

Acceleration of electrolyte membrane degradation by frequent activation in PEMFC electrochemical durability evaluation

Donggeun Yoo, Byungchan Hwang, Sohyeong Oh, and Kwonpil Park[†]

Department of Chemical Engineering, Sunchon National University, 255, Jungang-ro, Suncheon-si, Jeollanam-do 57922, Korea
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Abstract—During the durability tests for PEMFC membranes, performance characterization is conducted to determine the degree of degradation, the interval for which is different for each durability test protocol. Before performance characterization, activation is carried out to determine the reliability. Most activations are accompanied by voltage changes, which can lead to electrode degradation. However, this has largely been neglected because the activation time is shorter than the durability test time. In this study, activation was conducted at 24, 48, and 144 h intervals, during the membrane durability test of a PEMFC, and the effect of activation on the degradation of the membrane and electrode was investigated. For a shorter activation interval during the durability test, the lifetime of the membrane was reduced by up to 35%. For the same durability test time, more activations led to greater electrode and membrane degradation. Through scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS) analysis, it was found that for a shorter activation interval, more Pt was deposited into the membrane and then the membrane was thinner. During the durability test, frequent activation accelerated membrane and electrode degradation.

Keywords: PEMFC, Activation, Durability Evaluation, Membrane Degradation, Electrode Degradation

INTRODUCTION

Fuel cells, which are in the spotlight as environment-friendly power generation devices, are divided into various types such as SOFC, DMFC, PEMFC, and PAFC depending on the electrolyte, and various studies have been conducted for developing the performance of PEMFC [1-6]. Among them, PEMFCs have attracted extensive attention for their high efficiency, high power density and low operating temperature. However, the high costs and low durability of PEMFCs have hindered their commercialization. The performance and durability of PEMFCs deteriorate owing to the degradation of various stack materials. Among the observed degradation phenomena, the degradation of the membrane electrode assembly (MEA) is a major cause for the aforementioned degradation. The degradation of the MEA is classified into electrode degradation and electrolyte membrane degradation. Electrode degradation includes catalyst degradation caused by the dissolution and sintering of Pt during load cycling [7], as well as the degradation of carbon supports by high temperature and high potential [8,9]. Membrane degradation includes mechanical degradation due to humidification/drying and electrochemical degradation due to formation of radicals at a high potential [10].

For improving the durability of PEMFCs, it is necessary to first evaluate their durability. The durability test is highly time- and cost-intensive because it typically takes several thousands to tens of thousands of hours. Therefore, accelerated stress test (AST) protocols have been developed for more efficient and quicker testing [11-13]. For

each AST protocol, not only the test conditions but also the characterization intervals are different. In the membrane degradation protocol established by the U.S. Department of Energy (DOE), the linear sweep voltage (LSV) is measured every 24 h and the changes in the hydrogen crossover current density (HCCD) and short resistance (SR) are monitored during the test [11]. In the membrane degradation protocol established by Japan's New Energy Industrial Technology Development Organization (NEDO), LSV measurements are carried out in every 50 to 100 h and the change in the HCCD is monitored during the test [12]. In the EU durability test protocol, the I-V is measured every 50 cycles of the durability test (approximately 17 h) [13].

In a durability test, degradation is classified as reversible degradation and irreversible degradation. Reversible degradation is the performance deterioration that depends on the state of membrane humidification and catalyst oxidation, and hence, is recoverable [14, 15]. Irreversible degradation is the performance deterioration induced by permanent change in the catalyst and membrane, and hence is not recoverable. During the durability test, characterization is performed to check for irreversible degradation. If characterization is conducted without eliminating the reversible degradation that occurs during the durability test, it is difficult to check the degree of degradation. To perform reliable characterization, an activation process that can eliminate reversible degradation is required.

In PEMFC, activation is also typically referred to in various terms, such as break-in and conditioning, and there are various methods for activation such as constant voltage, constant current, step/cycling of voltage or current, and shut off [14]. Since most activations involve changes in the voltage and current, frequent activation can degrade the electrodes of the MEA. In the membrane degradation protocol, if electrode degradation and membrane degradation occur to-

[†]To whom correspondence should be addressed.

