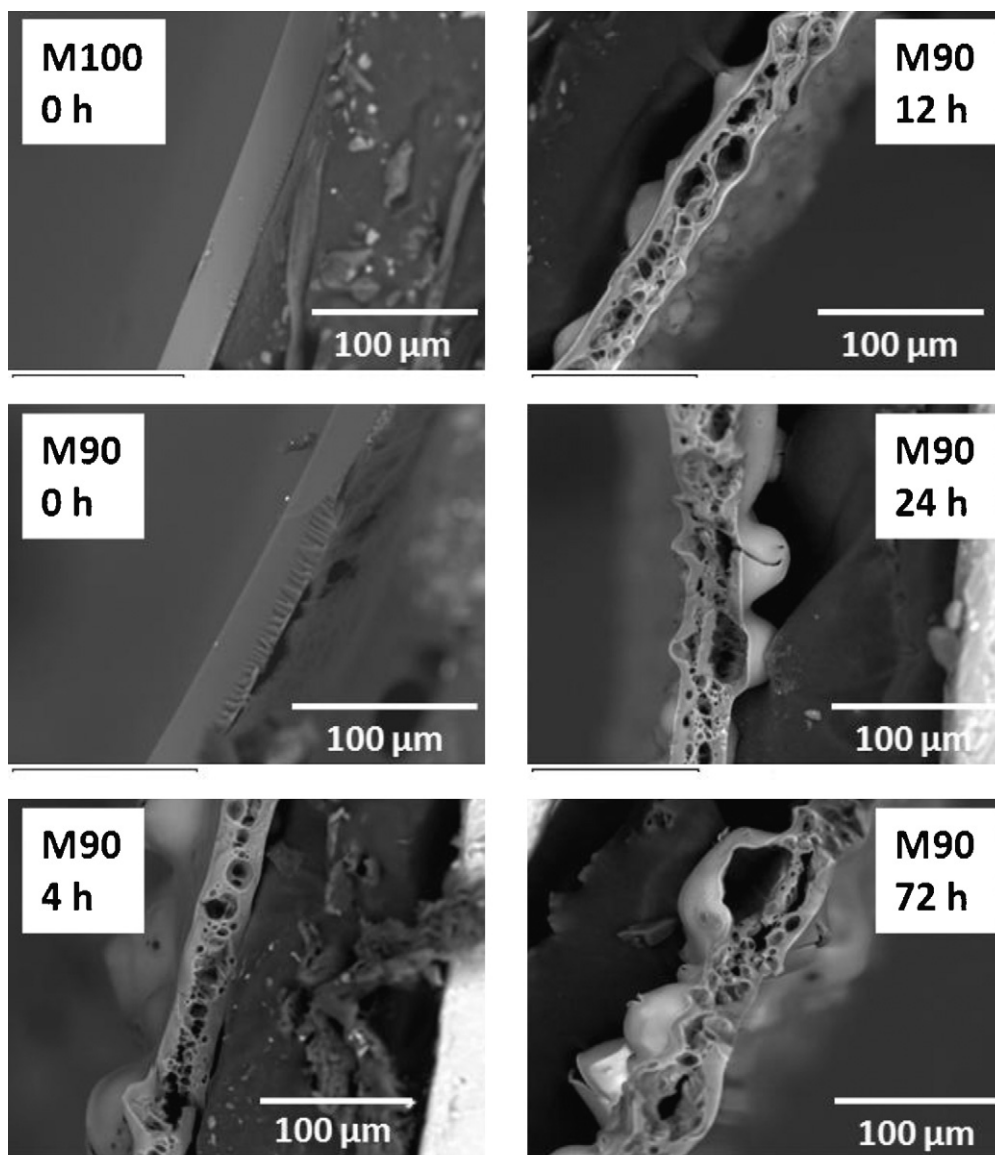


Fig. 5. Cross-sectional images of a non-H<sub>2</sub>O<sub>2</sub> treated Nafion membrane (M100-0 h) and H<sub>2</sub>O<sub>2</sub>-treated M90 membranes after treatment for various times.

values in those studies are the average FER values over 24 h. It can be seen in Table 2 that most of average FERs given in the literature are lower than those found in this study, which is partly attributed to lower total amount of H<sub>2</sub>O<sub>2</sub> during 24 h treatment in those studies than in this study. The treatment solutions in those investigations were not changed over the 24 h period, while they were changed 6 times in this work. It is well known that H<sub>2</sub>O<sub>2</sub> molecules are not stable in the presence of Nafion-Fe<sup>2+</sup>/Fe<sup>3+</sup> as indicated in Eqs. (1) and (2). Thus, the H<sub>2</sub>O<sub>2</sub> concentration continuously decreases with immersion time and, subsequently, the rate of radical attack decreases corresponding to the decrease in H<sub>2</sub>O<sub>2</sub> concentration. In addition, it has been reported that small fluorine-containing fragments (e.g., HF, CF<sub>3</sub>COOH, HCOOH-CF<sub>2</sub>-SO<sub>3</sub>H), derived from the cleavage of the polymer chain, evaporate during treatment [15]. In order to insure a constant H<sub>2</sub>O<sub>2</sub> concentration and minimize fluorine loss from a Fenton/H<sub>2</sub>O<sub>2</sub> reagent, the treated solution should be replaced as often as possible, but not too frequently as the concentration of fluorine leached out may be below detection limit. Consequently, in this study, used solution was replaced with freshly prepared solution every 4 h period to ensure constant H<sub>2</sub>O<sub>2</sub> concen-

tration and to still be able to accurately measure fluorine content. Since the loss of fluorine from degraded membranes was determined by the concentration of fluorine in used solutions and a long treatment time period (24–96 h) may result in a decrease in H<sub>2</sub>O<sub>2</sub> concentration and the evaporation of low-boiling point fluorine species, the observed FER values in the literature may be slightly underestimated and lower than values reported in this study. However, as seen in Table 2, the FER reported by Wang et al. [35] is the lowest although they renewed the solution the most often. They also stated that the collected solution was subsequently concentrated prior to the fluorine analysis which could have led to evaporation of fluorine-containing species, but they did not describe the technique or conditions in detail.

