Pinhole formation in PEMFC membrane after electrochemical degradation and wet/dry cycling test

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Abstract−During the operation of a PEMFC, the polymer membrane is degraded by electrochemical reactions and mechanical stresses. We investigated the effects of repeated electrochemical and mechanical degradations in a membrane. For mechanical degradation, the membrane and MEA were repeatedly subjected to wet/dry cycles; for electrochemical degradation, the cell was operated under open-circuit voltage (OCV)/low-humidity conditions. The repeated wet/dry cycles led to a decrease in the mechanical strength of the membrane. When the MEA was degraded electrochemically, repeated wet/dry cycling resulted in the formation of pinholes in the membrane. In the case of different MEAs that were first degraded electrochemically, the extents of their hydrogen crossover currents increased due to repeated wet/dry cycling being different. Therefore, these results indicated that the membrane durability could be evaluated by these methods of repeated electrochemical degradation and wet/dry cycles.

Key words: Polymer Electrolyte Membrane Fuel Cell, Durability, Membrane Degradation, Mechanical Degradation, Wet/Dry Cycling

INTRODUCTION

Degradation of an electrode and a polymer membrane, which are the key components of a PEMFC, is the major factor affecting the lifetime of the PEMFC. Degradation of a polymer membrane can be classified into chemical degradation and mechanical degradation. Chemical degradation is caused by membrane contamination and H_2O_2/radicals formed by electrochemical reactions. Contamination caused by cations such as Ca^{2+}, Fe^{3+}, Cu^{2+}, Na^{2+}, and K^+ seriously affects the cell performance [1-3]. This contamination originates from fuel cell components or the outer environment. The membrane is particularly vulnerable to contamination because of the affinity of the sulfonic acid group for cations [4].

To understand the membrane degradation mechanism, many studies have been performed, and degradation mechanisms involving some sources such as thermal degradation and contamination have been already proved. However, the electrochemical degradation of a membrane is still under debate.

The mechanism by which a polymer membrane in a PEMFC can undergo electrochemical degradation was established by General Electric (GE) in the 1960s. According to GE's mechanism [5], the H_2O_2 generated at the anode diffuses into the membrane and reacts with bivalent metal cations, present as impurities in the membrane, to form active oxygen species, which can then attack the polymer and degrade the membrane. However, this mechanism is not consistent with recent reports [6,7]. It was found that the membrane degradation was accelerated under open-circuit voltage (OCV) in low-RH conditions. Therefore, extensive researches have been conducted under these conditions [8-14].

Thermal stress and mechanical pressure applied to a membrane cause mechanical degradation. It has been reported that during fuel cell operation, variations in temperature and humidity cause cyclic stress and strains in the membrane and result in mechanical failure (pores/cracks) in the membrane [15-18]. While electrochemical degradation begins to occur after many thousands of hours of operation, mechanical degradation mainly causes early life failures (<1,000 h) [5]. However, studies on the combined chemical and mechanical effects acting together have not been carried out sufficiently.

During fuel cell operation, electrochemical degradation and mechanical degradation can occur simultaneously or sequentially. So far, studies on electrochemical and mechanical degradations of a membrane have been performed separately. However, in this study, we investigated the synergetic effects of electrochemical and mechanical degradations when they occurred sequentially. For mechanical degradation, repetitive wet/dry cycles were applied to MEAs; for electrochemical degradation, the cell was operated under repetitive OCV/low-humidity conditions.

EXPERIMENTAL

For a wet/dry cycling test, a membrane (Nafion 112) and a commercial MEA were fixed in an acrylic frame. Fig. 1 shows the temperature and humidity profile used for the wet/dry cycling test. The membrane and MEA were humidified at 70 °C (90% RH) for 2 h and dried at 70 °C for 2 h. Then they were cooled to −25 °C for 1.5 h and humidified again. This RH cycle was repeated.

An electrochemical-degradation test was performed in a 25-cm² single cell. The cell assembled with an MEA, GDL, Teflon gaskets, bipolar plates, and end plates was installed in a fuel cell test station (CNL Energy Co.) After cell activation, the MEA was held at 80 °C and under OCV for 144 h. During cell operation, hydrogen crossover

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was measured. 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 0.4 V was applied to the cathode by using a potentiostat (Solartron, SI 1287). The hydrogen that crossed over to the cathode was oxidized by the application of a voltage, and the resulting currents were measured.