E-mail: parkkp@scnu.ac.kr

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gether, the membrane durability cannot be accurately determined. In addition, electrode degradation accelerates membrane degradation [16,17]; therefore, the former must be minimized in the membrane durability test. However, in most cases, the activation time is shorter than the degradation time, due to which degradation by activation has been neglected thus far.

This study investigates the effect of activation on a PEMFC membrane durability test. Open circuit voltage (OCV) holding was conducted to test the electrochemical durability of the membrane. And activation and characterization were performed at different intervals during OCV holding, following which the membrane and electrode degradation were compared for different activation intervals. The aim of this work is to clarify the importance of activation and characterization intervals in the durability test, and hence, help develop more accurate membrane durability test protocols.

EXPERIMENTAL

1. Cell Conditions and Activation

In this study, a single cell was used with an active area of 25 cm². The MEA was fabricated by hot pressing and using a Pt/C catalyst loading of 0.4 mg Pt/cm² for both electrodes on a Nafion XL (Dupont, USA) electrolyte membrane. The cell was assembled with the MEA using gas diffusion layers (SGL 10BC, Germany) and gasket. Durability test and electrochemical characterization were conducted on a test station (CNL Energy, Korea), and the cell temperature, humidity, and gas flow rate were controlled. Characterization and activation, except for the durability test, were performed at a cell temperature of 70 °C, ambient pressure, and relative humidity (RH) of 100%.

The durability test of the MEA was performed under OCV holding, which is an electrochemical durability test mode. OCV holding was conducted by supplying hydrogen to the anode and oxygen to the cathode at 829 mL/min at a cell temperature of 90 °C, with the anode at 10% RH, and cathode at 30% RH. The OCV holding intervals were set to 24, 48, and 144 h, and after each durability test interval, activation and characterization were performed.

Activation was carried out using a voltage step method by lowering the voltage from the OCV to 0.4 V at constant voltage intervals and then raising the voltage from 0.4 V to the OCV at constant voltage intervals. The cells were activated until their performance no longer increased, approximately 2 h right after cell assembly, and approximately 40 min after the durability test.

2. Fluoride Emission Rate (FER) Measurement

During OCV holding, the FER was measured quantitatively using the Ion Selective Electrode Meter (PH-250L, ISTEK, Korea). The calibration curve was prepared with a sodium fluoride 1,000-100 ppm standard solution. The condensate was collected by condensing the gas coming out of the cell outlet at 4 °C.

3. Cell Characterization and Post Analysis

To analyze the degree of the electrode and membrane degradation of the MEA during the durability test, cyclic voltammetry (CV) and LSV measurements were performed using a potentiostat (Solatron, SI 1287). Hydrogen to the anode and argon to the cathode were supplied at a flow rate of 40 mL/min, and 200 mL/min respectively. All characterizations were conducted after every durability

test. Before each characterization the cell was activated.

LSV measurements were performed in the potential range of 0-0.5 V at a scan rate of 1 mV/s, the potential range 0-0.5 V. The HCCD is an oxidation current of hydrogen that has passed through the electrolyte membrane from the anode to the cathode. The hydrogen oxidation current reaches the limiting current density in the range of 0.3 to 0.35 V [18]. Therefore, the current density value at 0.3 V was considered as the HCCD. The short resistance (SR) was calculated to range from 0.4 to 0.5 V using Ohm's law.

CV measurements were conducted for 15 cycles at a scan rate of 30 mV/s in the potential range of 0.05-1.2 V. The electrochemical surface area (ECSA) was calculated using the current density from the 0-0.4 V hydrogen desorption region as the area above the trend line in the 0.4 V electric double layer region.

After the durability test, the membrane thickness of the MEA and Pt content inside the membrane were analyzed using cross-sectional scanning electron microscope/energy dispersive X-ray spectroscopy (SEM-EDS, JSM-7100F, JEOL, Japan). The MEAs were coated with Au and observed in the beam potential range of 5-15 kV.

RESULTS

1. Irreversible Degradation Changes During OCV Holding

Fig. 1 shows the OCV change during the electrochemical durability test (OCV holding). To determine the effect of activation on the durability test, the activation intervals were set at 24, 48, and 144 h. The end point of the durability test was set when the voltage decreased by 20% compared to the initial voltage (0 h) of OCV holding.