As shown in Table 2, treatment conditions as well as the introduction of Fe and H<sub>2</sub>O<sub>2</sub> in each study were also quite different, but the average FERs were comparable. It is well known that treatment conditions, for example temperature and amounts of catalyst (Fe<sup>2+</sup> ions) and reactant (H<sub>2</sub>O<sub>2</sub>), significantly affect the kinetics, rate of H<sub>2</sub>O<sub>2</sub> decomposition, and eventually rate of Nafion degradation. Moreover, while some studies pre-ion exchanged Fe<sup>2+</sup> ions

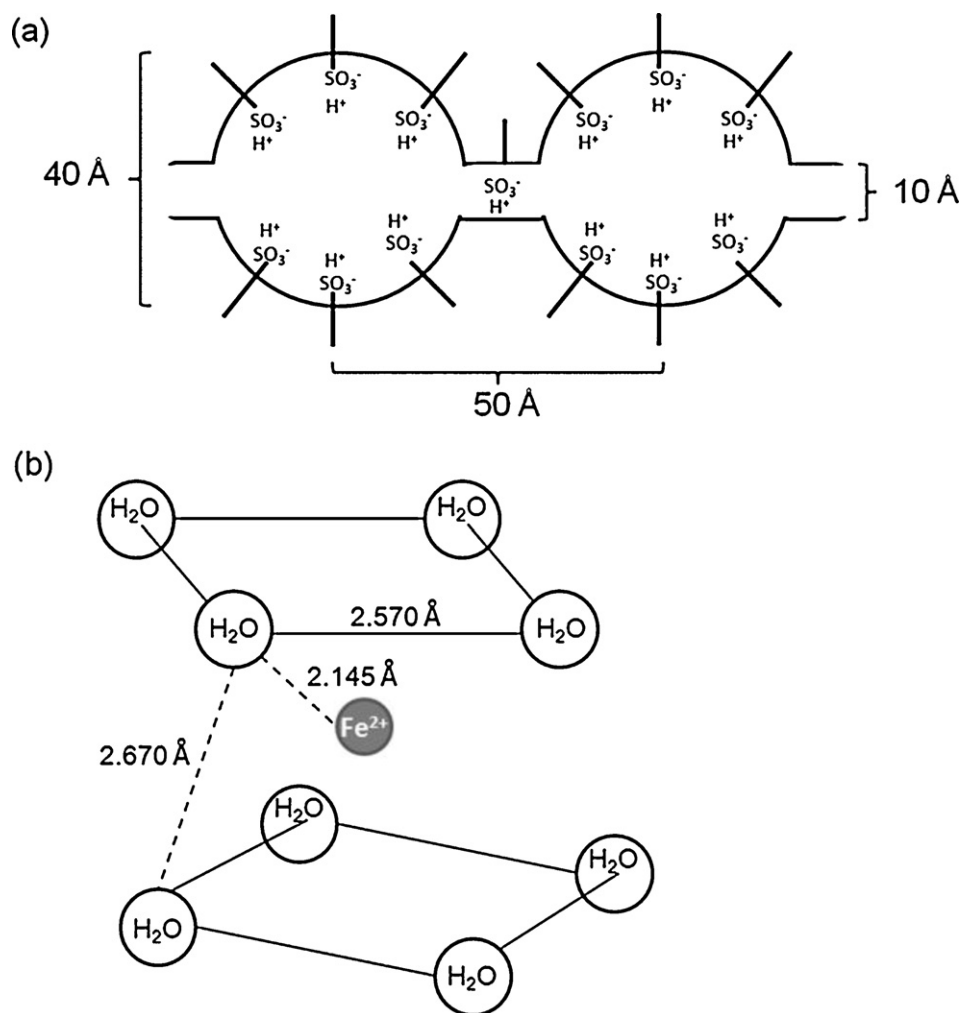


Fig. 6. (a) Ionic cluster of hydrated Nafion ionomer (redrawn from Ref. [51]) and (b) optimized structure of a  $[\text{Fe}(\text{H}_2\text{O})_8]^{2+}$  cluster (redrawn from Ref. [52]).

into a membrane before exposure to a  $\text{H}_2\text{O}_2$  solution (defined as the exchange technique), others concurrently introduced a membrane to ppm levels of  $\text{Fe}^{2+}$  ions and  $\text{H}_2\text{O}_2$  reagent (defined as the solution technique). For the exchange technique (such as used in this study),  $\text{Fe}^{2+}$  ions are allowed to penetrate into the Nafion membrane to form Nafion- $\text{Fe}^{2+}$ . Once  $\text{H}_2\text{O}_2$  reagent is introduced, the reactive radicals ( $\text{OH}^\bullet$ ,  $\text{OOH}^\bullet$ ) are formed in the proximity to the Nafion matrix, which readily facilitates chemical decomposition (more detailed discussion in section 3.3). On the other hand, for the solution technique, the presence of both  $\text{Fe}^{2+}$  ions and  $\text{H}_2\text{O}_2$  generates free radical species in the solution. Some of these active radicals recombine and form  $\text{H}_2\text{O}$  and  $\text{O}_2$  before reaching the membrane, while some initially attack the outer surface of the membrane before they diffuse into and deteriorate the interior of the membranes. Also, as Fenton's reagent ( $\text{H}_2\text{O}_2$  solution containing  $\text{Fe}^{2+}$  ions) is periodically changed, the accumulation of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions in the membrane proceeds over time since multivalent cations have much higher preference for sulfonic sites than protons [29,33,34,43]. Therefore, after prolonged exposure, the membrane is chemically attacked both internally inside the Nafion structure due to the presence of Nafion- $\text{Fe}^{2+}$ /Nafion- $\text{Fe}^{3+}$  and externally at the contact surface due to radicals derived from the addition of  $\text{Fe}^{2+}$  ions and  $\text{H}_2\text{O}_2$  in the new solution. However, if the same total concentrations of  $\text{Fe}^{2+}$  ions and  $\text{H}_2\text{O}_2$  are used, the exchange technique should degrade the membrane to a higher degree than the solution technique, which contradicts the conclusion of Kundu

