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Development of shut-down process for a proton exchange membrane fuel cell

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Abstract

Several different shut-down procedures were carried out to reduce the degradation of membrane electrode assembly (MEA) in a proton exchange membrane fuel cell (PEMFC). The effects of close/open state of outlets of a single cell and application of a dummy load during the shut-down on the degradation of the MEA were investigated. Also, we elucidated the relationship between the thickness of the electrolyte membrane and the degradation of the MEA for different shut-down procedures. When a thin electrolyte membrane was used, the closer of outlets mitigated the degradation during on/off operation. For the thicker electrolyte membrane, the dummy load which eliminates residual hydrogen and oxygen in the electrodes should be applied to lower the degradation.

Keywords: Dummy load; Membrane electrode assembly (MEA); Polymer electrolyte membrane; Proton exchange membrane fuel cell (PEMFC); Shut-down process

1. Introduction

Fuel cells have been spotlighted for their high conversion efficiency and environmental cleanliness. Among several fuel cells, proton exchange membrane fuel cell (PEMFC) is the most promising kind, which is considered for transportation usage. It can be operated at mild temperature (5–120 °C) and its start-up time is relatively short. Also, its performance decay by the on/off operation is low compared to other types of fuel cell such as molten carbon fuel cell (MCFC) and solid oxide fuel cell (SOFC). Even though the PEMFC has several advantages, it still has some problems, which have to be overcome for the commercialization. Especially, its long-term durability has to be improved to 5000 h (including thermal and realistic cycle operation) for the power generation system for fuel cell vehicles [1]. To improve the durability of PEMFC, the degradation phenomena of PEMFC components have to be examined thoroughly. There are lots of publications, which are related to the degradation of PEMFC components. Mostly, the degradation of an electrolyte membrane (Nafion-type perfluorosulfonated polymers) and electrodes (anode and cathode) in a membrane electrode assembly (MEA) has been investigated.

In case of the Nafion membrane, the formation of H_2O_2 at the anode side, which is followed by its decomposition to $^{\bullet}OH$ or $^{\bullet}OOH$ radicals could be the main reason for the degradation of the electrolyte membrane [2,3]. The radicals attack the Nafion's end group and initiate the polymer decomposition [3]. Kinumoto et al. reported that the presence of Fe^{2+} or Cu^{2+} enhances the decomposition rate of Nafion [4]. They found that main and side chains of the Nafion are decomposed by peroxide radical attack. They analyzed the decomposition using FT-IR and ^{19}F NMR. Recently, Mittal et al. measured fluoride emission rate (FER) from the fuel cell effluent water to quantify the membrane degradation [5]. According to their results, low relative humidity

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caused high degradation. Also, they reported that the operation at low current region produced high FER.

The long-term durability of electrode is also an important factor for the commercialization of PEMFC. The PEMFC operation under constant potential loses catalytic active surface area by the catalyst particle growth [6,7]. The potential cycling could accelerate the rate of surface area loss [8,9]. Yasuda et al. and Bi et al. studied the Pt dissolution and deposition between electrode and membrane or in the membrane with H_2/air or H_2/N_2 potential cycles. Also, Liu et al. studied the degradation of the MEA by cyclic current loading conditions, which simulate real driving conditions for automotives, with different analytical methods such as cell polarization, impedance spectra and hydrogen crossover rate [10]. They reported that the degradation of the MEA under the cyclic current loading conditions was different from that of the MEA under constant current mode. From the results, new model was established to incorporate the aging observations and describe the cell performance along with time. Another severe degradation is carbon corrosion in the electrodes. If the hydrogen is not supplied properly to the fuel cell, the carbon support at the anode side starts to react with water to generate proton [11], resulting in severe degradation.