During OCV holding, the cell voltage decreases with time, initially in an exponential manner and then linearly and slowly. The exponential voltage degradation is almost recovered after activation and is a reversible degradation phenomenon. On the other hand, the linear voltage degradation is only recovered partially after activation, and hence, is an irreversible degradation phenomenon [15, 19,20]. In Fig. 1, the linear degradation rate for the 24, 48, and 144 h intervals increases sharply at 140, 168, and 230 h, respectively. Approximately 20 h after these points, durability tests were terminated. Thus, as the number of activations increases for the same time, the time point at which the irreversible degradation rate increases is advanced and the durability evaluation time is reduced.

Fig. 2 shows the change in the HCCD during the durability test. The HCCD increases due to membrane degradation (thinning) in which radicals attack the membrane [21]. After OCV holding for 144 h, as the activation interval is shorter, the HCCD increase rate plot is steeper. The acceleration of the linear voltage degradation in Fig. 1 is affected by an increase in the HCCD due to membrane degradation. Thus, the HCCD increases with irreversible degradation of the membrane in the MEA leading to irreversible OCV reduction.

2. Electrode Degradation in the Electrochemical Durability Test

During the OCV holding test, the changes in the ECSA were compared using CV (Fig. 3). After OCV holding for 144 h, the ECSAs decreased to 25, 19, and 16%, respectively, at intervals of 24, 48 and 144 h. Although OCV holding is an electrolyte membrane degradation protocol, the electrode is also degraded due to the high-voltage conditions. The ECSA reduction increases as the number

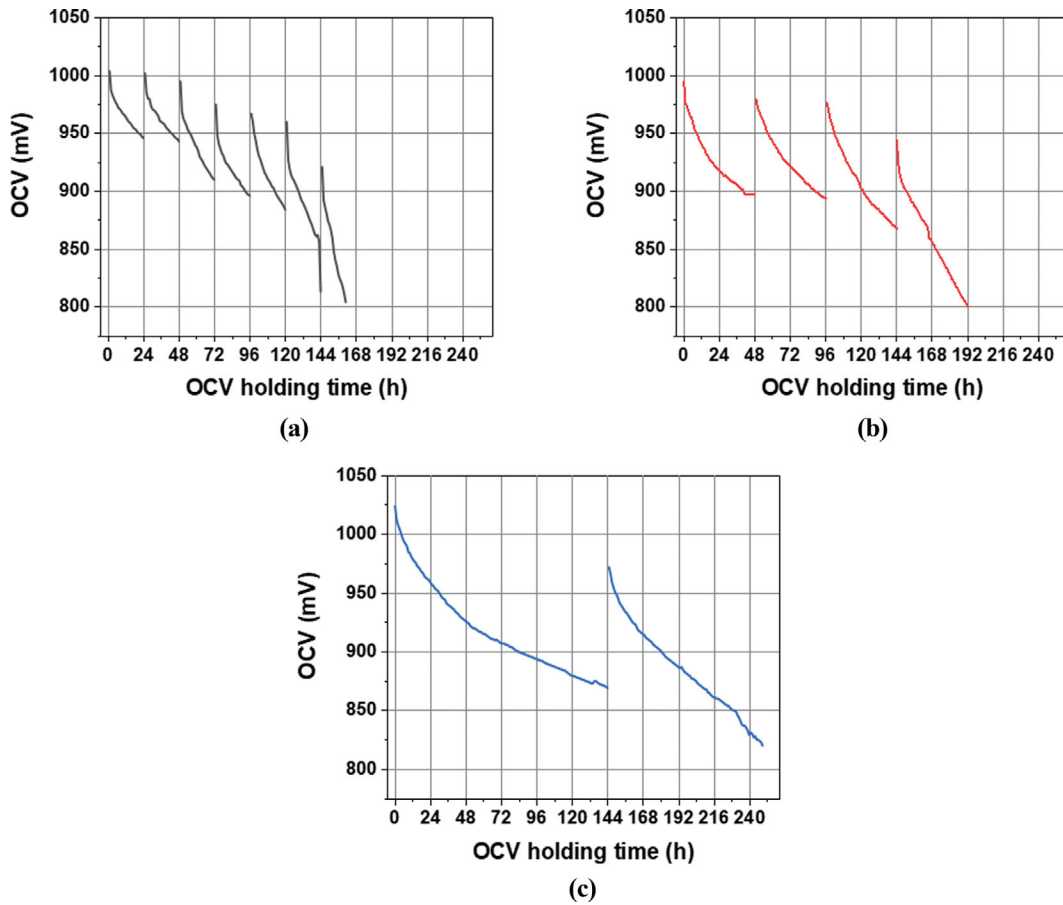


Fig. 1. Voltage changes during the durability test for each activation interval (a) 24 h interval (b) 48 h interval (c) 144 h interval.

