Degradation of proton exchange membrane by Pt dissolved/deposited in fuel cells

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Abstract−An accelerated single cell test and single electrode cell test were carried out to investigate membrane degradation by Pt dissolved/deposited on the membrane. For a cell operating under accelerated conditions (OCV, 90 °C, anode RH 0%, cathode O_2 supply), MEA analyses revealed that Pt particles were deposited in the membrane at the anode side, with a decrease in F, O, and C content near the anode side of the membrane. Dissolved Pt from the cathode showed that Pt existed mainly in the form of Pt^{2+} ionic species. Oxygen and hydrogen helped Pt dissolution from the cathode and Pt deposition in the membrane, respectively. Radical formation on deposited Pt in the membrane was detected by electron spin resonance (ESR). Fluoride emission rate (FER, an indicator of membrane degradation rate) increased with an increase in the amount of Pt in the membrane.
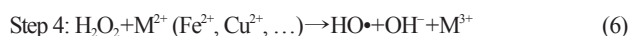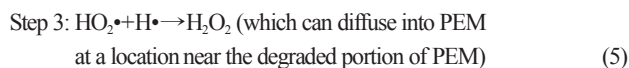
Key words: PEMFC, Membrane Degradation, FER, Pt Dissolution, Oxygen Radical

INTRODUCTION

In proton exchange membrane fuel cell (PEMFC) commercialization, durability and lifetime are the most important issues. Fuel cell lifetime requirements range from hundreds of hours for potable applications to 5,000 h or longer for automotive applications to 40,000 h or longer for stationary applications [1]. But, sufficient durability to meet this demand has not been established. Membrane degradation is one of the most important factors limiting the lifetime of PEMFC. So it is important to understand the mechanism of its degradation.

The mechanism by which the polymer membrane in PEMFC can undergo electrochemical degradation was established by General Electric (GE) in the 1960s. However, this mechanism continues to be debated.

According to mechanism established by GE [2], as shown below, H_2O_2 generated at the anode diffuses into the membrane and reacts with bivalent metal cations (M^{2+}) present as impurities in the membrane to form active oxygen species, which can then attack the polymer and degrade the membrane.

Step 1: $H_2 \rightarrow 2H\bullet$ (via Pt catalyst) $\qquad$ (3)

Step 2: $H\bullet + O_2$ (diffused through PEM) $\rightarrow HO_2\bullet$ $\qquad$ (4)

Step 3: $HO_2\bullet + H\bullet \rightarrow H_2O_2$ (which can diffuse into PEM
$\qquad$ at a location near the degraded portion of PEM) $\qquad$ (5)

Step 4: $H_2O_2 + M^{2+}$ (Fe^{2+}, Cu^{2+}, …) $\rightarrow HO\bullet + OH^- + M^{3+}$ $\qquad$ (6)

Step 5: $\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet$ $\qquad$ (7)

In 2005, Liu et al. [3] reported that radicals could be formed directly on the Pt surface by the reaction between H_2 and O_2 without H_2O_2 formation. Mittal et al. [4] reported that H_2O_2 was not the main cause of membrane degradation.

Since the early 2000s, several studies on membrane degradation have focused mainly on Pt catalyst. In 2007, Mittal et al. [5] reported that the yield of the membrane-degrading species was affected by a change in Pt surface properties. In 2002, Patterson et al. [6] first reported that dissolved Pt from the electrode existed in the membrane. Wang et al. [7] found that the equilibrium concentration of dissolved Pt increased monotonically from 0.65 to 1.1 V and decreased at potentials >1.1 V. According to the study of Ohama et al. [8], Pt bands present in the membrane caused membrane degradation. These recent studies throw considerable doubt on the mechanism established by GE.

In 2004, Endoh et al. [9] observed the radical generation under PEMFC operation. Detection of oxygen radicals such as $\bullet OH$ or $HO_2\bullet$ is difficult because of their short lifetime. Therefore, these researchers clarified the existence of oxygen radicals through indirect measurement of carbon radicals. If radicals that attack the membrane have a short lifetime, degradation should occur only on the portion of the membrane close to the catalyst. However, there are many examples in our experiments where membrane degradation was not limited to the area of the membrane near the catalyst. Our recent findings on Pt dissolution/deposition in the membrane help to explain these membrane degradations.

Using MEA we performed we investigated the mechanism by which dissolved/deposited Pt causes membrane degradation by performing accelerated single cell operation and cell operation assembled

with a single electrode. In this study, various postmortem analyses.

EXPERIMENTAL

1. Cell Test

1-1. Single Cell Test

Accelerated degradation tests were performed using a 25-cm^2 single cell. This cell assembled with commercial MEA, GDL, teflon gaskets, bipolar plates, and end plates was installed in a fuel cell test station (C&L Co.).