et al. [24]. They studied properties of degraded Nafion membranes after treatment by the solution and exchange techniques. However, they did not investigate Fe content in the post-decomposed membranes. It is possible that the disagreement is due to differences in Fe content for membranes treated by these two techniques.

It is important to note that the Nafion ionomer is vulnerable to the reactive radicals produced by the decomposition of  $\text{H}_2\text{O}_2$  catalyzed by  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions. Accordingly, the comparison of the degree of chemical degradation and performance of treated membranes among studies in the literature should also take into account the Fe composition in a membrane and treatment conditions. In summary, regardless of differences in experimental procedures and variation in treatment conditions, the average FERs reported in this work are in the same range as those in other studies.

### 3.3. Investigation of changes in Nafion morphology after $\text{H}_2\text{O}_2$ treatment

The decomposition of the  $\text{H}^+$ -form of the Nafion membrane (M100) was investigated and no significant physical change for the membrane immersed in water or  $\text{H}_2\text{O}_2$  solution at  $80^\circ\text{C}$  for 24 h was observed (data not shown here). However, after  $\text{H}_2\text{O}_2$  treatment of Fe-containing membranes, remarkable physical changes (i.e., evolution of bubbles, significant change in the membrane's color from clear transparent to light yellow opaque, changes in membrane dimensions, etc.) were observed. The length and width



of membrane changed only slightly after  $\text{H}_2\text{O}_2$  exposure, but the thickness increased (ca. 1.5 times) due to the formation of bubbles. Fig. 4 shows the change in morphology of the membrane with  $y_{\text{H}^+-\text{Fe}}^0 = 0.90$  (M90). It can be seen that the amount and size of bubbles increase and pinholes are observed as chemical degradation proceeds. Fig. 5 presents the cross-section images of Nafion membrane samples. The progression of the decay process initially introduces small pinholes at the center of the membrane and finally splits the membrane into two halves. This finding is not consistent with results reported by Kundu et al. [24]. They observed very small bubbles that originated at the membrane surface and a non-damaged region in the center of the membrane. Since the pre-ion exchanged membranes were treated in an  $\text{H}_2\text{O}_2$  aqueous solution at  $80^\circ\text{C}$  in their study, the membranes should have been in the swollen state, and the rate of degradation should not have been limited by the rate of  $\text{H}_2\text{O}_2$  diffusion. The fact that Kundu et al. [24] did not observe the degradation (bubbles/pinholes) in the inner phase of the membrane suggests non-uniform and incomplete Fe-ion exchange in their study.

It has been previously found that the exchange process for cations (e.g.,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ) and protons ( $\text{H}^+$ ) with sulfonic groups in Nafion membranes {N-117 (175  $\mu\text{m}$ ), NRE-211 (25  $\mu\text{m}$ )} takes ca. 7–10 days to achieve equilibrium [29,50]. However, Kundu et al. [24] pre-ion exchanged membranes {N-112 (50  $\mu\text{m}$ )} in saturated solutions of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  for only 24 h. Their cross-section images suggest that 24 h was apparently not enough time for  $\text{Fe}^{2+}$  ions to neutralize all available sulfonic sites. Only the proton sites towards the exterior of the membranes were possibly ion-exchanged with the  $\text{Fe}^{2+}$  ions and formed Nafion- $\text{Fe}^{2+}$ , while the interior of the membrane was still in the  $\text{H}^+$ -form. The non-uniformly Fe-distributed membranes in their study may have possibly been due to the slow diffusion of  $\text{Fe}^{2+}$ -water clusters in the Nafion network. Fig. 6(a and b) shows the morphology of the Nafion ionomer in the hydrated form [51] and the optimum structure of  $\text{Fe}^{2+}$ -water clusters  $\{[\text{Fe}(\text{H}_2\text{O})_8]^{2+}\}$  [52], respectively. It can be seen that the size of  $[\text{Fe}(\text{H}_2\text{O})_8]^{2+}$  clusters ( $\geq 3 \text{ \AA}$ ) is relatively large compared to that of the limiting diameters of the channels of Nafion (10  $\text{\AA}$ ). It is likely that the interaction of  $[\text{Fe}(\text{H}_2\text{O})_8]^{2+}$  with sulfonic acid groups and exchange of  $\text{H}^+$  by  $\text{Fe}^{2+}$  significantly decrease the effective diameter of these channels and hinder further diffusion, resulting in non-uniform Fe distributions within the thickness direction of the membrane if sufficient time for equilibration is not allowed.

In this study, membranes {NRE-211 (25  $\mu\text{m}$ )} were allowed to ion-exchange for 7 days until no change in conductivity was observed, and this appeared to ensure equilibrium and a relatively homogeneous Fe distribution in the membranes.