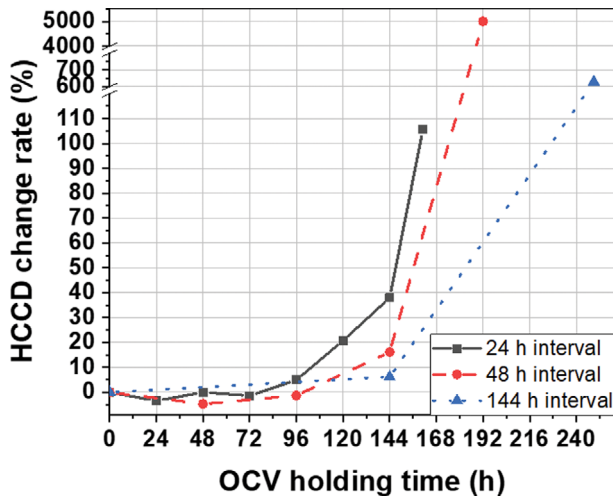


Fig. 2. Comparison of the HCCD change rate with the OCV holding time.

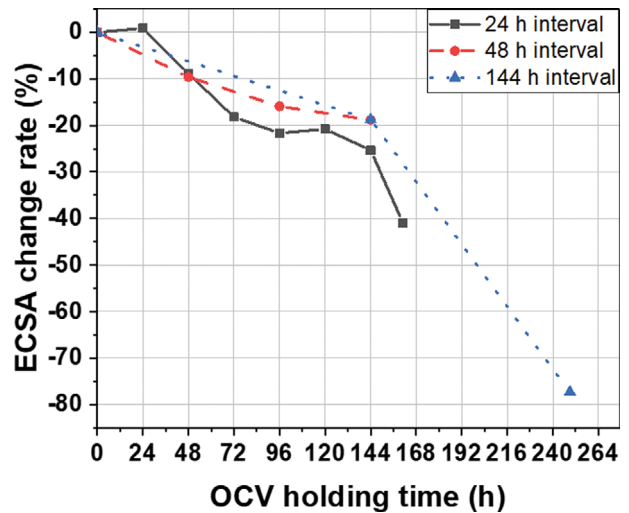


Fig. 3. Comparison of ECSA change rate with OCV holding time for each activation interval.

of activations increases. This leads to electrode degradation during activation. Activation is generally carried out by changing the voltage under high-humidity conditions, which is also a conducive to electrode degradation [22]. Therefore, the more the number of activations during OCV holding, the greater the electrode degradation.

FER measurement is used to confirm the degree of the mem-

brane degradation [23,24]. Therefore, the FER was measured during the durability test for quantitatively analyzing the irreversible degradation of the membrane (Fig. 4). During OCV holding, the FER temporarily decreases after activation. The Pt in the membrane causes membrane degradation by forming radicals inside the membrane.

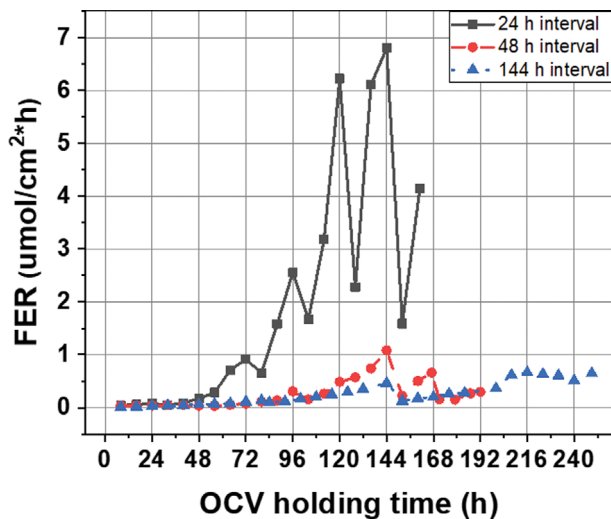


Fig. 4. Change in the FER during OCV holding for each activation interval.