To attain the highest level of performance, the cell was preconditioned for 24 h under a constant current mode.

Initial cell performance was measured at 70 °C with hydrogen and air gases humidified at 70 °C. After operating under OCV/anode dry conditions for 144 h, the cell was preconditioned once again, and the cell performance was measured and compared with the initial performance.

Membrane degradation was evaluated by measuring OCV changes, hydrogen crossover, and AC impedance. Used membrane was observed by scanning electron microscopy (SEM)/EDS and transmission electron microscopy (TEM).

Hydrogen crossover was determined electrochemically [10]. The hydrogen side was used as the reference and counter electrode, and the nitrogen side was used as the working electrode. H$_2$ and N$_2$ gases were fed into the anode and cathode at 40 and 200 ml/min, respectively, at atmospheric pressure. Voltage from 0 to 0.5 V was introduced in the cathode by using a potentiostat (Solatron, SI 1287). Hydrogen that crossed over to the cathode was oxidized by the application of a voltage, and the resulting currents were measured.

1-2. Cell Test with a Single Electrode

A Nafion 112 membrane (DuPont) and an E-TEK electrode (0.4 mg Pt/cm^2) were used in the cell operation with a single electrode (anode only or cathode only) [11]. In the anode only mode, the electrode was exposed to H$_2$, and air (or O$_2$) was used as the reactant on the other side. In the cathode only mode, the electrode was exposed to air (or O$_2$), and H$_2$ was used as the reactant on the other side. The cell with 5 cm^2 active area was operated at 90 °C and 30% RH under OCV conditions. The reactant gas flow rates of the anode and cathode were set at 300 ml/min.

2. Analyses

Water from the anode and cathode effluents was analyzed for the presence of fluoride ions with a fluoride ISE meter (ion selective electrode meter, PH-250L, ISTEK, Inc.). FERs were calculated from the concentration of fluoride in the effluent water and the condensation rate of water.

The dissolved Pt ionic species in the membrane were analyzed by using a UV-visible spectrophotometer (UV-1650PC, SHIMADZU). The fresh and used membranes were immersed in 1.33 M NaCl at room temperature for 12 days. The solutions were filtrated and absorption spectra were recorded from 200 to 400 nm.

Pt deposited in the membrane was observed with a transmission electron microscope (TEM, Tecnai F20, Philips) at an accelerating voltage of 200 kV. The membrane used in the analysis was sliced by ultramicrotome.

Amounts of dissolved/deposited Pt in membranes were measured by inductively coupled plasma (ICP) spectrometry. Membrane samples were immersed in aqua regia (HCl : HNO$_3$=3 : 1) for 24 h to extract Pt particles and Pt ionic species that existed in the membrane.

The generation of radicals on Pt in the membrane was measured by an electron spin resonance (ESR) spectrophotometer (JEOL, JES-FA200).

RESULTS AND DISCUSSION

1. Location of Pt and Membrane Degradation After Acceleration Test

The cell was operated under OCV/anode dry conditions at 90 °C for 144 h. Instead of air, oxygen gas at RH 65% was supplied to the cathode to enhance the Pt dissolution rate. The use of pure oxygen gas increases the rate of oxygen crossover through the membrane because the partial pressure of oxygen increases five times as much as that of air. This process also raises the voltage at the
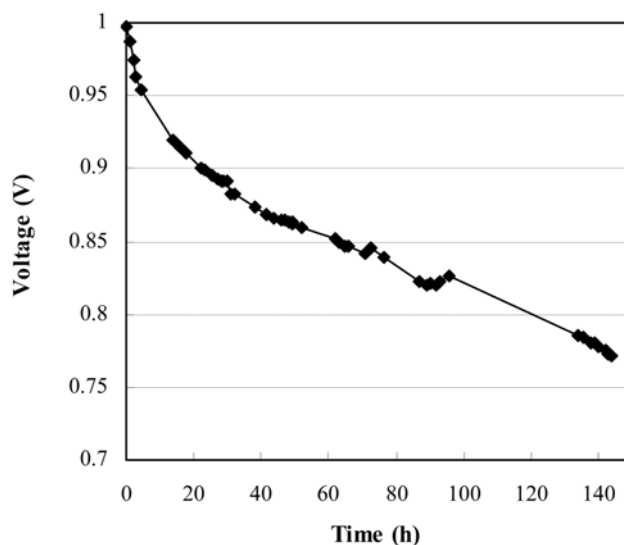