#### 3.4. Investigation of Fe content in $\text{H}_2\text{O}_2$ -treated membranes

Since the uptake of cations considerably influences conductivity [29], Fe content in  $\text{H}_2\text{O}_2$ -treated membranes was also investigated to prevent misinterpretation of the effect of Nafion degradation degree on conductivity. The Fe contents of M90 membranes measured before and after 24 h  $\text{H}_2\text{O}_2$  treatment were 0.224 and 0.240 wt.%, respectively. Since the change in Fe composition of the degraded membrane was minor (7%) and the difference was within experimental error, we consider that the concentrations of Fe in the membrane were relatively constant for all membrane compositions and for all treatment times studied.

#### 3.5. Investigation of molecular structural changes in $\text{H}_2\text{O}_2$ -treated membranes

Fig. 7(a and b) presents FTIR spectra of non- $\text{H}_2\text{O}_2$  treated membranes (M100-0 h, M22-0 h) and  $\text{H}_2\text{O}_2$ -treated Fe-containing

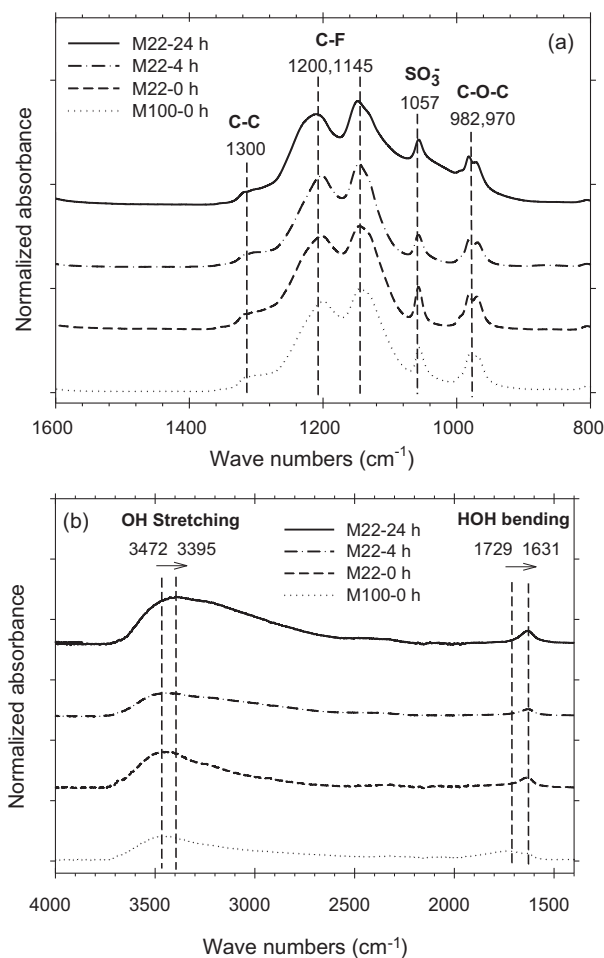


Fig. 7. FTIR spectra of non- $\text{H}_2\text{O}_2$  treated (M100-0 h, M22-0 h) and  $\text{H}_2\text{O}_2$ -treated Nafion membranes (M22): (a) wave number range 800–1600  $\text{cm}^{-1}$  and (b) wave number range 1400–4000  $\text{cm}^{-1}$ .

membrane (M22) after various exposure times. In Fig. 7(a), the C–F peaks at 1145 and 1200  $\text{cm}^{-1}$  and the C–C peak at 1300  $\text{cm}^{-1}$  represent the PTFE backbone (main chain) of a Nafion membrane. The double peaks at 970 and 982  $\text{cm}^{-1}$  assigned to the C–O–C bond, and the vibration at 1057  $\text{cm}^{-1}$  assigned to the S–O bond are characteristic peaks of the pendant side chain and sulfonic groups of Nafion, respectively. It can be seen that the heights of these normalized peaks for the main chain of all membranes appear to be similar. However, the normalized intensity of FTIR spectra for  $\text{SO}_3^-$  and C–O–C peaks of Fe-containing membranes (M22) decreases as  $\text{H}_2\text{O}_2$  treatment time increases. These results suggest that the degradation in Nafion takes place more preferentially at the sulfonic end groups and at the ether linkages located in the side chains than at the PTFE hydrophobic backbone. It has been reported that the steps for membrane deterioration is first the breaking of C–S and C–O–C bonds in the pendant side chains, followed by attack of the PTFE main chain [13]. Our finding is consistent with results in the literature [10,14,15,21,22,47,53]. However, some authors have reported that  $\text{H}_2\text{O}_2$  treatment decomposes the main chain, the side chain, and the sulfonic group with a similar rate [35,38,49].

In Fig. 7(b), the IR spectra of a non- $\text{H}_2\text{O}_2$  treated membrane (M100-0 h) show peaks at 1729 and 3472  $\text{cm}^{-1}$ , which are attributed to HOH bending and OH stretching, respectively. It can be seen that after Fe-containing membranes (M22) were subjected to  $\text{H}_2\text{O}_2$  treatment, the water vibration bands shifted to lower wave numbers (1631 and 3395  $\text{cm}^{-1}$ ). This observation indicates that the hydrogen bond of water molecules in ionic clusters is weak-

ened after  $\text{H}_2\text{O}_2$  decomposition, which is in accordance with the conclusions of Qiao et al. [13].