As we mentioned above, there are several factors for the degradation of PEMFC. However, some of them do not really happen during the real PEMFC operation for fuel cell vehicles such as the operation under long OCV state and H_2/air potential cycles. If more realistic situation has to be considered, the degradation of the MEA during PEMFC on/off operation should be investigated. It was reported that start-up/shut-down process caused the oxidation of carbon support [12,13]. Hydrogen and air boundary developed at the anode after fuel cell shut-down or during its start-up caused the severe cathode carbon corrosion. In the case, thickness and catalytic active surface area of the cathode were reduced significantly.

In this study, we investigated several different kinds of situations, which could arise during real shut-down of PEMFC. For the shut-down process of PEMFC, we changed the conditions such as the open/close state of outlets and the application of dummy load [13] to remove residual hydrogen and oxygen in the electrodes. We report the best procedure for the shut-down process which lowers the degradation of MEA in the PEMFC.

2. Experimental

2.1. Materials

On/off operation cycles were carried out with commercially available membrane electrode assembly (commercial MEA). Also, in order to investigate the effect of the electrolyte membrane on the degradation by on/off operation, MEAs (25 cm^2) were prepared with Nafion 115 and Nafion 112 (Nafion 115-based MEA and Nafion 112-based MEA). They were fabricated by decal method [14]. Catalyst ink was prepared by mixing 45.5 wt.% Pt/C (Tanaka) with isopropyl alcohol (Baker Analyzed HPLC Reagent) and Nafion solution (EW1100, 5 wt.%, DuPont Inc.). The catalyst ink was sonicated for 0.5 h and applied to inert substrate (keptone film). Then, the catalyst layer was transferred to Nafion membrane by hot pressing (140 °C, 4 min, 100 kgf cm^{-2}). The Pt loading was 0.3 mg cm^{-2} and 0.4 mg cm^{-2} for anode and cathode, respectively.

2.2. PEMFC operation

The single cell was fabricated with MEA, gas diffusion media, Teflon gaskets and graphite blocks. To activate the cell, the gases (H_2 and O_2) were passed through bubble humidifiers (gas flow rate: 400 mL min^{-1} under ambient pressure) before entry via the fuel cell inlets.

I–V characteristics were evaluated using an electric load (Daegil Electronics, EL500P) at 70 °C under 100% relative humidity. H_2 and air were passed through humidifiers before they were allowed to enter the fuel cell inlets under ambient pressure.

2.3. On/off operation of PEMFC

On/off repetition (200 cycles) of PEMFC was carried out with three consecutive steps. In step 1, 100% humidified hydrogen and air were fed to anode and cathode for 10 s. In step 2, dry hydrogen and air were supplied to the fuel cell for 10 s. The outlets of anode and cathode were open in steps 1 and 2. Then, in step 3, inlets of anode and cathode were closed and several on/off techniques (processes 1–4) were carried out such as open/close state of outlets and the application of dummy load to remove residual hydrogen and oxygen in anode and cathode (Table 1). From step 2 to step 3, the OCP (open-circuit potential) was decreased to 0 V and from step 3 to step 1, voltage increased to OCP.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize changes in the Nafion 115- and Nafion 112-based MEAs after on/off repetition test.

3. Results and discussion

3.1. On/off operation of PEMFC

On/off repetition (200 cycles) of PEMFC using commercial MEA was carried out with different shut-down processes (processes 1–4). Fig. 1 shows the voltage response of the MEAs at the stage of step 3. When outlets of anode and cathode were open for the shut-down (process 1; Fig. 1(a)), the OCP decreased to 0 V in 40 min. If the dummy load was applied (process 2; Fig. 1(b)), the OCP decreased to 0 V in 10 s. The processes 3 and 4 also

Table 1
Experimental details for step 3 for shut-down process

	Anode outlet	Cathode outlet	Application of dummy load
Process 1	Open	Open	No
Process 2	Open	Open	Yes
Process 3	Close	Close	No
Process 4	Close	Close	Yes

