

Effects of On/Off Cycles on the Degradation of PEMFCs

Recently, it was reported that degradation of the MEAs could be attributed to chemical attack of hydrogen peroxide on Nafion membrane and ionomer in the catalytic layer.¹⁻⁴ As a possible mechanism, it was suggested that hydrogen peroxide radical is formed at the anode side by the reaction of residual hydrogen with oxygen diffused from the cathode through the membrane.¹⁻⁴ Diffusion rate of oxygen is relatively high at open circuit voltage (OCV) during the idle period due to large oxygen concentration difference between anode and cathode.⁴ Thus, during the idle period, formation of hydrogen peroxide is facilitated resulting in degradation of MEAs.

To prevent formation of hydrogen peroxide and degradation of MEAs according to the mechanism described above, hydrogen or oxygen could be removed from the anode and the cathode gas channel, respectively, after operation. Since it is not economical to purge the anode and the cathode gas channel with an inert gas such as nitrogen or to purge the cathode gas channel with hydrogen, purging the anode gas channel with air would be a feasible method for fuel cell vehicles. However, in that case, carbon corrosion might occur to degrade performance of PEMFC.^{5,6} Supplying air to the anode gas channel creates a moving boundary between fresh air and residual hydrogen. The boundary makes a shorted cell in the anode side and results in a high voltage around 1.6 V at the cathode side opposite to the anode portion that sees air causing carbon corrosion.^{5,6} Even though these degradation mechanisms have been suggested, effects of hydrogen removal using air-purging on durability of PEMFCs operating with repetitive on/off cycles have not been reported. In this study, to development a durable shutdown process for PEMFCs, degradation of the MEAs operating with repetitive on/off cycles with or without hydrogen removal process was investigated by evaluating performance of single cells. Characteristics of the MEAs were analyzed by AC impedance spectroscopy, cyclic voltammetry, gas leak, cross-sectional SEM images, and TEM images.

Experimental

The load cycle employed in this study to simulate an on/off procedure consisted of 4 steps; in step 1, as reactant gases, hydrogen and air were supplied to the anode and the cathode, respectively, for 15 minutes without applying load; in step 2, load was increased from 0 to 15 A (0.6 A/cm^2) at an increment rate of 1 A/min for 15 minutes; in step 3, the cell was operated at the constant load of 15 A for 30 minutes; in step 4, with keeping air supply to the cathode, load was removed and simultaneously the anode gas line was switched to and fed with a idle-purging gas for 15 minutes. As the purging gas, hydrogen or air was used. The former case was called 'hydrogen/air purging' and the latter 'air/air purging'.

Results and Discussion

Performance decay – With repeating the load cycle, cell voltage was measured at every cycle at the end of step 1 and 3 as represented in Fig. 1. As shown in Fig. 1(a), for the hydrogen/air purging cycle, open circuit voltage (OCV) measured at the end of step 1 decreased by 0.35 V during 50 cycles while remained almost constant for the air/air purging load cycle. Decrease in OCV could be attributed to gas crossover through the membrane.⁸ It was reported that oxygen diffused from cathode to anode and react with hydrogen to form hydrogen peroxide at relatively high rate at OCV.²⁻⁴ Hydrogen peroxide radicals attack the polymer electrolyte membrane, resulting in a decrease in cell performance.²⁻⁴ Therefore, in the hydrogen/air purging cycle, more amount of hydrogen peroxide could be formed and attacked the membrane than in the air/air purging cycle, leading to degradation of membrane and an increase in gas crossover. Fig. 1(b) exhibits that cell voltage measured at a current density of 0.6 A/cm^2 at the end of step 3 decreased by 0.21 and 0.13 V during 50 cycles and the decay rate was estimated to be 4.2 and 2.6 mV/cycle in hydrogen/air and air/air purging cycle, respectively.