Fig. 1. OCV changes during cell operation under OCV/anode dry conditions at 90 °C for 144 h.
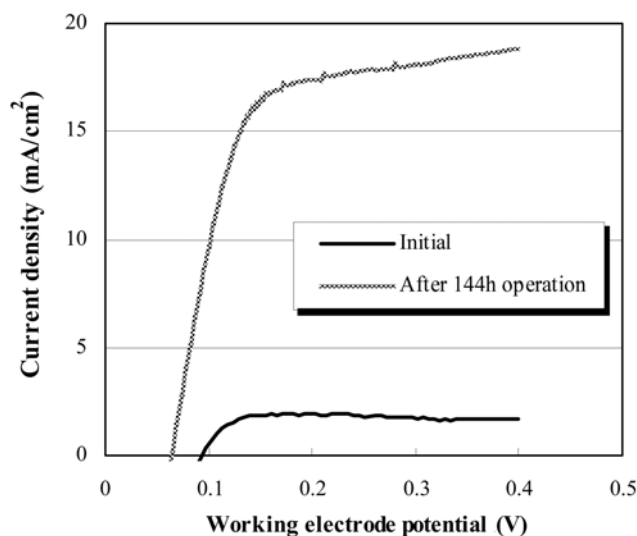

Fig. 2. Hydrogen crossover current of a cell operated under OCV/ anode dry conditions at 90 °C for 144 h.

cathode and results in an increase in the Pt dissolution rate.

Fig. 1 shows the remarkable OCV decrease during cell operation under OCV/anode dry conditions. Initially, the value of OCV was very high because of the partial pressure increase caused by oxygen gas supply. However, the increase in gas crossover (Fig. 2) by membrane degradation decreased the partial pressure of hydrogen and oxygen on the electrodes and resulted in an OCV decrease. Because of the increase in hydrogen crossover and the decrease in the efficiency of the electrodes, as measured by ac impedance (Fig. 3), cell performance greatly decreased after cell operation under the accelerating condition, as shown in Fig. 4. The value of FERs (data not shown) also increased remarkably. Therefore, a severely degraded membrane sample was obtained.

After removing the electrodes, we analyzed the membrane was analyzed by SEM/EDS (Fig. 5). In the left side of the graph, corresponding to the anode side, a significant decrease in the quantities of F, O, and C was observed. This reduction was caused by the relatively greater amount of Pt that existed on the anode side than that on the cathode side. Although Pt catalysts were dissolved from the cathode, they diffused through the membrane and were deposited by contact with hydrogen supplied from the anode and generated radicals that caused membrane degradation. Thus, chemical bonds of the membrane were decomposed by this radical attack, and accordingly, the F, O, and C concentrations in the membrane near the anode side decreased. The existence of Pt particles deposited in the
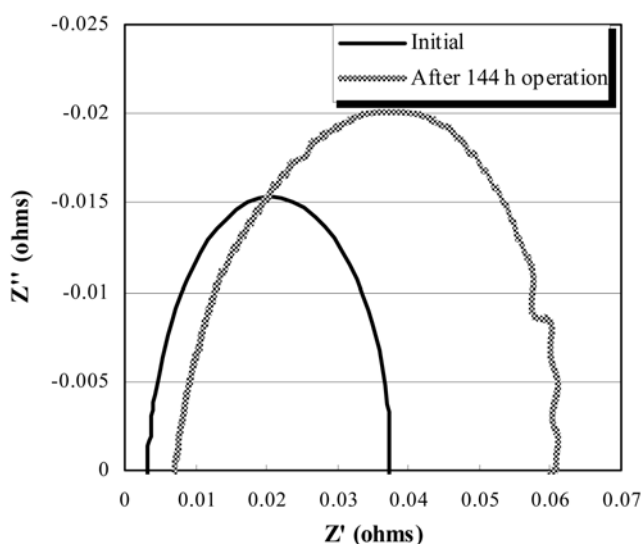

Fig. 5. SEM/EDS spectrum of the membrane after cell operation under OCV/anode dry conditions at 90 ºC for 144 h.