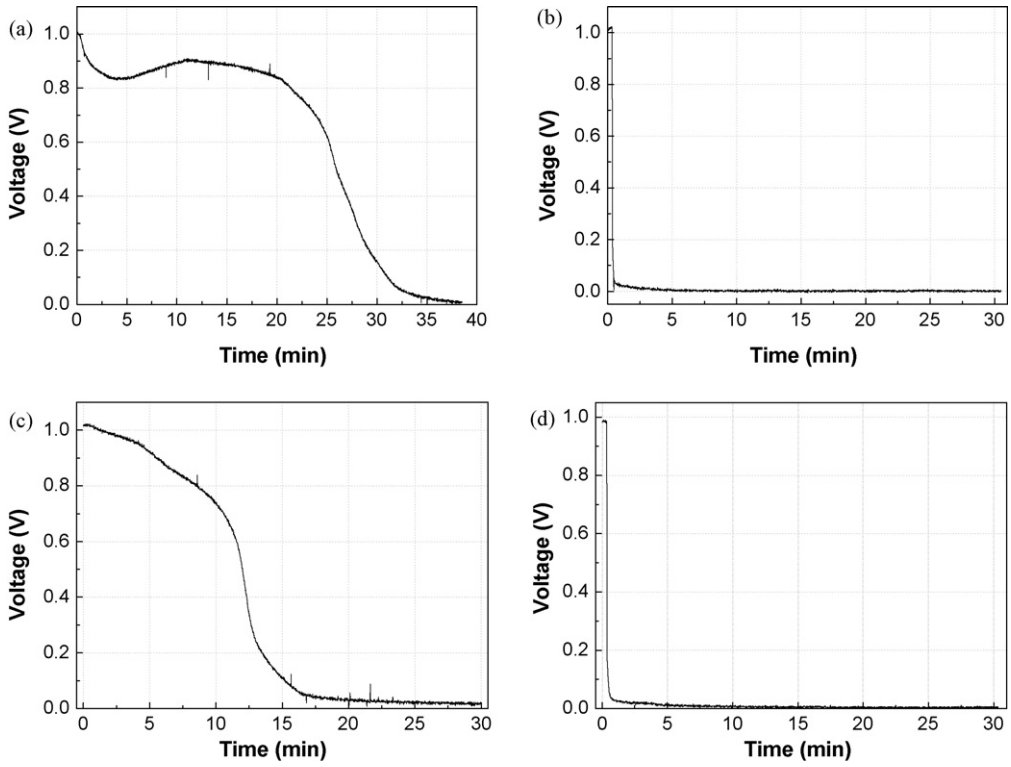

Fig. 1. Voltage responses during step 3 with shut-down processes 1 (a), 2 (b), 3 (c) and 4 (d) using commercial MEA.

showed same voltage responses as processes 1 and 2 (Fig. 1(c) and (d)), respectively.

After 200 on/off cycles of shut-down processes 1–4, *I–V* characteristic of the cell was analyzed. The results are presented in Fig. 2. When the outlets were open at the stage of step 3 for the cycles of shut-down process (process 1), the degradation of cell performance was severe (Fig. 2(a)). However, when dummy load was applied during step 3, the degradation of cell perfor-