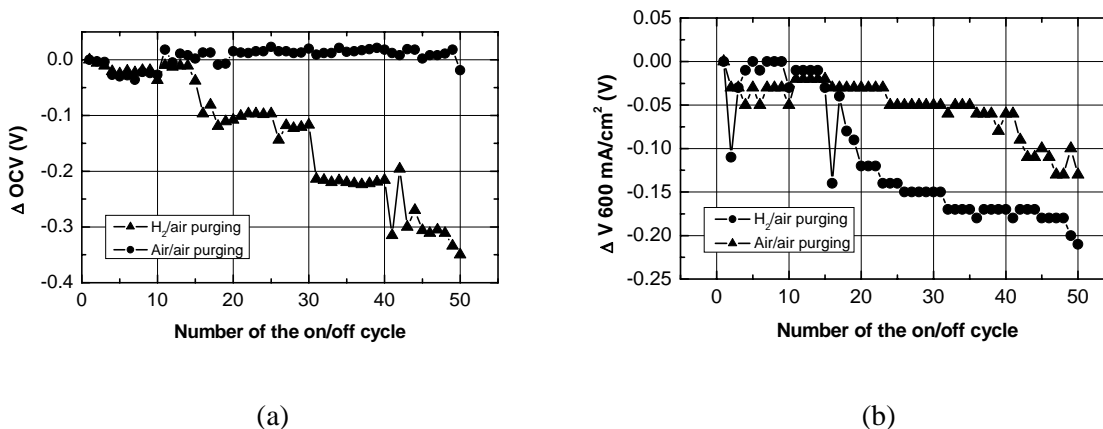


Figure 1. Effects of the idle-purging gases on (a) open circuit voltage (OCV) and (b) cell voltage at 600 mA/cm^2 measured at the end of step 1 and 3, respectively.

Electrochemical Analysis – To examine electrochemical degradation of the MEAs, impedance spectroscopy and cyclic voltammetry were performed after every 10 cycles. AC impedance of the single cells was measured to obtain polarization resistances of the single cell. As shown in Fig. 2(a), charge transfer resistance of the single cell increased more rapidly in the hydrogen/air purging cycle (from 3.1 to $19.5 \text{ } \Omega\text{cm}^2$ in 30 cycles) than in the air/air purging cycle (2.8 to $4.7 \text{ } \Omega\text{cm}^2$ in 50 cycles). For hydrogen/air purging cycle, impedance spectroscopy could not be measured after 30 cycles since open circuit voltage of the cell was lower than the measurement potential of 0.85 V . Those results imply that the residual hydrogen in the anode gas channel increased charge transfer resistance and hence activation loss possibly by sintering Pt catalyst and/or destruction of three-phase boundaries. The increase in charge transfer resistance could be effectively prevented removing the residual hydrogen from anode gas channel by air-purging. Fig. 2(b) shows utilization of Pt particles calculated from the charge. In the case of hydrogen/air purging, Pt utilization decreased from 39.6 to 27.4% in 30 cycles while in the case of air/air purging from 39.1 to 25.0% in 50 cycles. These results demonstrate that with repeating load cycles reduced the electrochemical active surface area and utilization of platinum catalysts and that the decrease in Pt utilization was faster in the hydrogen/air

purging cycle than in the air/air purging cycle.