Fig. 3. Nyquist plots of cell performance before and after cell operation under OCV/anode dry conditions at 90 ºC for 144 h.
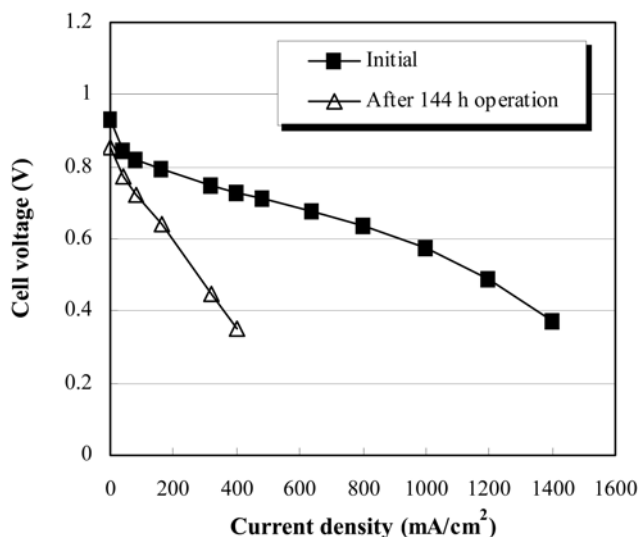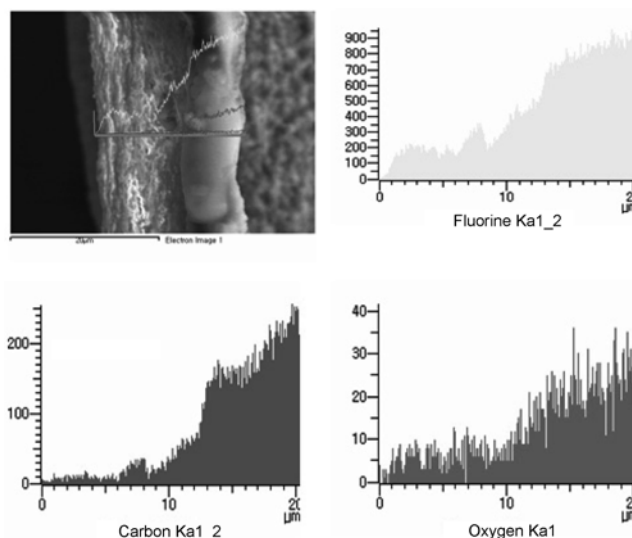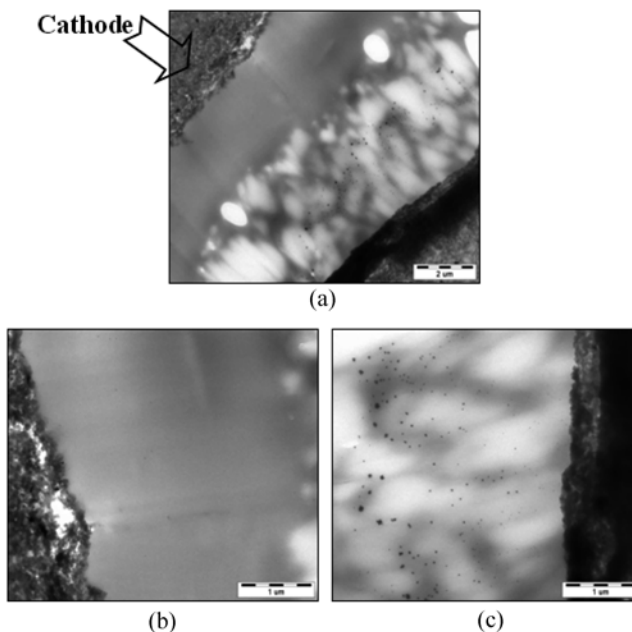

Fig. 6. Cross-sectional TEM images of the membrane degraded under OCV/anode dry conditions at 90 ºC for 144 h.
(a) TEM image of the entire membrane area; (b) TEM image of the membrane near the cathode, and (c) TEM image of the membrane near the anode

Fig. 4. Comparison of cell performance before and after cell operation under OCV/anode dry conditions at 90 ºC for 144 h.

membrane near the anode side was confirmed by TEM (Fig. 6).

2. Correlation between Dissolved/Deposited Pt and FER

To further understand membrane degradation caused by Pt dissolved/deposited in the membrane, cells assembled with only a single electrode were tested, and the disassembled MEAs were analyzed.

To dissolve Pt catalyst from the electrode onto the membrane, the cells were operated in the cathode only mode for three different times (10, 20 and 30 h). Air was supplied to the electrode side, and H_2 was supplied to the nonelectrode side. The reactant gas was switched by the cell hardware switch, and the cells were operated for 10 h. Before gas switching, the cells were purged for 2 h with N_2 on both sides of the anode and cathode.