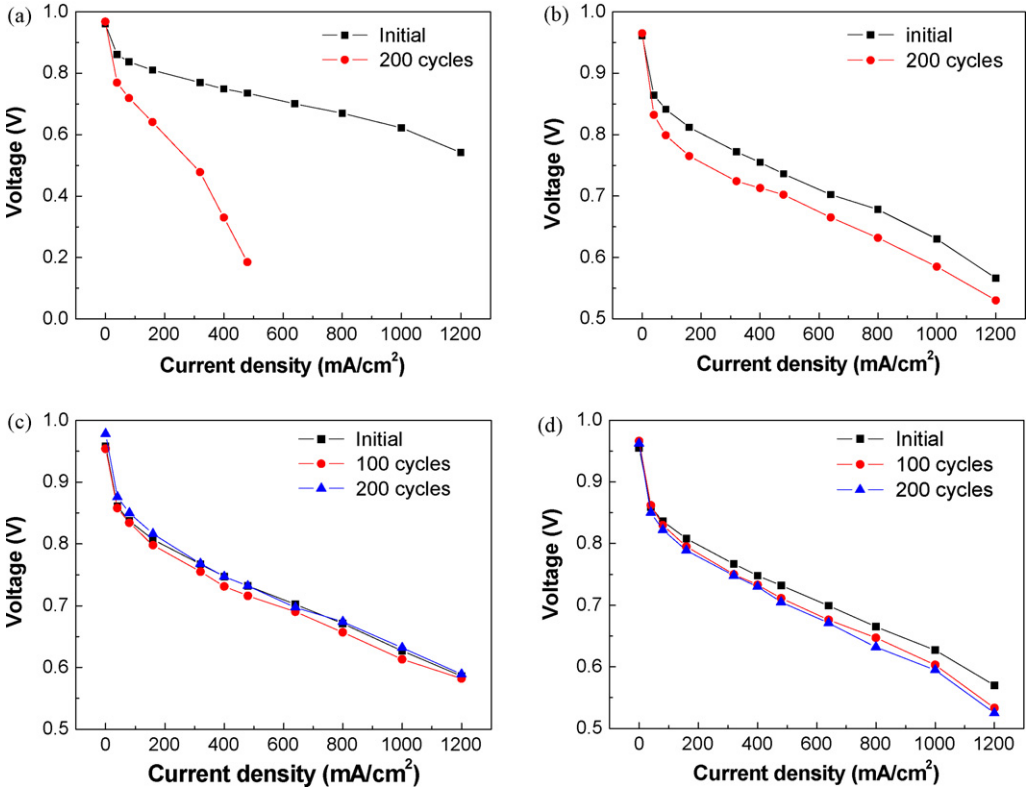

Fig. 2. Polarization curves after 200 cycles of shut-down processes 1 (a), 2 (b), 3 (c) and 4 (d) using commercial MEA.