### 3.6. Discrepancy in the literature about loss of IEC for $\text{H}_2\text{O}_2$ -treated membranes

There is a discrepancy in the literature as to the effect of Nafion decomposition on IEC loss. Some authors have observed a loss in IEC for Nafion membranes after ex-situ treatment in a Fenton/ $\text{H}_2\text{O}_2$  reagent [10,35,44], as we observed in this study. Other investigations, however, reported no loss [4,24]. These differences are probably due to differences in membrane treatment applied before IEC determination. In this study, the IEC of degraded membranes was determined immediately after the conductivity measurement, and our results are consistent with those authors who did not modify the degraded membrane prior to IEC measurement by an ion-exchange technique. On the other hand, other authors, who did not observe any changes in IEC after chemical attack by radicals, first immersed the degraded samples in acidic solutions (e.g.,  $\text{H}_2\text{SO}_4$ , HCl) at 80–100 °C for hours or days in order to remove  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions from the membrane prior to IEC characterization [4,24].

It was found that after acid treatment, IEC of Fe-containing membranes (M22) before and after 4 h  $\text{H}_2\text{O}_2$  exposure were 897 and 891 ( $\mu\text{mol H}^+$ )  $\text{g}^{-1}$ , respectively, which were very similar within experimental error to the IEC of a Nafion membrane in the original  $\text{H}^+$ -form [928 ( $\mu\text{mol H}^+$ )  $\text{g}^{-1}$ ]. This finding provides an explanation for the discrepancy in IEC loss results reported by researchers who did or did not perform acid treatment prior to IEC analysis. It is important to note that a decrease in the absorbance intensities for the  $\text{SO}_3^-$  bond in  $\text{H}_2\text{O}_2$ -treated M22 was observed (see M22-4 h in Fig. 7(a)), which indicates the lost of sulfonic sites [Eq. (12)] from the membrane. Surprisingly, it was found that the IEC of M22 did not decrease after exposure to both  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  solutions (891 ( $\mu\text{mol H}^+$ )  $\text{g}^{-1}$ ). It has been proposed that the  $\text{H}_2\text{O}_2$  degradation process via side chain cleavage during exposure to  $\text{H}_2\text{O}_2$  produces carboxylic acid end groups [15] and forms carbonyl functional groups on the Nafion matrix [3]. It is possible that these weak polymer groups are replaced by sulfonic acid moieties [54] and the cross-linked bonds of S-O-S,  $\text{SO}_2\text{-O-SO}_2$ , and/or  $\text{SO}_2\text{F}$  are modified during treatment in a  $\text{H}_2\text{SO}_4$  solution at high temperature (80 °C) for a long period of time, causing reformation of exchangeable sulfonic sites.

FTIR analysis was also performed to study the change in molecular structure due to acid treatment. Fig. 8(a and b) presents FTIR spectra of  $\text{H}_2\text{O}_2$ -treated membranes (M22) before and after acidic treatment and of a non- $\text{H}_2\text{O}_2$  treated membrane (M100-0 h). The spectrum for M100-0 h is included in order to study the recovery of the state of water upon acid treatment, which will be mentioned later. Fig. 8(a) illustrates that the peak height at 1057  $\text{cm}^{-1}$  (representing the existence of  $-\text{SO}_3\text{H}$  groups) of a  $\text{H}_2\text{O}_2$  treated membrane after acid treatment [M22-4 h (after acid treat.)] is similar to that of a non- $\text{H}_2\text{O}_2$  treated membrane (M100-0 h) and slightly higher than that before acid treatment (M22-4 h). This suggests that an increase in sulfonic acid groups occurred as a result of acid exposure. As shown in Fig. 8(b), shifts in the vibration bands for HOH bending and OH stretching to lower wave numbers for the  $\text{H}_2\text{O}_2$ -treated membranes were observed and the position for water peaks of the degraded membranes after acidic treatment [M22-4 h (after acid treat.)] look very similar to those of the non- $\text{H}_2\text{O}_2$  treated membrane. Thus, although cross-linking between two sulfonic end groups can occur and the hydrogen bonding of water molecules in the ionomer be weakened during  $\text{H}_2\text{O}_2$  exposure, an IEC investigation and FTIR study suggest that both can be recovered upon acid treatment.

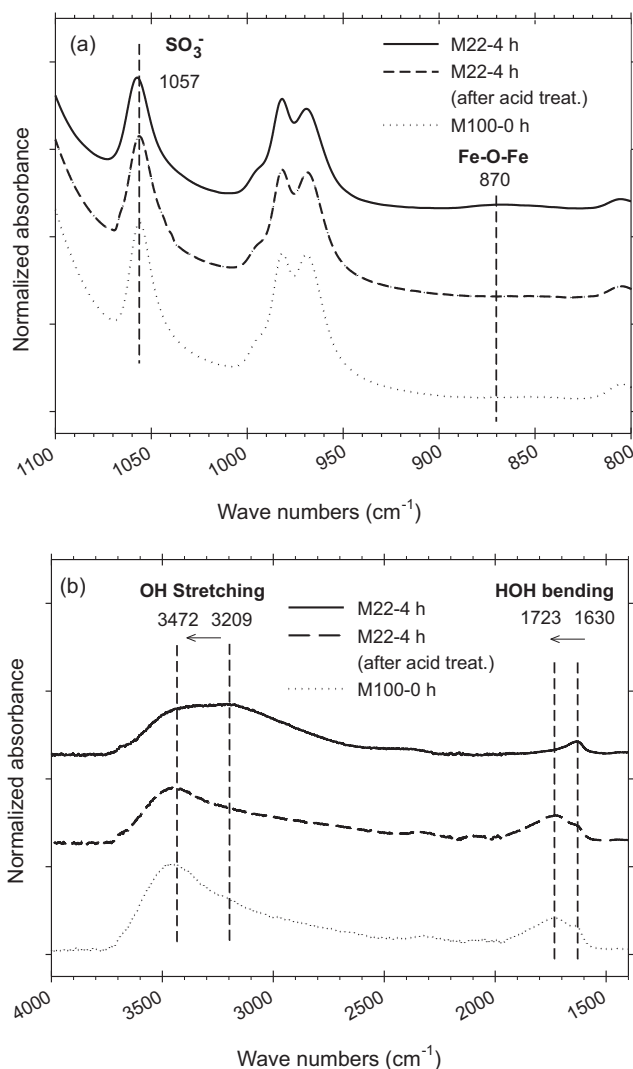


Fig. 8. FTIR spectra of  $\text{H}_2\text{O}_2$ -treated (4 h) Nafion membranes (M22) before and after acidic treatment: (a) wave number range 800–1100  $\text{cm}^{-1}$ , and (b) wave number range 1400–4000  $\text{cm}^{-1}$ .