After the electrochemical degradation and wet/dry cycling test, the pinholes formed in the membrane were observed with a scanning electron microscope (SEM, JEOL JSM-T330A; HITACHI S-4700).

RESULTS AND DISCUSSION

1. Accelerated Degradation Test of Membrane/MEA Clamped in an Acrylic Frame

First, a 25-cm^2 MEA was clamped in an acrylic frame, and a wet/dry cycle was repeated six times by using the method shown in Fig. 1. This MEA stressed by wet/dry cycling was set in a single-cell test fixture. For electrochemical degradation, the cell was activated under the constant-current mode, and then it was operated at 80 °C and under OC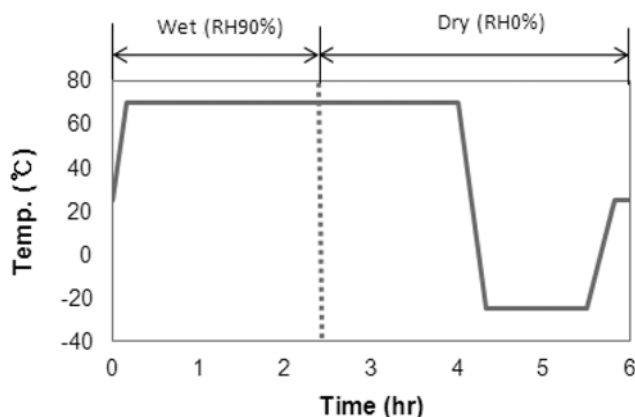V for 144 h while dry hydrogen (0% RH) and fully hydrated air (100% RH) were fed into the anode and the cathode, respectively.

For comparison, another 25-cm^2 MEA was prepared and first degraded electrochemically. Then, wet/dry cycles were applied in the same manner as described earlier.

Fig. 2 shows the stress-strain response of the Nafion 112 membrane subjected to the wet/dry cycling test. With an increase in the number of repeated wet/dry cycles, the yield strain decreased, that is, the mechanical strength of the membrane decreased.

In Figs. 3 and 4, the cell performance and hydrogen crossover currents of the two MEAs subjected to the electrochemical-degradation test and the wet/dry cycling test in different orders are plotted and compared. In the case of the MEA subjected to the wet/dry cycling test before electrochemical degradation, the cell performance and hydrogen crossover current were similar to their respective initial data.

However, in the case of the MEA that was first subjected to the electrochemical-degradation test, the cell performance greatly decreased, and the hydrogen crossover current drastically increased,

Fig. 1. Temperature and humidity profile for wet/dry cycling test.

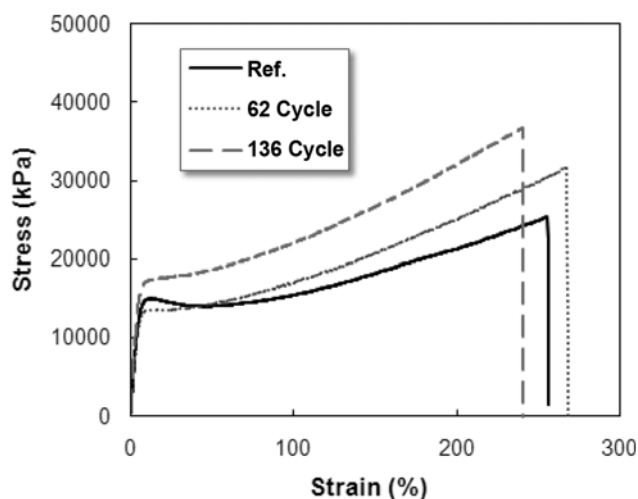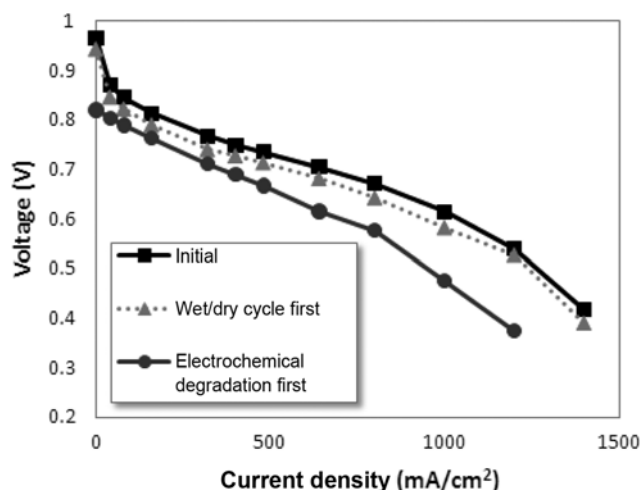Fig. 3. Comparison of cell performances of the two MEAs degraded in different order.