Fig. 7 shows the result of FERs before and after gas switching. After gas switching, FER values increased markedly. In Fig. 7(b), FER increased with contact time increase in air, and FER values on the nonelectrode side (air contact) were higher than those on the electrode side (hydrogen contact). After FER measurement, the cells were disassembled, and the amount of Pt dissolved/deposited in
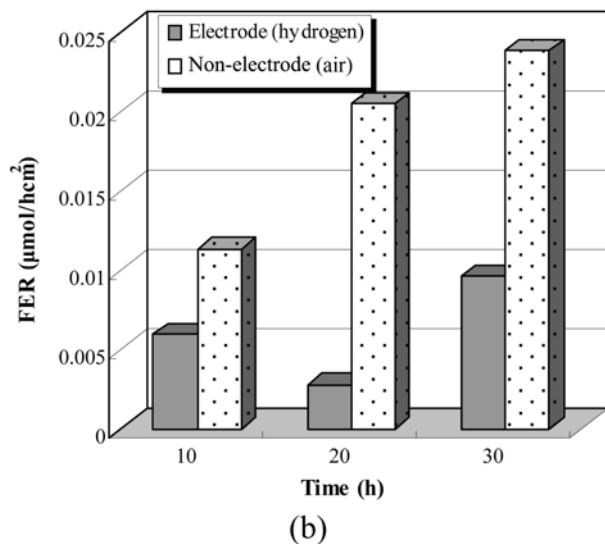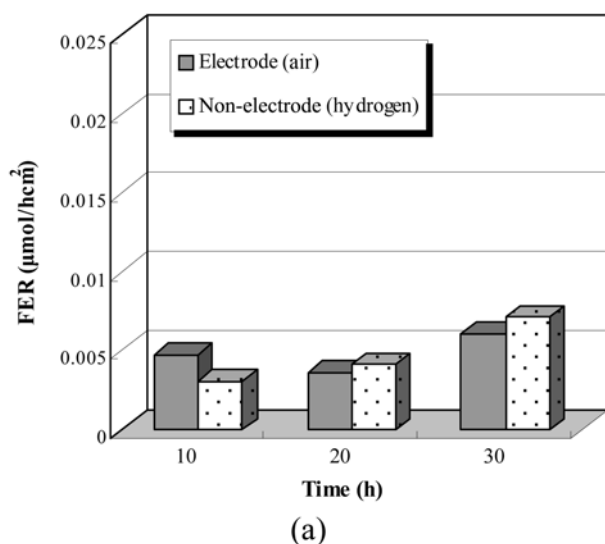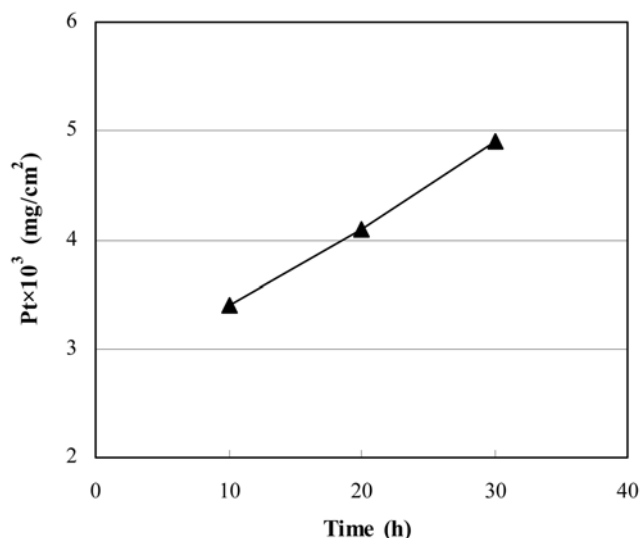

Fig. 8. Amount of Pt dissolved/deposited in the membrane after cell operation with a single electrode.
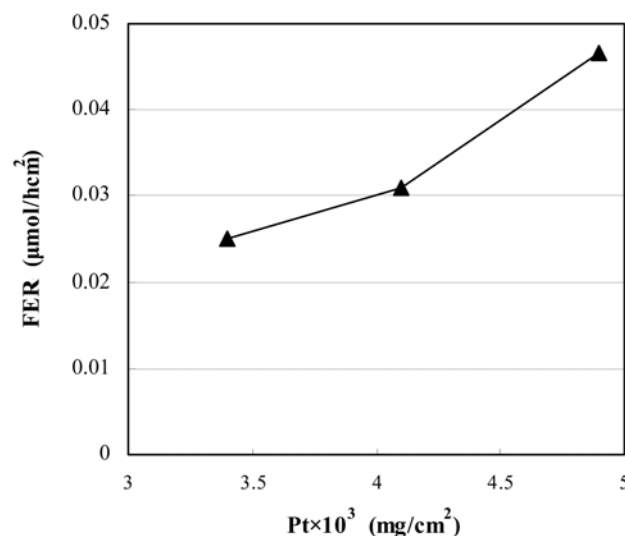

Fig. 9. Correlation between FER and the amount of Pt dissolved/deposited in the membrane after cell operation with a single electrode.

the membrane was measured by ICP spectrometry (Fig. 8). With an increase in test time, the amount of Pt dissolved/deposited in the membrane increased.