### 3.7. Effect of $\text{H}_2\text{O}_2$ treatment and Fe composition on water content of Nafion membranes

It is known that protons are transported in Nafion by the Grötthuss and vehicle mechanisms [55,56] and that these processes involve the hopping of protons via the water network and the diffusion of  $\text{H}_3\text{O}^+$  ions through the Nafion structure, respectively. Therefore, the efficiency of proton transport depends very strongly on the amounts of water adsorbed [57] and the state of water in the Nafion ionomer. A quantitative investigation of water content is, thus, necessary for the full understanding of conductivity behavior. To date, there are few investigations examining water uptake of  $\text{H}_2\text{O}_2$ -treated membranes. A few studies have reported measuring the water content of degraded membranes equilibrated in DI water at ambient temperature [5,13], but such conditions are not related to optimum fuel cell operation (50–100%RH and 60–80 °C). It was found that, under those conditions (DI water at ambient temperature), protons are mainly transported via bulk water existing at the middle of ionic clusters, not via the water attached to sulfonic sites, and these two kinds of water decrease with an increase in  $\text{H}_2\text{O}_2$  treatment time [13]. Accordingly, in this study, the water uptake of Nafion membranes with various degradation degrees at

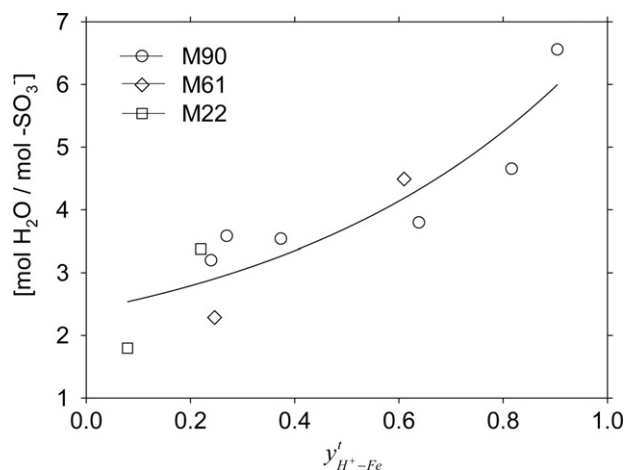


Fig. 9. Water uptake at 100%RH and 80 °C of H<sub>2</sub>O<sub>2</sub>-treated Nafion membranes as a function of  $y_{H^+-Fe}^t$ .

typical conditions for a stationary PEMFC (100%RH and 80 °C) was quantitatively investigated for the first time.

Fig. 9 shows the influence of proton composition ( $y_{H^+-Fe}^t$ ) on water adsorption ( $\lambda_{H_2O}$ ) of Fe-containing membranes (M90, M61, M22) at 100%RH and 80 °C. The water content of these membranes prior to H<sub>2</sub>O<sub>2</sub> exposure agrees well with the previous findings [28]. It can be seen that as  $y_{H^+-Fe}^t$  decreases due to radicals attack from H<sub>2</sub>O<sub>2</sub> decomposition, water uptake of the membranes decreases. This finding is consistent with Qiao et al. [13], who observed a decrease in water uptake of degraded membranes equilibrated in DI water at ambient temperature. It was found that the kinetics of  $X_{IEC}$  decrease correspond with those of water content for M90 (data not shown here). This observation suggests that the amount of water adsorption depends strongly on the proton concentration in a membrane.

### 3.8. Effect of H<sub>2</sub>O<sub>2</sub> treatment on Nafion conductivity at fuel cell conditions

Fig. 10(a and b) illustrates the influence of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> treatment of on Fe-containing membranes (M90) on conductivity at various humidities and 80 °C. It can be seen that the effect of water treatment on the conductivity of the M90 membrane was minor. The conductivity slightly increased with an increase in H<sub>2</sub>O immersion time, possibly because of membrane swelling after long exposure time to hot water. However, the effect of H<sub>2</sub>O<sub>2</sub> treatment on the conductivity of the Fe-containing membrane (M90) was severe. The conductivity significantly decreased with H<sub>2</sub>O<sub>2</sub> exposure time and reached a plateau after 24 h, corresponding very well with the characterizations of degraded membranes as shown in Fig. 1.

Fig. 11(a–d) demonstrates the effect of Nafion degradation and Fe composition on conductivity at typical fuel cell conditions (30–100%RH and 80 °C). The conductivities of all Fe-containing membranes prior to H<sub>2</sub>O<sub>2</sub> exposure were consistent with the results from our previous study [29]. It can be seen that, for the same Fe content, a lesser effect on the conductivity at higher humidities is observed, which is probably because of the higher water adsorption and a more flexible structure at higher humidities.