Fig. 2. Strain-stress curves of Nafion 112 membrane subjected to different numbers of wet/dry cycles in an acrylic frame.
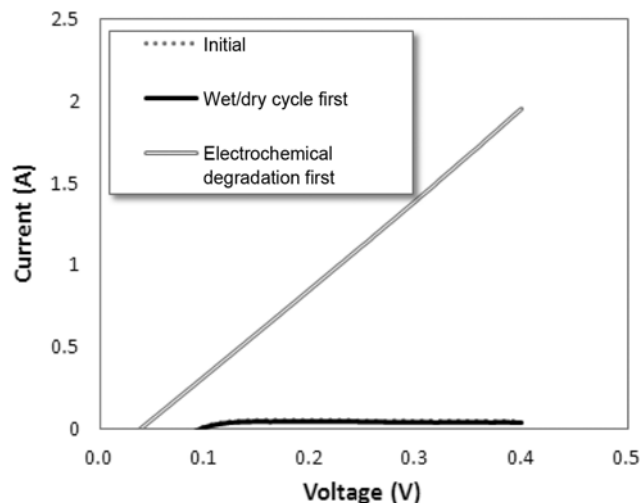

Fig. 4. Comparison of hydrogen crossover currents of the two MEAs degraded in different order.

Fig. 5. SEM surface image of MEA degraded electrochemically first.

Fig. 6. Comparison of cell performances of MEAs after electrochemical degradation and wet/dry cycling test.

Fig. 7. Comparison of hydrogen crossover currents of MEAs after electrochemical degradation and wet/dry cycling test.

exceeding the measuring extent.

The decrease in the OCV, as revealed by the I-V curve, and the dramatic increase in the hydrogen crossover current support the conclusion that pinholes were formed in this MEA. Moreover, the linear slope of the hydrogen crossover current also revealed that many pinholes were formed in the membrane. Further, after removing the electrodes from the MEA, the membrane surface was observed by using the SEM (Fig. 5). A very large pinhole was observed, mainly at the membrane edge, but not at the center. In the case of the MEA that was first subjected to the electrochemical-degradation test, the membrane might be degraded by H_2O_2 or radicals formed by OCV/ anode dry condition. In addition, the subsequent wet/dry cycling led shrinkage/expansion of the degraded membrane. Therefore, mechanical stress was produced at the weak parts of the degraded membrane and led to the formation of pinholes in the membrane.

On the other hand, in the case of the MEA subjected to wet/dry cycling test first, the effect of mechanical stress was small because the weak parts did not exist in the membrane. Although the membrane was also degraded by the following electrochemical degradation, no pinhole was formed because the mechanical stress was not applied after the electrochemical degradation.