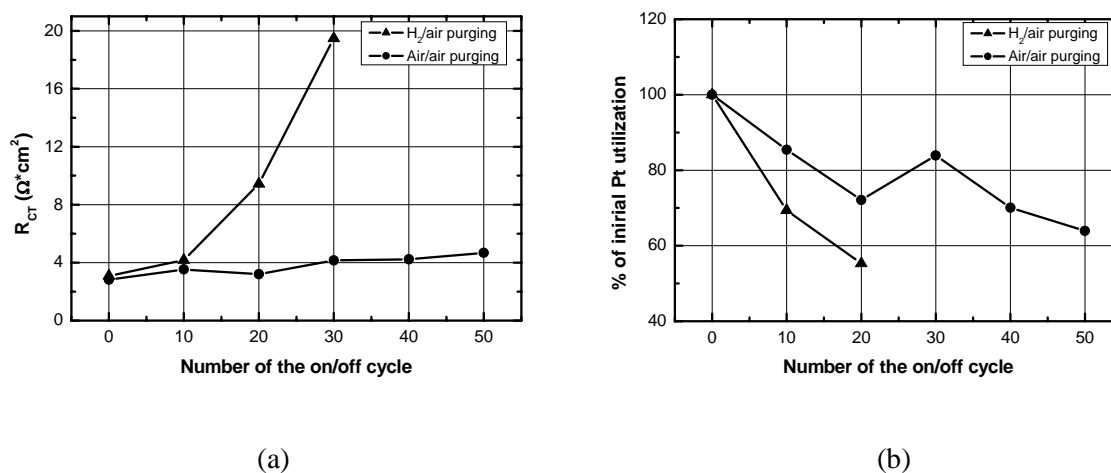


Figure 2. Effects of the idle-purging gases on (a) charge transfer resistance and (b) Pt utilization of the single cells.

Post Analysis – To measure gas crossover through the membrane, gas leak was measured before and after 50 cycles. Since the gas leak test might cause physical damage to the membrane, gas leak was not measured during the cycling. Before cycles, neither internal nor external gas leak was detected for both single cells. After 50 cycles, external leak was not detected implying no gasket failure. For the hydrogen/air purging cycle, internal leak through the membrane was measured to be 435 and 1,180 mL/min at pressure difference between anode and cathode of 0.5 and 1.0 bar, respectively. In contrast, for the air/air purging cycle, internal gas leak was not detected. The high gas crossover through the membrane in the hydrogen/air purging cycle could be attributed to degradation of the membrane such as thinning and pinhole formation.

Fig. 3 presents cross-sectional SEM images of the MEAs before and after 50 cycles. Thickness of the fresh membrane was 50 μm as shown in Fig. 3(a). After 50 cycles, thickness of the membrane was reduced to 15 and 35 μm in the hydrogen/air and air/air purging cycle, respectively. Decomposition of Nafion® membrane and the resulting emission of fluorine by chemical attack of

hydrogen peroxide radical have been reported.^{2,3} Thus, it could be concluded that, during on/off cycles, gas crossover facilitated the membrane thinning was one of the reasons to degrade PEMFC performance and that by removing the residual hydrogen from the anode gas channel, formation of hydrogen peroxide and thinning of the membrane could be effectively prevented.

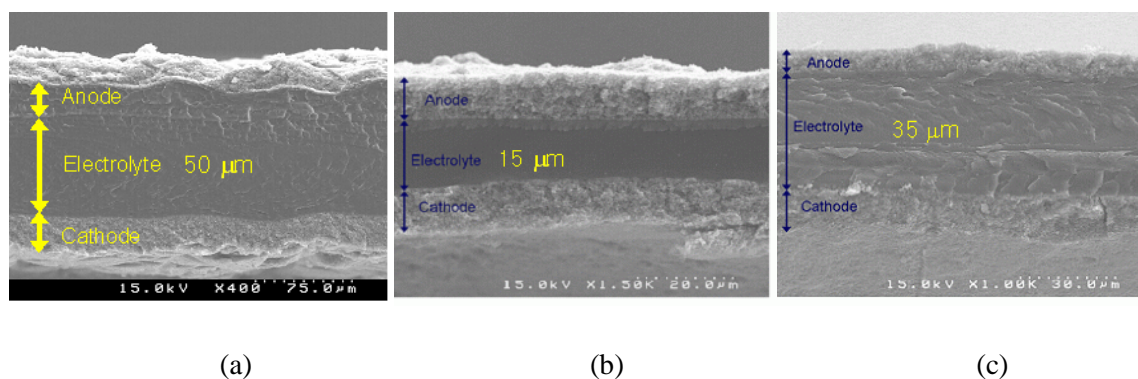


Figure 3. Cross-sectional SEM images of the MEAs (a) before and after 50 on/off cycles employing (b) hydrogen/air and (c) air/air as the idle-purging gases.