Fig. 9 shows the correlation between FER and the amount of Pt dissolved/deposited in the membrane. The increase in FER value was directly related to the increase in the amount of Pt in the membrane. As shown by Ohma et al. [8], this increase in FER values reflects H_2O_2/radical generation that leads to membrane degradation, which is ultimately caused by Pt deposited in the membrane. The increase in FER values on the nonelectrode side after gas switching seems to depend on the increase in the amount of Pt deposited in the membrane as well as on the gas diffusion rate. Because the Pt particles were deposited in the membrane near the nonelectrode side, O_2 might easily reach to the deposited Pt because of the short

(a)

(b)

Fig. 7. FER from the electrode and nonelectrode sides (a) before and (b) after gas switching.

diffusion distance despite the slow diffusion rate of O_2.

3. Cell Operation by Gas Switching and TEM Analysis

In the anode only mode, the reactant gases were switched repeatedly, and the change in FER values was measured. The electrode was contacted with H_2-air-H_2-air-H_2 in that order. The cell was operated at 90 °C and 30% RH. As shown in Fig. 10, when air made contact with the electrode, a dramatic increase in FER values was observed. Mittal et al. [4], in a study similar to our experiment, explained this phenomenon, as a surface change of Pt catalyst during
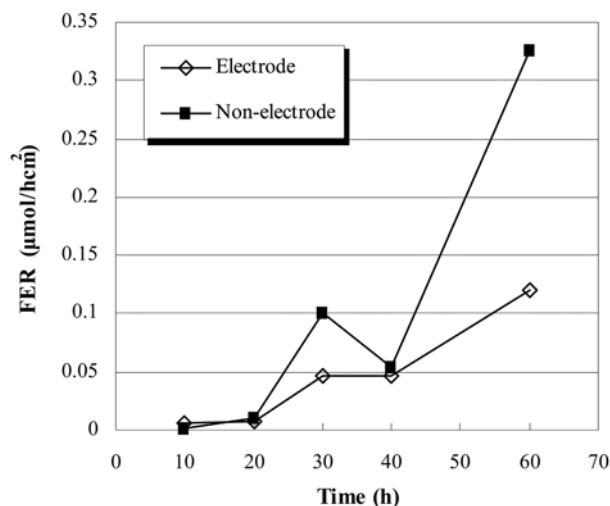

Fig. 10. Change in FER from electrode and nonelectrode sides during repeated reactant gas switching.
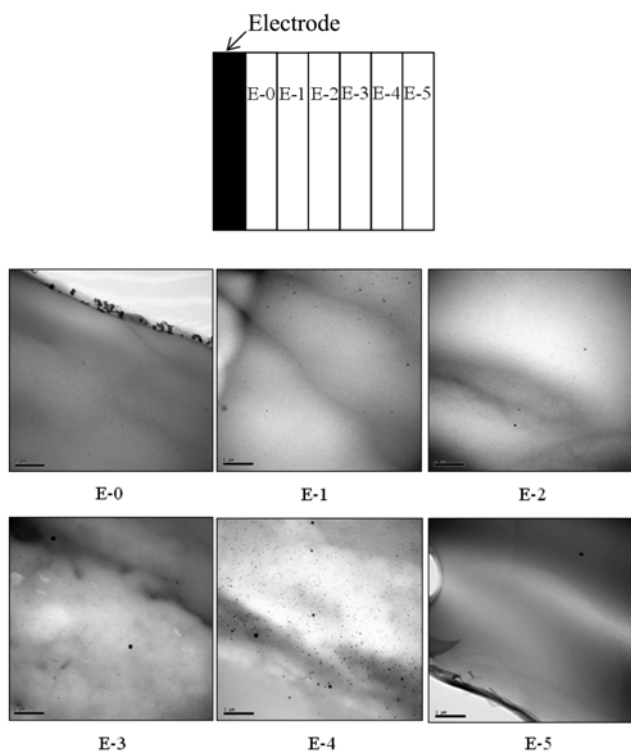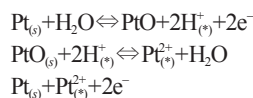

Fig. 11. Cross-sectional TEM images of the membrane after repeated reactant gas switching.

air contact, although they could not comprehend the reason for it.

We observed an increase in FER on the nonelectrode side rather than on the electrode side. Therefore, this result cannot be explained as a surface change of Pt catalyst. Further, as in Fig. 7, while air made contact with the electrode, Pt was dissolved, diffused, and deposited in the membrane near the nonelectrode side. Therefore, H_2O_2/radicals were generated by the supply of oxygen on Pt deposited in the membrane near the nonelectrode side. Thus, we conclude that the membrane was degraded by the attack of these radicals and, accordingly, FER was increased. When hydrogen again made contact with the electrode, FER on the nonelectrode side decreased because the air supply was far from the deposited Pt. After the end of this test, the membrane disassembled from the cell was observed by TEM. Fig. 11 shows cross-sectional TEM images of the membrane sectioned into six slices. Deposited Pt particles were observed near the nonelectrode side. This result clearly supports our explanation as to why a higher FER was measured on the nonelectrode side.