2. In-cell Degradation

In the case of the MEA clamped in an acrylic frame, the excessive expansion/shrinkage was observed by wet/dry cycles. Therefore, this phenomenon was expected to occur during fuel cell operation because the MEA is clamped on four edges in the cell. After MEA activation, the cell was operated at 80 °C and under OCV conditions for 144 h while dry hydrogen and humidified (100% RH) oxygen were introduced into the anode and the cathode, respectively. After this electrochemical degradation, wet/dry cycling was carried in this single cell as follows. The cell was cooled from 70 °C to 30 °C in 60 min while 300 ml/min of dry N_2 gas was supplied to it. Then, the cell temperature was raised from 30 °C to 70 °C at 100% RH in 30 min. After 18 cycles of wet/dry, a single cell was activated and the cell performance was measured (Fig. 6). It was found that the degradation in the cell performance was more than that after the electrochemical-degradation test. Furthermore, the remarkable OCV reduction supported the fact that pinholes were formed in the membrane after the wet/dry cycling test.
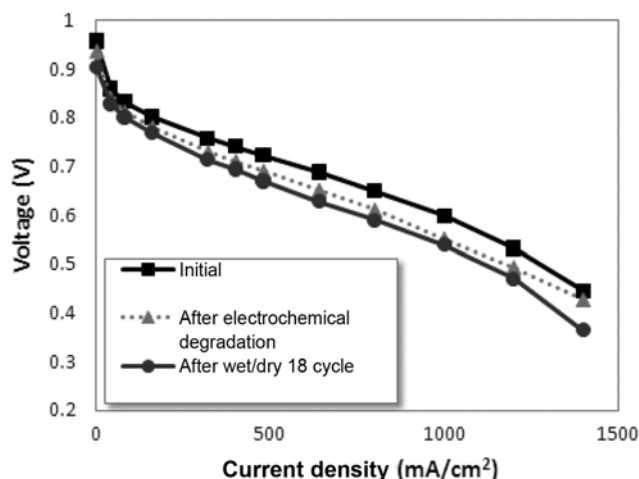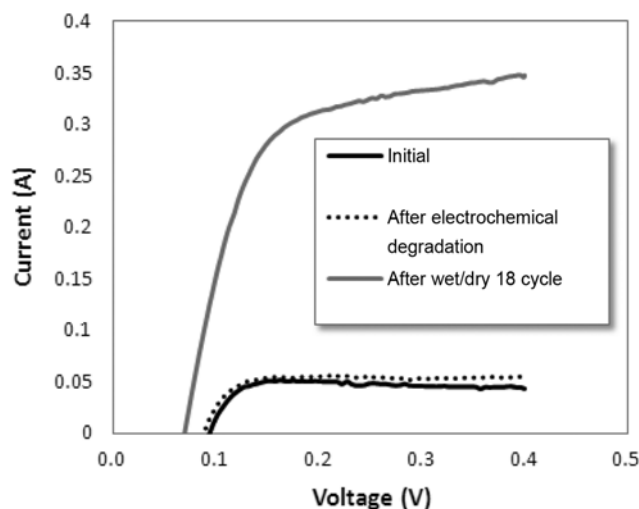
Fig. 7 shows the results for hydrogen crossover. After electrochemical degradation only, no change was observed in the hydrogen crossover current. However, after repeated wet/dry cycling, the hydrogen crossover current increased by ten times. However, as compared to the wet/dry-cycled membrane clamped in the acrylic frame, the pinhole size and the range of increase in the hydrogen crossover were small. Nevertheless, we confirmed that the repeated wet/dry cycling of the electrochemically degraded membrane in cell can lead to the formation of pinholes.