To analyze particle size of Pt catalyst, TEM images were taken before and after 50 cycles for anode and cathode. For the anode represented in Fig. 4, average particle size was measured to be 2.4 nm for fresh MEA while 4.9 and 4.3 nm after 50 cycles employing hydrogen/air and air/air purging respectively. Similarly for the cathode, during 50 cycles average particle size increased from 2.5 to 5.1 and 4.3 nm for the hydrogen/air purging cycle and the air/air purging cycle, respectively. Thus, during the on/off cycles, particle size of the catalyst increased for both the anode and cathode and sintering of Pt catalyst was faster in the hydrogen/air purging cycle than in the air/air purging cycle. These results demonstrate that the decrease in surface area of Pt catalyst could reduce the electrochemical active surface area and cell performance by increasing charge transfer resistance and activation loss and that sintering of Pt catalyst could be mitigated by removing hydrogen from anode gas channel during idle period.

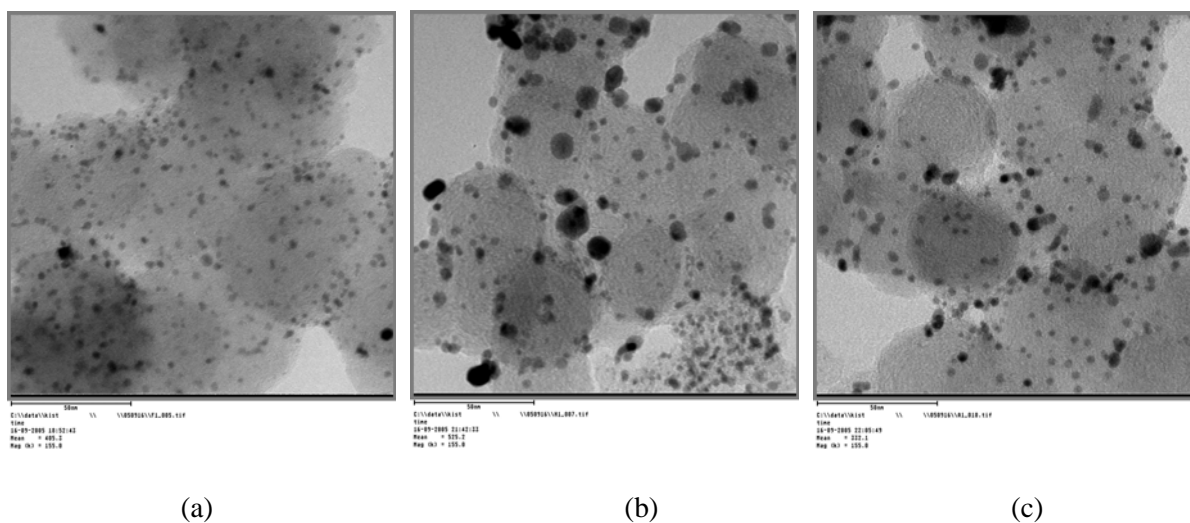


Figure 4. TEM images of anode of the MEAs (a) before and after 50 on/off cycles employing (b) hydrogen/air and (c) air/air as the idle-purging gases.

Conclusions

Effects of hydrogen removal during idle period on performance and characteristics of MEAs were investigated. With repeating load cycle including hydrogen/air purging during idle period, open circuit voltage (OCV) and voltage at low current densities i.e. below 100 mA/cm^2 was rapidly lowered implying an increase in gas crossover through the membrane and an increase in activation loss. The increase in gas crossover was confirmed by an incline of cyclic voltammograms and gas leak test and could be attributed to thinning of the membrane as observed on cross-sectional SEM images for the MEA. The increase in activation loss could be associated with an increase in charge transfer resistance revealed by ac impedance spectroscopy and with a decrease in electrochemical active surface area evaluated by cyclic voltammograms, that resulted from sintering of Pt catalyst as observed on TEM images for the electrodes. Degradation of the MEA exposed to the repetitive on/off cycle was significantly reduced by purging the anode gas channel with air to remove the residual hydrogen during idle period.

References

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