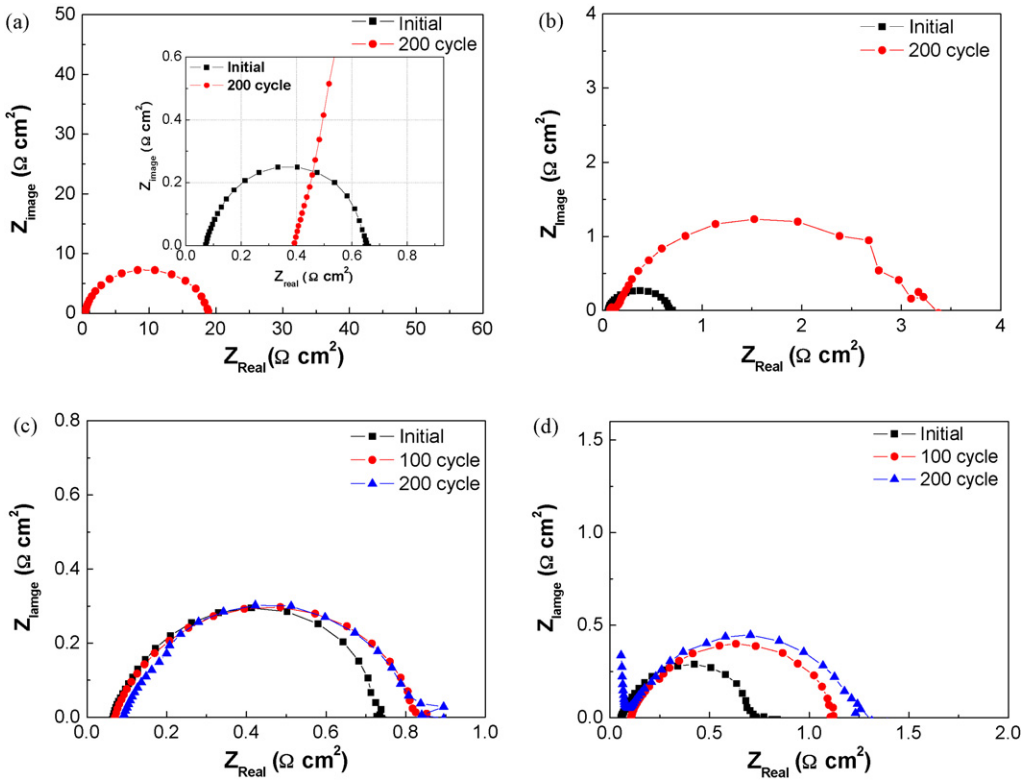

Fig. 3. Effects of the cycle on impedance of processes 1 (a), 2 (b), 3 (c) and 4 (d) using commercial MEA.

mance was reduced remarkably (process 2, Fig. 2(b)). When the outlets were closed at the stage of step 3 for 200 on/off cycles of shut-down process (process 3), the degradation of cell performance was not observed (Fig. 2(c)). Also, the degradation was very little when we applied dummy load to shut-down (process 4, Fig. 2(d)).

Fig. 3 shows the impedance analyses after 200 on/off cycles with shut-down processes 1–4. When the outlets were open during step 3 for on/off cycles (processes 1 and 2), charge transfer resistance increased dramatically. Also, it was observed that ohmic resistance increased without the application of the dummy load. Unlike processes 1 and 2, processes 3 and 4 showed relatively small increase of charge transfer resistance.

From four sets of on/off operation, we can obtain an idea for ideal shut-down process to reduce the degradation of PEMFC. The outlets of anode and cathode should be closed for the shut-down to improve the long-term durability. As reported previously [12,13], hydrogen and air boundary developed at the anode during shut-down caused the severe degradation of the cathode. Therefore, the outlets should be closed not to make hydrogen and air boundary.

As shown in Fig. 1(c), the OCP decreased to 0 V in 25 min during step 3 for the shut-down process 3. It could happen by the crossover of hydrogen and oxygen. Presumably, hydrogen, which comes from the anode, and oxygen are consumed in the cathode by catalytic activity. Also, oxygen, which is migrated from the cathode, and hydrogen are reacted in the anode. Therefore, after the OCP decreased to 0 V, there might be the mixture of small quantity of hydrogen and nitrogen in the electrode of the fuel cell. If the MEA is kept under the condition, hydrogen

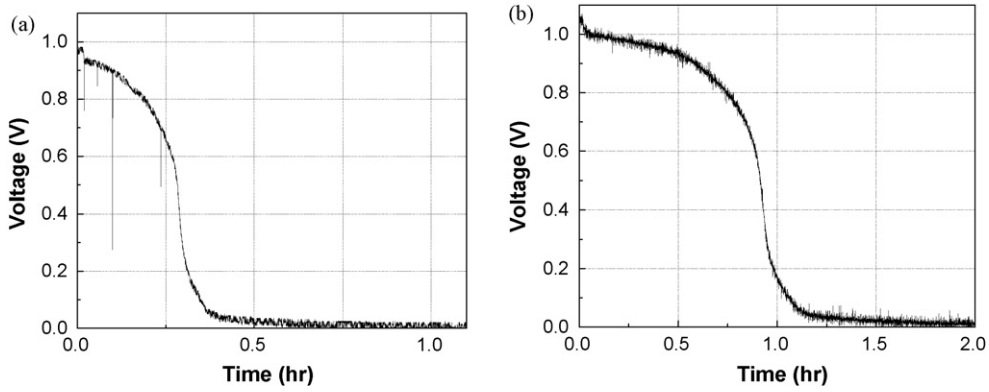

Fig. 4. Voltage responses during step 3 with shut-down process 3 using Nafion 112-based MEA (a) and Nafion 115-based MEA (b).