Fig. 8 shows an SEM image of the membrane degraded electrochemically for 144 h. Partial membrane thinning was observed. Under the accelerated electrochemical degradation, H_2O_2 or radicals were formed by the electrochemical reaction that might attack the polymer chains in the membrane; therefore, the membrane content such as fluoride and carbon was swept, and accordingly, the membrane was thinned. Mechanical stresses such as shrinkage and expansion applied to this thinned membrane seem to form pinholes or cracks in the membrane.
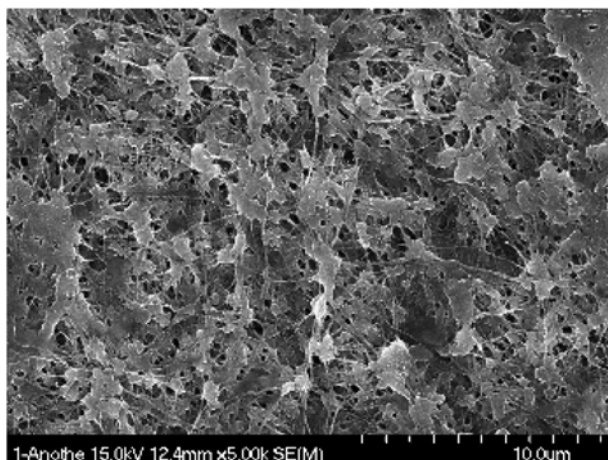
Fig. 8. SEM image of the membrane after electrochemical degradation under OCV/anode dry conditions at 80 ºC for 144 h.
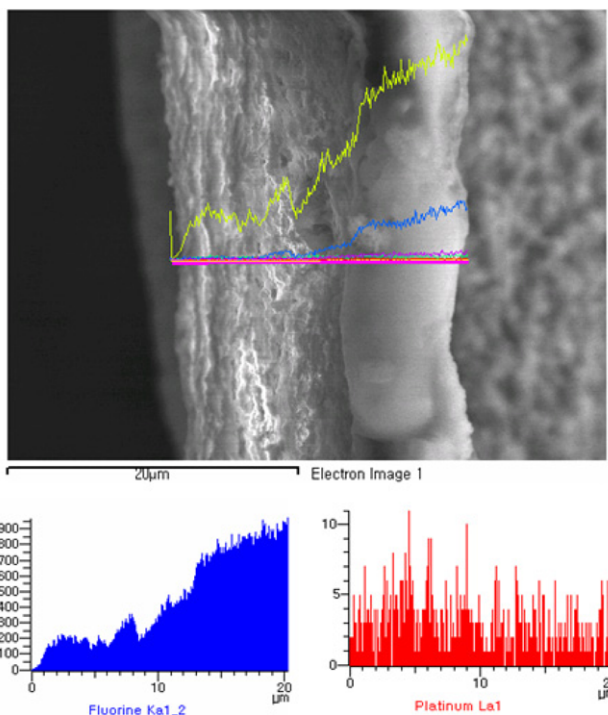

Fig. 9. SEM/EDS spectrum of the membrane after electrochemical degradation under OCV/anode dry conditions at 80 ºC for 144 h.

This thinned membrane was examined by SEM/EDS (Fig. 9) measurement. The membrane degradation was mainly observed on the anode side, and accordingly, the F, O, and C concentrations decreased near the anode side of the membrane. In addition, a large number of Pt particles were observed on the anode side in the membrane. Such membrane degradation on the anode side was considered as being due to the Pt particles, which dissolved from the cathode side and deposited on the anode side, acting as a catalyst for radical generation in the membrane.

3. Durability Test of Membrane

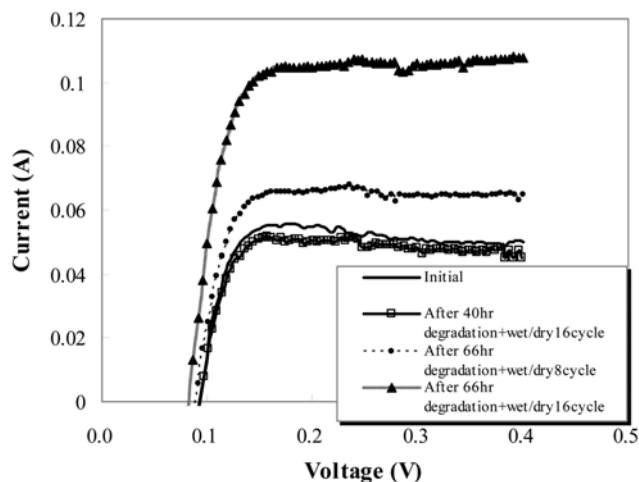Thermal degradation of a membrane occurs at a temperature ex-

Fig. 10. Change in hydrogen crossover current of MEA A with the electrochemical degradation time and the number of wet/dry cycles.
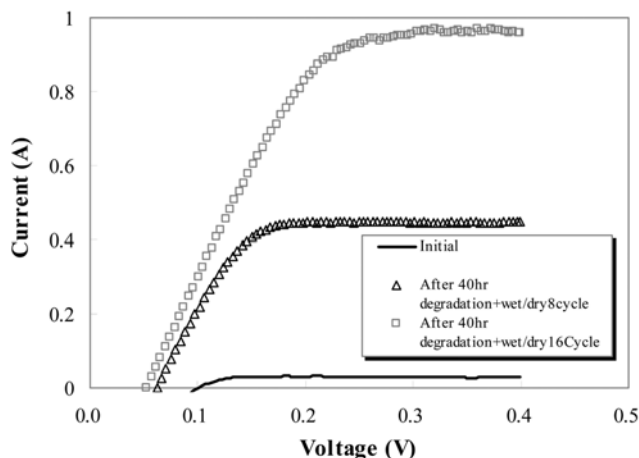