In this case, the degree of membrane degradation due to radicals depends on the size of the Pt particles and the distance between the particles. Activation by load cycling can influence the size and distance between the Pt particles, and hence, the rate of radical formation can be reduced [25]. Thus, a short activation interval can be expected to mitigate membrane degradation. However, the over-

all increase rate of the FER was higher. This is the result that activation accelerates electrode degradation. In electrode degradation, the dissolved Pt can be deposited on the membrane, which accelerates membrane degradation. Therefore, the increase in the FER is a result of electrode degradation during activation.

3. Postmortem Analysis of the MEA

After the durability test, the SEM cross-sectional images of the MEA were measured to compare the degree of membrane degradation for each activation interval (Fig. 5). After the durability test, the membrane thickness decreased from the initial 25.6 μm to 13.9, 18.8, and 20.0 μm at intervals of 24, 48, and 144 h, respectively. In the MEA subjected to the 24 h activation interval, the membrane thickness reduction rate was the highest despite the shortest test time of 161 h. On the other hand, in the MEA subjected to the 144 h activation interval, thickness reduction rate was the lowest despite the longest durability test time of 249 h.

Fig. 6 shows the amount of Pt in the membrane determined by EDS. The Pt contents inside the membrane are 3.81, 2.39, and 1.71 wt%, at activation intervals of 24, 48, and 144 h, respectively. As for shorter activation intervals, more Pt exists in the membrane. The number of activations until the end of durability test was 8, 5, and 3 times at activation intervals of 24, 48, and 144 h, respectively. The correlation between the number of activations and Pt content in the membrane was linear (Fig. 7(a)).

Fig. 7 shows the relationship among the number of activations, Pt concentration in the membrane, and durability test time. As the