4. Pt Ionic Species and the Effect of Pt Reduction by H_2

In the cell operation with a single electrode, O_2 was supplied to the electrode side and N_2 was supplied to the nonelectrode side to prevent the reduction of dissolved Pt. After 24 h at 90 °C, the membrane was immersed in 1.33 M NaCl solution for 12 days, and the solution was analyzed by UV-visible spectrophotometry (Fig. 12). For comparison, a fresh Nafion 112 membrane was also analyzed under the same conditions. A large peak at 216 nm attributable to $PtCl_4^{2-}$, and a small peak at 262 nm attributable to $PtCl_6^{2-}$ were detected. Therefore, we conclude that Pt traces that existed in the membrane were in the form of Pt^{2+}. Pt dissolution which occurred by the following reaction [12]:

$$Pt_{(s)} + H_2O \Leftrightarrow PtO + 2H_{(*)}^+ + 2e^-$$
$$PtO_{(s)} + 2H_{(*)}^+ \Leftrightarrow Pt_{(*)}^{2+} + H_2O$$
$$Pt_{(s)} + Pt_{(*)}^{2+} + 2e^-$$

where (*) indicates ionic species present in the water or in the ionomer phase.

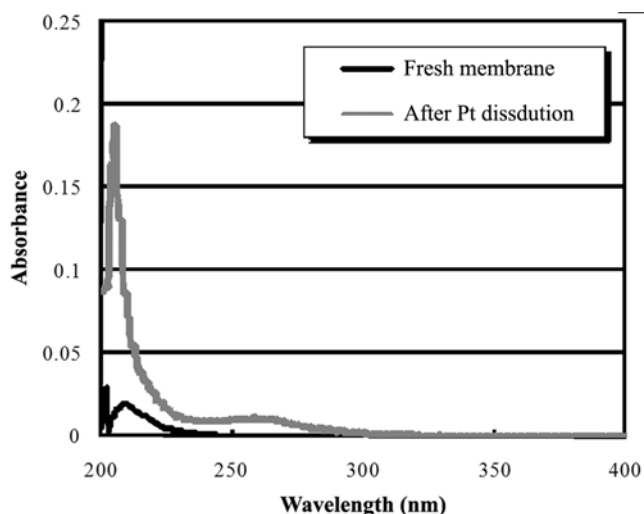When Pt ions exist in the membrane, they cannot serve as a cat-

Fig. 12. Comparison of UV spectra of fresh and Pt dissolved membranes.

alyst to generate H_2O_2/radicals that contribute to membrane degradation. However, when Pt ions are reduced and deposited in the membrane as Pt metal, they can play a role as a catalyst for radical formation. To validate this theory, two cells were tested under different conditions. First, in order to dissolve the Pt into the membrane, 300 ml/min of nitrogen at the nonelectrode side and oxygen at the electrode side were supplied to the two cells. These cells were then disassembled, and the electrodes were removed from the membrane. The cells were reassembled with only the membrane (without the electrode). Thus, the generation of H_2O_2/radicals on the electrode surface was excluded completely. To reduce the Pt ions that existed on the membrane, hydrogen and nitrogen gases were supplied to the single cell, while Pt reduction was omitted in another cell. Oxygen and hydrogen gases were then supplied to two different cells, and FER values were measured and compared. As shown in Fig. 13, higher FERs were observed in the cell that had undergone Pt reduction. This result confirms that membrane degradation is enhanced by radical formation catalyzed by Pt that has been reduced on the membrane by the hydrogen gas supply.
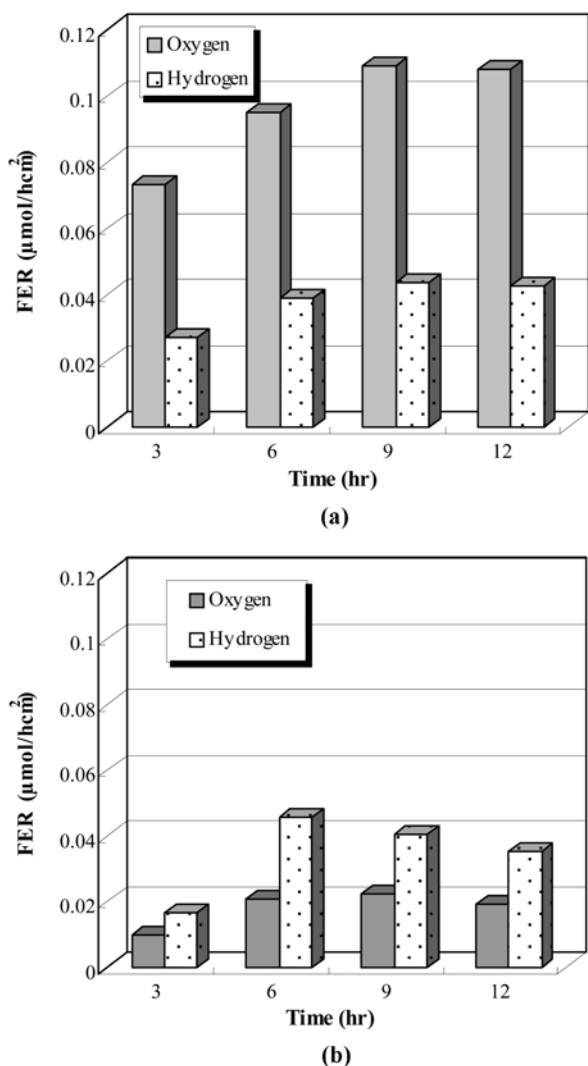