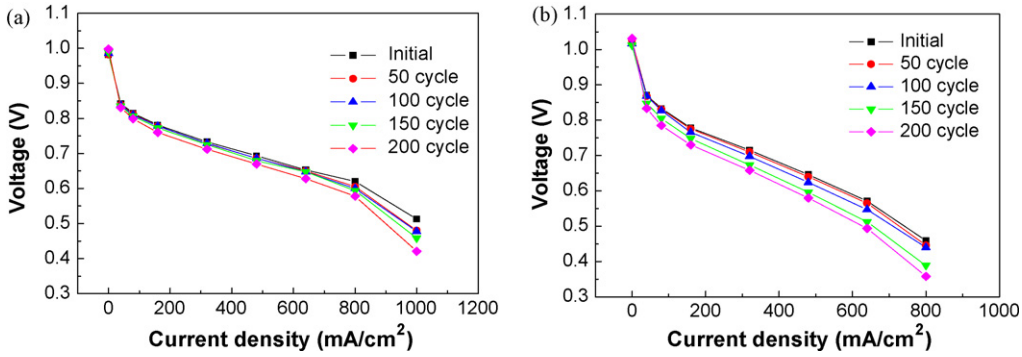

Fig. 5. Polarization curves of Nafion 112-based MEA (a) and Nafion 115-based MEA (b) after 200 cycles of shut-down process 3.

and air boundary is not formed during start-up, resulting in the mitigation of fuel cell degradation.

3.2. Effect of the membrane thickness on on/off operation of PEMFC

On/off repetition (200 cycles) of PEMFC was performed using Nafion 112- and 115-based MEAs with shut-down process 3. Fig. 4 shows the voltage response of the MEAs during step 3. Nafion 112- and 115-based MEAs needed longer time for voltage reduction (0.5 h and 1.5 h, respectively) than commercial MEA (Fig. 1(c)). The thickness of the electrolyte membrane of the commercial MEA is about 20–30 μm. Therefore, when the outlets of a single cell were closed during step 3, the crossover of hydrogen and air is relatively fast. However, electrolyte membranes of Nafion 112- and 115-based MEAs are much thicker than that of the commercial MEA. So, the crossover of hydrogen and air is slower, resulting in longer voltage reduction time from OCP to 0 V.

As reported previously [5,15], long duration of a PEMFC at high voltage accelerates the degradation of MEA. According to Fig. 4(b), Nafion 115-based MEA stayed for 45 min above 0.8 V during step 3 with shut-down process 3. It caused severe degradation by on/off repetition, resulting in low cell performance (Fig. 5(b)). Unlike Nafion 115-based MEA, Nafion 112-based MEA showed little performance degradation (Fig. 5(a)). It stayed for 10 min above 0.8 V during step 3 (Fig. 4(a)). This could relatively lead to low degradation with shut-down process 3.

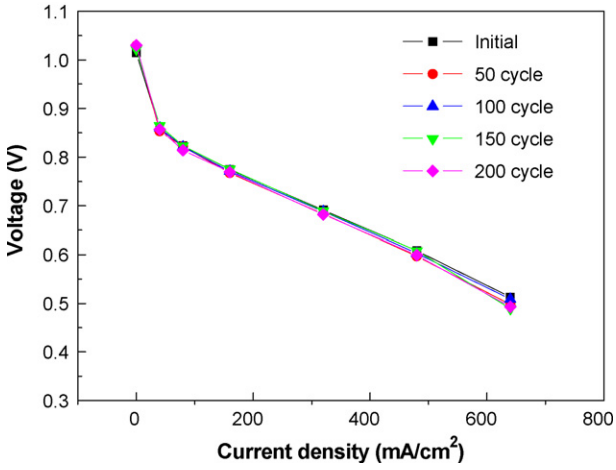

Fig. 6. Polarization curves of Nafion 115-based MEA after 200 cycles of shut-down process 4.