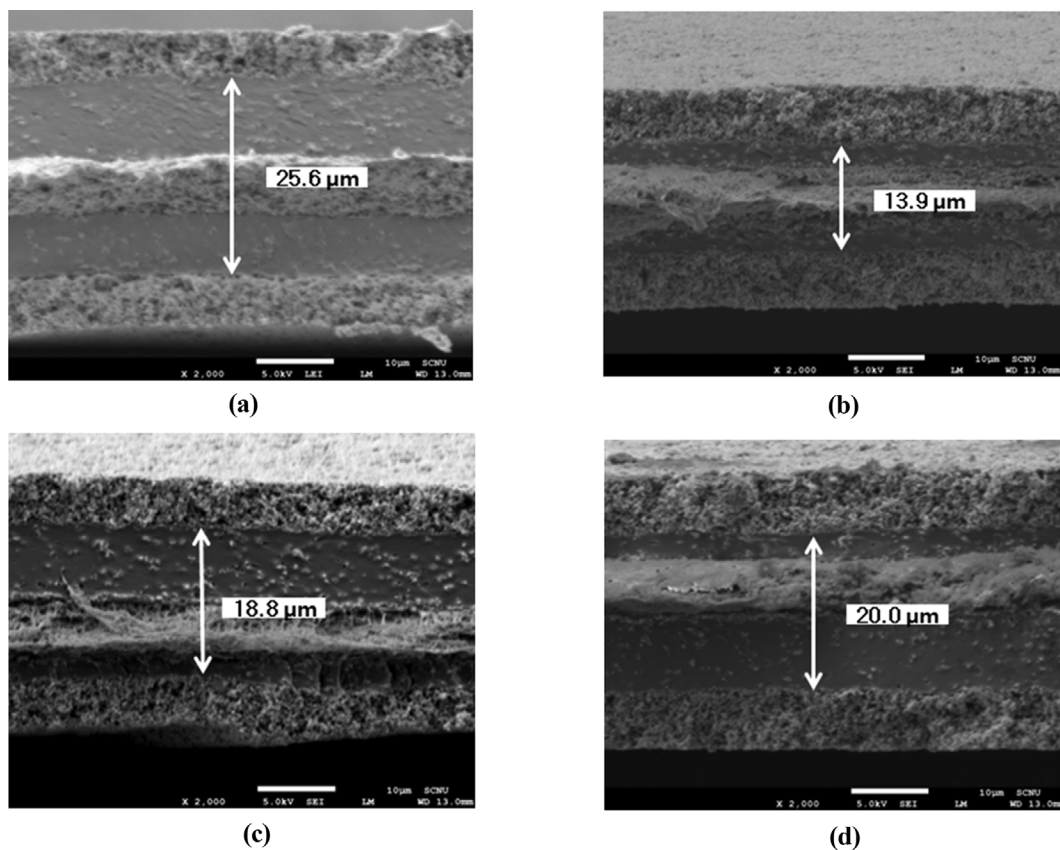


Fig. 5. SEM cross-section image of MEA after durability test (a) Pristine, (b) 24 h interval, (c) 48 h interval, (d) 144 h interval.

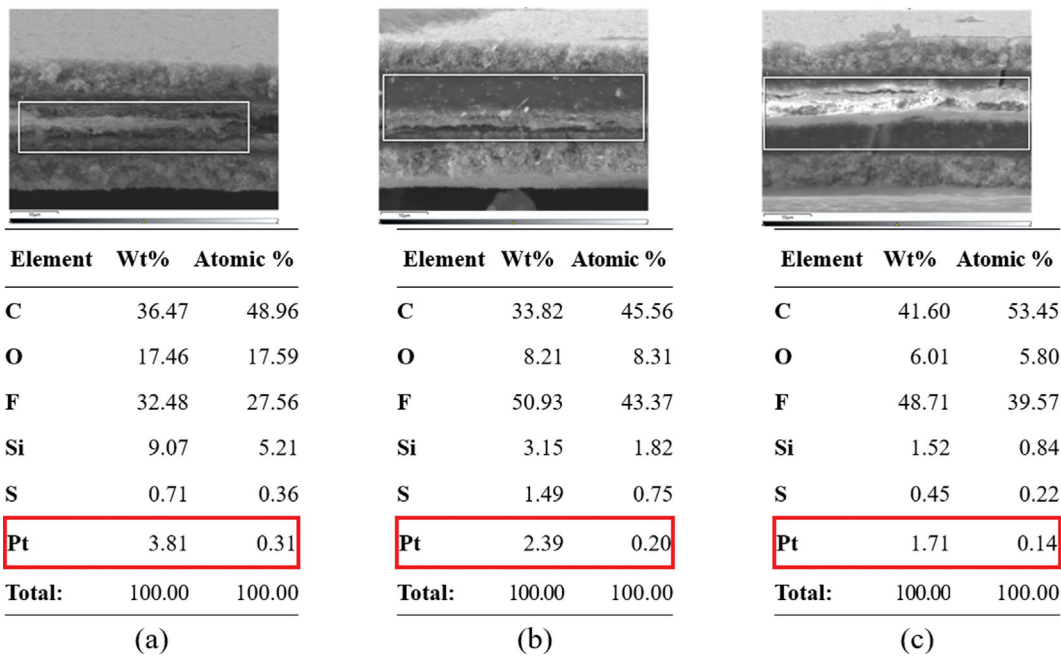


Fig. 6. Comparison of Pt concentration in membrane after durability test (a) 24 h interval, (b) 48 h interval, (c) 144 h interval.