Fig. 11. Change in hydrogen crossover current of MEA B with the number of wet/dry cycles.

ceeding 150 ºC. However, except in special cases, cells or stacks of PEMFCs are not operated at high temperature. Hence, electrochemical and mechanical degradations are the main factors of membrane degradation. Therefore, we examined the possibility of durability prediction by performing the repetitive electrochemical-degradation test and wet/dry cycling test within short-time operation. Two MEA types, referred to as "A" and "B" and supplied by company A and company B, respectively, were tested in the same manner.

Fig. 10 shows the results for the hydrogen crossover current of MEA A. After electrochemical degradation for 40 h, the wet/dry cycle was repeated 8 and 16 times. However, no change was observed in the hydrogen crossover current. After the additional electrochemical degradation for 26 h, the wet/dry cycling test was carried out 8 and 16 times, and the hydrogen crossover current was measured again. After 8 times of wet/dry cycling, the hydrogen crossover current began to increase. That is, the electrochemical degradation for 66 h led to mechanical breach in the membrane, and the repeated shrinkage/expansion formed pinholes in the membrane. This resulted in the increased hydrogen crossover.

For comparison (Fig. 11), MEA B was tested in the same manner. After 40 h electrochemical degradation, wet/dry cycling was carried out 8 and 16 times. At this time, the hydrogen crossover current increased considerably. The hydrogen crossover current of MEA B increased in 40 h, that is, the MEA degradation time was 26 h shorter than that of MEA A. So, the electrochemical durability of MEA B was about 60% that of MEA A.

We roughly calculated the mechanical strength with the increasing ratio of the hydrogen crossover currents by shrinkage/expansion in the two MEAs already degraded electrochemically.

After wet/dry cycles were conducted 8 and 16 times, the increase in the hydrogen crossover current of MEA B was 8 and 10 times more than that of MEA A, respectively, that is, the membrane B developed pinholes easily and exhibited weak mechanical strength. Therefore, these results indicated that the membrane durability could be evaluated by these methods of repeated electrochemical degradation and wet/dry cycles.

CONCLUSION

During the operation of a PEMFC, electrochemical and mechanical degradations can occur simultaneously or sequentially and repetitively. So far, in many studies on membrane degradation, electrochemical and mechanical degradations have been performed individually. However, we investigated the effects of these two different degradations when they occurred repeatedly. In an acrylic frame, a membrane was repeatedly subjected to wet/dry cycles from $-25\,^{\circ}C$ to $70\,^{\circ}C$. It was found that with an increase in the number of repeated wet/dry cycles, the mechanical strength of the membrane decreased. Further, after wet/dry cycling of an MEA, which was first degraded under accelerated electrochemical conditions, the cell performance degraded and the hydrogen crossover current increased greatly. As a result of SEM measurement, this increase in the hydrogen crossover current was due to the pinholes formed in the membrane. It is inferred that wet/dry cycling caused mechanical stress in the weak parts of the degraded membrane and resulted in the formation of pinholes in the membrane. In addition, the same results were obtained for a membrane installed in a cell. Two different MEAs, referred to as "A" and "B", respectively, were subjected to repeated electrochemical degradation and wet/dry cycling. The hydrogen crossover current of MEA B increased in 40 h: its MEA degradation time was 26 h shorter than that of MEA A. In other words, its electrochemical durability was about 60% that of MEA A. After wet/dry cycles were performed, the increase in the hydrogen crossover current of MEA B was 8-10 times more than that of MEA A: membrane B developed pinholes easily and exhibited weak mechanical strength. Therefore, these results indicated that the membrane durability could be evaluated by these methods of repeated electro-

chemical degradation and wet/dry cycles.

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