Instead of process 3, process 4 was used for the Nafion 115-based MEA for shut-down to mitigate the degradation. The result is presented in Fig. 6. Unlike on/off operation with process 3, the degradation of the cell was not observed. We believe that the dummy load to remove hydrogen and oxygen in step 3 is highly required for the MEA using a thick polymer electrolyte membrane such as Nafion 115.

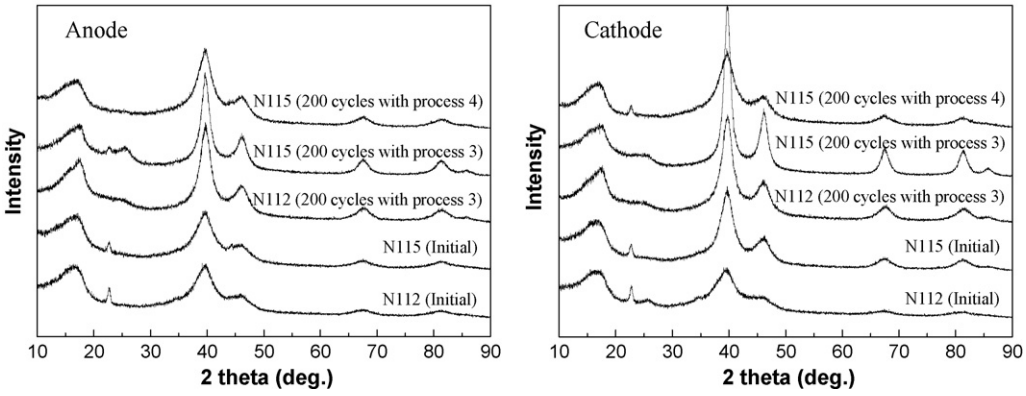

Fig. 7. X-ray diffraction patterns for anode and cathode of the MEAs using Nafion 112 and 115 before and after 200 on/off repetition with different shut-down method.

Table 2
The size of Pt particles from the X-ray patterns for anode and cathode of the MEAs using Nafion 112 and 115 before and after 200 on/off repetition

MEAs	Anode (nm) Pt (1 1 1)/Pt (220)[a]	Cathode (nm) Pt (1 1 1)/Pt (2 2 0)[a]
Nafion 112-based MEA (initial)	2.9/2.3	3.1/2.0
Nafion 115-based MEA (initial)	2.5/2.3	3.4/3.2
Nafion 112-based MEA (After 200 cycles with process 3)	3.4/3.9	3.7/3.8
Nafion 115-based MEA (After 200 cycles with process 3)	4.7/4.8	5.9/6.3
Nafion 115-based MEA (After 200 cycles with process 4)	3.3/2.8	3.3/2.7

[a] The particle size was calculated by the peak Pt (1 1 1) and Pt (2 2 0), respectively.