Surprisingly, although minor degradation of the non-Fe containing membrane (M100) subjected to H<sub>2</sub>O<sub>2</sub> treatment was observed (Table 1), the conductivity at a given %RH as shown in Fig. 11(a) decreased to a much lower extent than for Fe-containing membranes. The slight decrease in conductivity was possibly due to changes in the state of water in the hydrophilic region. FTIR spec-

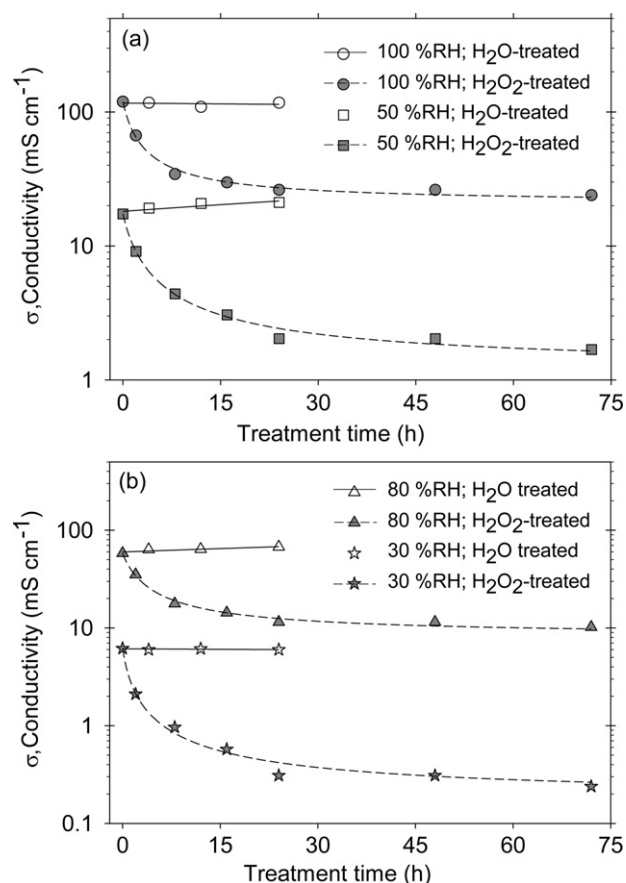


Fig. 10. Conductivities at 80 °C of M90 membranes as a function of H<sub>2</sub>O or H<sub>2</sub>O<sub>2</sub> treatment time: (a) 50 and 100%RH, (b) 30 and 80%RH.

tra for M100 revealed that the position for water peaks was slightly shifted after 24 h exposure to H<sub>2</sub>O<sub>2</sub> (data not shown).

In Fig. 11(b–d), on the other hand, a significant decrease in conductivity for Fe-containing membranes subjected to H<sub>2</sub>O<sub>2</sub> treatment can be observed, which was attributed to chemical decomposition of Nafion samples and lower water uptake in the Nafion structure. Qiao et al. [13] reported that H<sub>2</sub>O<sub>2</sub> treatment also influences the entanglement level and the evolution of cross-linking between two sulfonic end groups in the hydrophilic cluster (S–O–S bond), resulting in a decrease in the strength of hydrogen-bonded water, lower water uptake, and ultimately lower ionic conductivity. As can be seen in Fig. 11(b–d), the change in conductivity upon exposure to H<sub>2</sub>O<sub>2</sub> increases as the Fe content in the membranes increases, except for M22. This may be due to major changes in the Nafion structure. Significant dimension changes in the decomposed membranes (M22) were clearly observed. The dimensions (length × width × thickness) before and after 24 h treatment were 5.5 cm × 1 cm × 0.035 cm and 3.5 cm × 0.6 cm × 0.054 cm, respectively. This observation implies that, at high Fe composition in the membrane, the process for ionomer scission is fast and Nafion structure is severely deteriorated. For that reason, the molecular weight of the Nafion ionomer may be decreased, and the state of water in the hydrophilic cluster may be affected, resulting in an open structure and an increase in water mobility. Also, since prior to H<sub>2</sub>O<sub>2</sub> exposure, the conductivity of the Fe-exchanged membrane (M22) had already been impaired by high Fe content, the effect of H<sub>2</sub>O<sub>2</sub> treatment on conductivities at 24 h relative to those at 0 h may appear to be moderate.

In addition, the conductivity of membranes containing various Fe contents but similar F losses was also studied. As can be seen