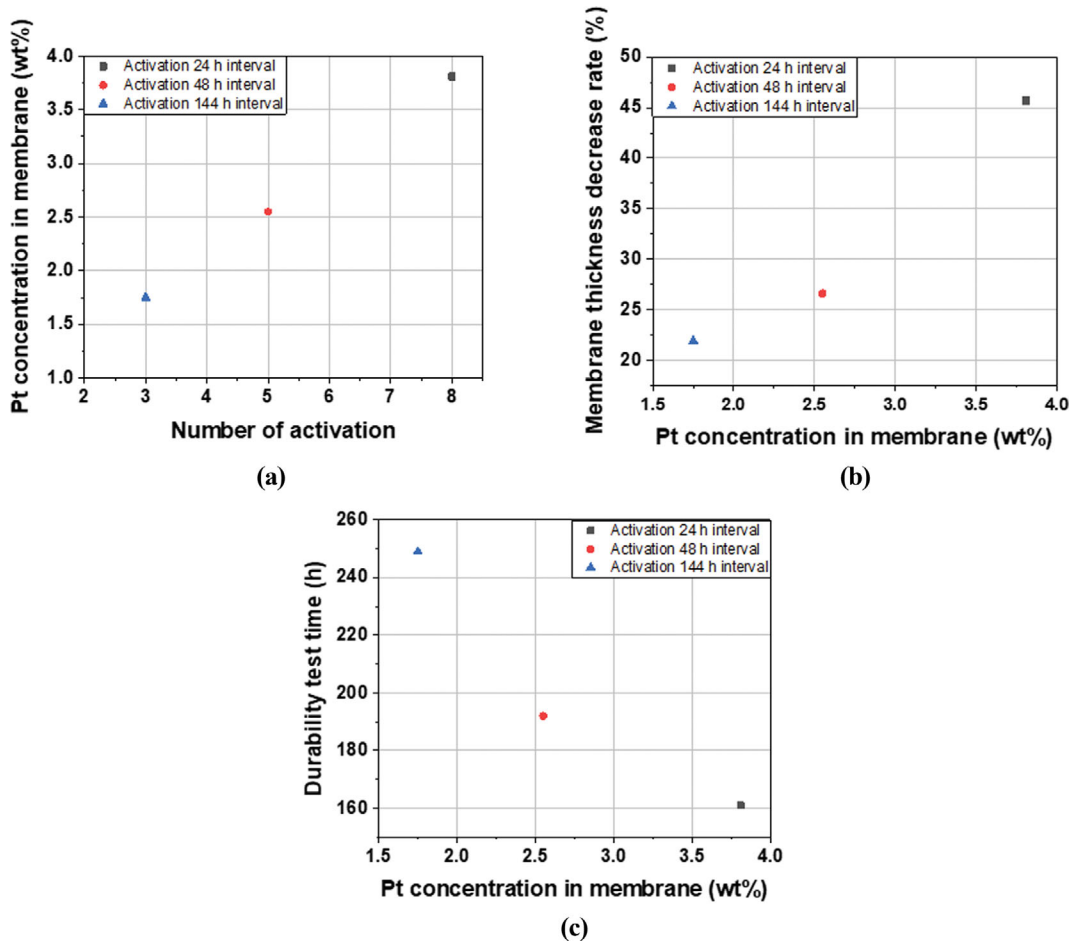


Fig. 7. Relationship among the number of activations, Pt concentration in the membrane, and durability test time. (a) Pt concentration in the membrane with number of activations, (b) membrane thickness decrease rate, and (c) durability test time with Pt concentration in the membrane.

number of activations increased, Pt content in the membrane increased (Fig. 7(a)), and the membrane was thinner, and the durability test time decreased (Fig. 7(b), (c)). These correlations directly show that the Pt in the membrane due to electrode degradation as the number of activations increased during the durability test, which accelerated membrane degradation.

Consequently, our results show that frequent activation accelerates the electrode degradation during electrochemical durability test, resulting in a decrease in the durability of electrolyte membrane. This degradation caused by activation should be minimized because it can lead to confusion in interpreting the degradation of durability test protocol, and it can be difficult to separate from the degradation by durability test protocol. Therefore, we suggest that, in addition to the durability test protocol, activation and characterization methods such as the duration, intervals, and number of cycles, should be carefully considered.

CONCLUSIONS

OCV holding was conducted in an electrochemical durability test using activation intervals. For a shorter activation interval, the irreversible voltage decrease rate was higher, and the lifetime of the membrane by 35% than that with a 144 h interval. With shorter activation intervals, the HCCD increased, confirming that more irreversible degradation occurred. For the same durability test time, as the number of activations increased, the ECSA decreased and FER increased. This shows that electrode degradation accelerated membrane degradation, which was directly confirmed through the change in the membrane thickness and Pt content in the membrane. During the durability test, as the number of activations increased, the Pt content in the membrane increased and the membrane thickness decreased. Finally, it was found that the electrode degradation caused by activation affected the membrane durability test, which was confirmed through the linear correlations among the number of activations, Pt concentration in the membrane and durability test time. Thus, extremely frequent activations can hinder the membrane durability test, making it important to consider the durability test activation and characterization intervals.

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