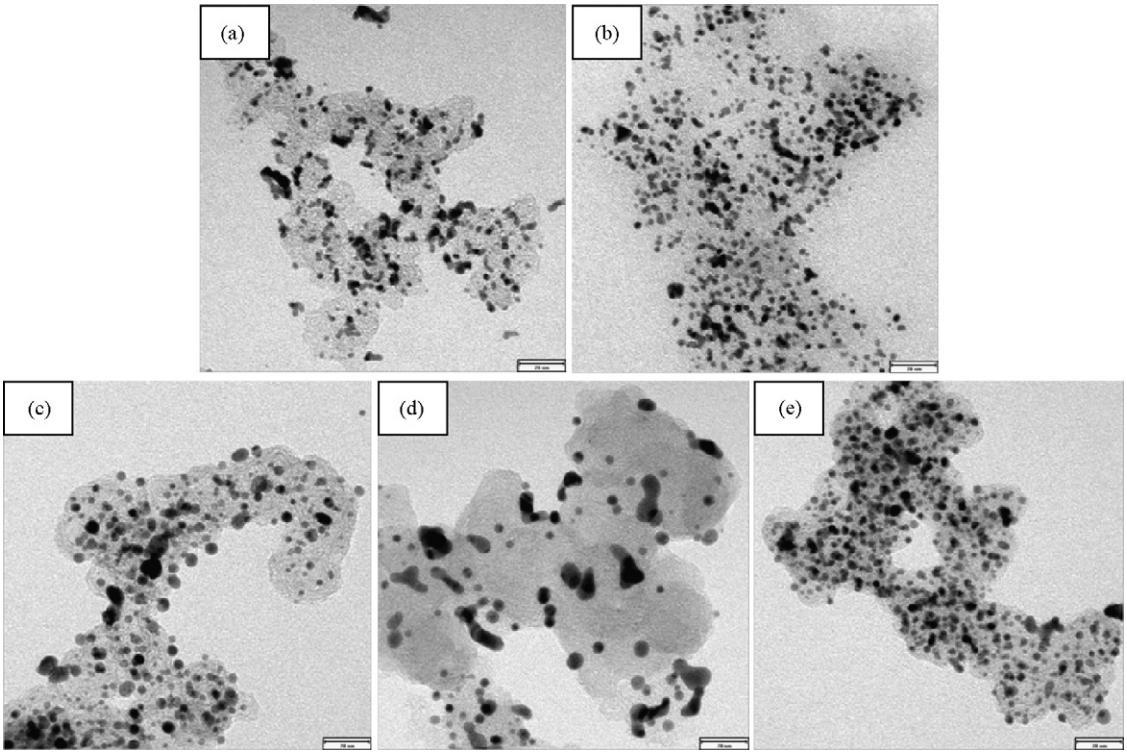

Fig. 8. TEM image for cathode of the MEAs using Nafion 112 and 115 before and after 200 on/off repetition with different shut-down methods: (a) N112 (initial), (b) N115 (initial), (c) N112 (after 200 cycles with process 3), (d) N115 (after 200 cycles with process 3), and (e) N115 (after 200 cycles with process 4).

The MEAs using Nafion 112- and 115-based electrolyte membrane were analyzed by XRD. Fig. 7 shows XRD of fresh MEAs and MEAs after 200 on/off repetition. Table 2 summarizes the results using the method, which was reported previously [16]. Pt particle size of the fresh MEAs was 2–3 nm. After 200 on/off cycles with process 3, Pt particle size of the MEA using Nafion 112 and 115 increased. Especially, in case of MEA using Nafion 115, Pt particle size increased dramatically. However, when the process 4 was used for the shut-down, the growth of the Pt particle was relatively mitigated. Fig. 8 shows TEM images of the MEAs before and after 200 on/off repetition. Fig. 8(a) and (b) presents fresh MEAs using Nafion 112 and 115. Also, Fig. 8(c)–(e) shows MEAs after 200 on/off cycles with different shut-down process. In case of the MEA using Nafion 115, severe Pt agglomeration was observed when on/off repetition was carried out with shut-down process 3, which agrees with the results by XRD analysis. The particle growth could arise by long duration at high voltage [17], resulting in low cell performance.

4. Conclusions

Four different procedures were performed to find a proper method for the shut-down of PEMFC. When a thin electrolyte membrane ($\leq$50 μm) was used for MEA, the closer of the outlets was very essential to mitigate the degradation of the MEA (namely, process 3). However, when the MEA with a thicker membrane (e.g. Nafion 115) was used, the closer of the outlets was not enough to reduce the degradation. Another approach has to be introduced to the shut-down process. Voltage response analysis during shut-down procedure using process 3 revealed that the MEA with a thicker electrolyte membrane stayed longer period above 0.8 V than that with a thinner electrolyte membrane. Especially, the MEA with Nafion 115 membrane was kept for 45 min above 0.8 V per one on/off cycle. This could cause severe degradation of Nafion 115-based MEA. For the MEA with a thick electrolyte membrane, a dummy load has to be applied to get rid of residual hydrogen and oxygen in the

electrodes (process 4). In the case, the degradation of the MEA was reduced dramatically.

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