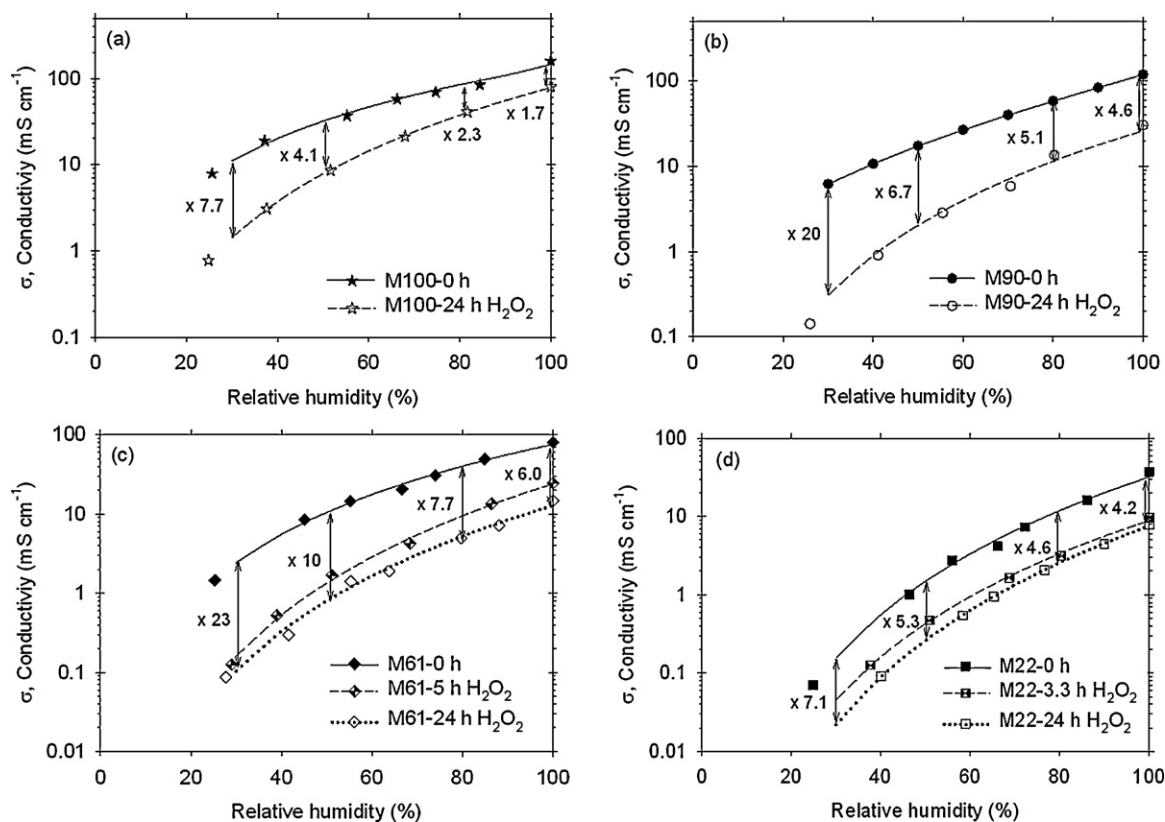


Fig. 11. Conductivities at 80 °C of Nafion membranes after various H<sub>2</sub>O<sub>2</sub> exposure times: (a) M100, (b) M90, (c) M61, and (d) M22.

from Fig. 2, the F loss of M90 after 24 h exposure to H<sub>2</sub>O<sub>2</sub> is ca. 4.24 mmol g<sup>-1</sup>. The exposure times required for M61 and M22 to lose similar F were 5 h and 3.3 h, respectively. In Fig. 11(b–d), it was found that the conductivities at 24 h of M90 (M90-24 h H<sub>2</sub>O<sub>2</sub>) were higher than those at 5 h of M61 (M61-5 h H<sub>2</sub>O<sub>2</sub>) and those at 3.3 h of M22 (M22-3.3 h H<sub>2</sub>O<sub>2</sub>), respectively. The differences in conductivities were probably because of the differences in  $y_{\text{H}^+ - \text{Fe}}^f$ .

#### 4. Conclusions

The effect of H<sub>2</sub>O<sub>2</sub> on Nafion properties and conductivity at conditions relevant for fuel cell operation was quantitatively investigated for the first time in this study. After Fe-contaminated membranes were subjected to H<sub>2</sub>O<sub>2</sub> solutions, major changes in physical morphologies and chemical properties of degraded samples were observed. The H<sub>2</sub>O<sub>2</sub>-treated membranes appeared to be more opaque and contained a lot of bubbles. Cross-section images show that the oxidative radicals (OH•, OOH•) internally and externally attacked the membranes, created pinholes, and finally split the membranes into two halves. The destruction of the Nafion matrix and chain shortening of the polymer structure after exposure to H<sub>2</sub>O<sub>2</sub> caused losses of sulfonic acid groups, ionic fragments, and polymer repeating units. In this study, the degree of degradation was measured by the fractional losses in ion-exchange capacity ( $X_{\text{IEC}}$ ), weight ( $X_W$ ), and fluorine content ( $X_F$ ). It was found that plots of these losses vs. H<sub>2</sub>O<sub>2</sub> treatment time for membranes with all Fe concentrations had similar trends, but the values for  $X_{\text{IEC}}$ ,  $X_W$ , and  $X_F$  were higher for membranes with higher Fe content. However, the values for  $X_{\text{IEC}}$  were always higher than those of  $X_W$  and  $X_F$  for all Fe compositions. The experimental results suggest that H<sub>2</sub>O<sub>2</sub> exposure not only causes the loss of sulfonic groups from the side chain by cleavage but also initiates the crosslinkage of sulfonic sites on the pendant side chains (S–O–S bond, SO<sub>2</sub>–O–SO<sub>2</sub>, and/or SO<sub>2</sub>F) in the

Nafion structure. In addition, FTIR results revealed that the hydrogen bond of water molecules in Nafion clusters was weakened upon H<sub>2</sub>O<sub>2</sub> treatment. However, both the reformation of –SO<sub>3</sub>H and the recovery in the state of water occur after acidic treatment.

The comprehensive comparison for Nafion degradation levels [e.g., fluorine loss (emission) rates (FERs),  $X_{\text{IEC}}$ , etc.] and explanation for the discrepancy of these values reported in many investigations have also been given and clarified. It was found that average FERs observed in this study were remarkably similar to the results available in the literature, considering differences in treatment conditions and variation in experimental procedures.

The water uptake ( $\lambda_{\text{H}_2\text{O}}$ ) and conductivity of degraded Nafion membranes at normal fuel cell conditions were quantitatively examined. It was found that H<sub>2</sub>O<sub>2</sub> treatment considerably decreases the H-bond strength among water molecules, water uptake, and conductivity of Nafion membranes. The water content of membranes for all Fe compositions decreased by ca. 50% after exposure to H<sub>2</sub>O<sub>2</sub> for 24 h, and the conductivity decreased by ca. 44–80% depending on H<sub>2</sub>O<sub>2</sub> treatment time.

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