Fig. 13. FERs obtained from two different cells, in which the stage of Pt reduction was (a) included and (b) excluded.
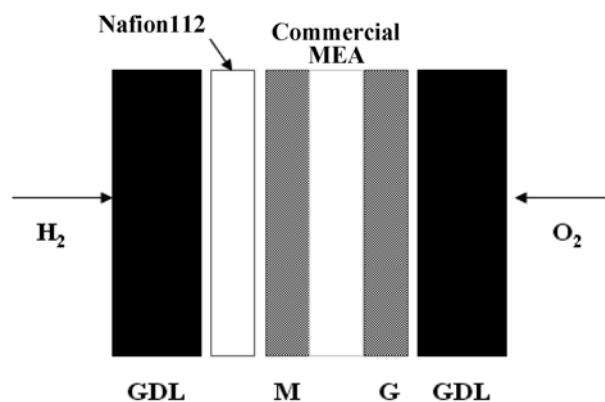
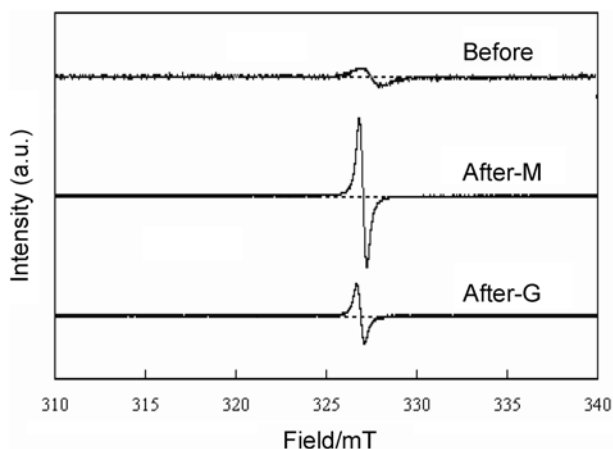Fig. 14. Cell configuration for measuring radical formation.

Fig. 15. Comparison of ESR spectra of fresh and degraded electrodes.

5. Detection of Radical Formed on Pt Inside of the Membrane

To ascertain radical formation on Pt deposited in the membrane, a test was carried out with the cell configured as shown in Fig. 14. The electrode was positioned inside the membrane. To accelerate radical formation, the cell was operated at 90 °C for 94 h with dry hydrogen and humidified oxygen (RH 65%). At the end of this period, we attempted to measure the presence of carbon radicals on both electrodes (designated M and G in Fig. 14) by ESR (Fig. 15). Larger ESR signals were detected at 327 mT (assigned for carbon radicals) on M and G electrodes than those detected on a fresh electrode. Carbon radical formation can be attributed to hydrogen abstraction by •OH and HO_2• radicals [9]. Thus, ESR detection of carbon radicals, which are more stable than hydrogen radicals (because the lifetime of the •OH or HO_2• radical is of the order of nanoseconds), provides evidence of indirect radical formation on Pt deposited in the membrane.

CONCLUSION

We investigated the mechanism of membrane degradation by Pt dissolved/deposited in the membrane by accelerated single cell test and single electrode cell test.

On MEA, which was tested under accelerated degradation con-

ditions (OCV, 90 °C, anode RH 0%, cathode O_2 supply), Pt was distributed on the anode-side membrane, and the membrane content of F, O, and C decreased on the anode-side membrane.

Membrane degradation by Pt dissolved/deposited in the membrane was investigated further by cell operation with a single electrode. By the applied high potential, Pt on the electrode was ionized in the form of Pt^{2+} ionic species. These species were then reduced by hydrogen coming from the anode and deposited in the membrane. This Pt deposited in the membrane played a role as a catalyst for H_2O_2/radical formation that led to membrane degradation. Through indirect measurement of carbon radicals using ESR, radical formation on the deposited Pt in the membrane was clarified.

ACKNOWLEDGMENT

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