



## Effects of MEA fabrication method on durability of polymer electrolyte membrane fuel cells

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### ABSTRACT

To study the effects of fabrication methods on the durability of polymer electrolyte membrane fuel cells (PEMFCs), membrane-electrode assemblies (MEAs) were fabricated using a conventional method, a catalyst-coated membrane (CCM) method, and a CCM-hot pressed method. Single cells assembled with the prepared MEAs were operated galvanostatically at  $600 \text{ mA cm}^{-2}$  for 1000 h for the conventional MEA and the CCM MEA and for 500 h for the CCM-hot pressed MEA. During operation, *i*-*V* curves, impedance spectra, and cyclic voltammograms were measured roughly every 100 h. Before and after long-term operation, the physical and chemical characteristics of the MEAs were analyzed using mercury porosimetry, X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and Fourier transformation infrared spectroscopy (FTIR). Under the operating conditions, the CCM MEA exhibited the lowest degradation rate as well as the highest initial performance.

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### 1. Introduction

In developing proton exchange membrane fuel cells (PEMFCs) for commercial applications, the durability of membrane-electrode assemblies (MEAs) is one of the vital issues [1]. Many articles have dealt with degradation of the electrodes in relation to loss of catalyst surface area caused by agglomeration, dissolution, migration, formation of metal complexes and oxides [2–5], and/or instability of the carbon support [6]. Membrane degradation can be caused by mechanical or thermal stress resulting in formation of pinholes and tears [7–9] and/or by chemical attack of hydrogen peroxide radicals [7,10] formed during the electrochemical reactions. Contamination of MEAs due to corrosion of the bipolar plate, cell assembly parts, humidifiers, and gaskets/sealing materials can reduce the proton conductivity of the electrolyte and oxygen reduction kinetics at the cathode [11–14]. MEAs can be degraded by severe operating conditions such as insufficient reactant flows [15,16], high or low humidification of the reactant gases [1,17–19], and high or low operating temperature [19]. Improper water management (too wet or too dry) may have detrimental effects on MEA degradation [20]. Even though extensive studies [1–20] have investigated degradation phenomena of PEMFCs, effects of MEA fabrication conditions on PEMFC degradation have not yet been elucidated.

In this work, the influence of the MEA fabrication method on the durability of PEMFCs were examined based on the long-term performance of single cells prepared by a conventional (hot-pressing) method, a catalyst-coated membrane (CCM) method, and a combination of the conventional method and the CCM method.

### 2. Experimental

#### 2.1. Fuel cell tests

Catalyst ink was prepared by mixing 40 wt% Pt/C (E-tek, Inc.) with isopropyl alcohol (Baker Analyzed HPLC Reagent) and then sonicating for 1 h. 5 wt% Nafion® solution (Du Pont, Inc.) was added to the catalyst ink, which was sonicated again for 1 h. MEAs were fabricated by a conventional method, a catalyst-coated membrane method, and a combination of the conventional method and the CCM (CCM-hot pressed) method. For the conventional MEA, the prepared catalyst ink was sprayed on a wet-proofed carbon paper (Sigracet®, SGL Carbon Inc.) to make an electrode. Then, the electrodes were placed on both sides of a pre-treated Nafion® 112 membrane and hot pressed. A CCM MEA was fabricated by spraying the prepared ink on both sides of a pre-treated Nafion® 112 membrane. The prepared CCM MEA was then dried at 70 °C prior to being assembled with wet-proofed carbon papers. To make a CCM-hot pressed MEA, a catalyst-coated membrane was prepared as described above for the CCM MEA and then hot-pressed with carbon papers. In all the methods, the active electrode area was  $25 \text{ cm}^2$  with catalyst loading of 0.3 and 0.4 mg Pt  $\text{cm}^{-2}$  for anode and cath-

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ode, respectively, and hot pressing was conducted at 140 °C with a compaction pressure of 200 kg cm<sup>-2</sup> for 90 s. Single cells were assembled with a prepared MEA, Teflon gaskets, and 5 channel semi-serpentine graphite blocks. H<sub>2</sub> and O<sub>2</sub> or air were fed to the anode and cathode, respectively. The stoichiometry of H<sub>2</sub> and O<sub>2</sub> or air was 1.5 and 3 with relative humidity of 100 and 55%, respectively. The cell temperature was 80 °C.

Before recording the initial *i*-*V* characteristics, all the MEAs were activated with H<sub>2</sub>/O<sub>2</sub> followed by H<sub>2</sub>/air for 24 h, respectively, at 0.6 V. The single cells were then operated galvanostatically with H<sub>2</sub>/air at 600 mA cm<sup>-2</sup> (15 A) and the cell voltage was recorded. During operation, electrochemical analyses were performed roughly every 100 h. For *i*-*V* measurements, the load of 15 A was removed from the cell without changing the gas supply. When the cell voltage reached open circuit voltage (OCV), current was applied to the cell as a step function of 40 or 100 mA cm<sup>-2</sup> and the cell voltage was recorded. Ohmic resistance and polarization resistance were estimated by measuring ac impedance for the cathode of the single cells, which was used as the working electrode. For impedance measurements, humidified air and H<sub>2</sub> were supplied to the cathode and the anode, respectively. The applied frequency was varied from 10 kHz to 10 mHz with an amplitude of 5 mV (peak-to-peak). Cyclic voltammograms (CVs) were measured at a scan rate of 50 mV s<sup>-1</sup>. During the measurement, humidified N<sub>2</sub> and H<sub>2</sub> were fed to the working electrode and the counter electrode, respectively. For the measurements of ac impedance and CVs, the counter electrode also served as a reference electrode, since the overpotential at the counter electrode for the hydrogen oxidation or evolution reaction is negligible [21].

## 2.2. MEA characterization

Chemical and physical characteristics of the MEAs were investigated by mercury porosimetry, X-ray diffraction (XRD), scanning electron microscopy (SEM) combined with electron probe micro analysis (EPMA), and Fourier transformation infrared spectroscopy (FTIR) before and after long-term operation. Pore structures of the electrodes were determined by using Micromeritics auto pore IV for both sides of the MEA simultaneously. Therefore, for measuring the pore structure, MEAs with the same catalyst layer on both sides of the membrane were prepared apart from the MEAs for performance measurements. XRD patterns were taken with a Rigaku DMAX 2500 to obtain the Pt crystallite size. To take cross-sectional SEM images of the MEAs, samples were prepared by cutting the MEAs in liquid nitrogen followed by impregnating into epoxy and polishing with sandpaper for EPMA. FTIR analysis was performed to analyze the chemical bonding structure of the MEAs. MEA samples were immersed in isopropyl alcohol and then gently wiped to remove the catalyst layer to separate membrane from MEA. The membrane was then washed several times with isopropyl alcohol and deionized water and finally dried before analysis.

## 3. Results and discussion

### 3.1. Single cell performance and durability

Fig. 1 presents cell voltage measured during operation at 600 mA cm<sup>-2</sup>. At the beginning of operation, the CCM MEA exhibited the highest cell voltage of 0.65 V, followed by the CCM-hot pressed (0.63 V) and the conventional MEA (0.61 V). However, during operation the cell voltage of the CCM-hot pressed MEA decreased faster (0.32 mV h<sup>-1</sup> on average) than that of the others (0.14 and 0.12 mV h<sup>-1</sup> for the conventional MEA and the CCM MEA, respectively, on average). Thus, the CCM-hot pressed MEA was operated only for 500 h while the other MEAs were operated for 1000 h.

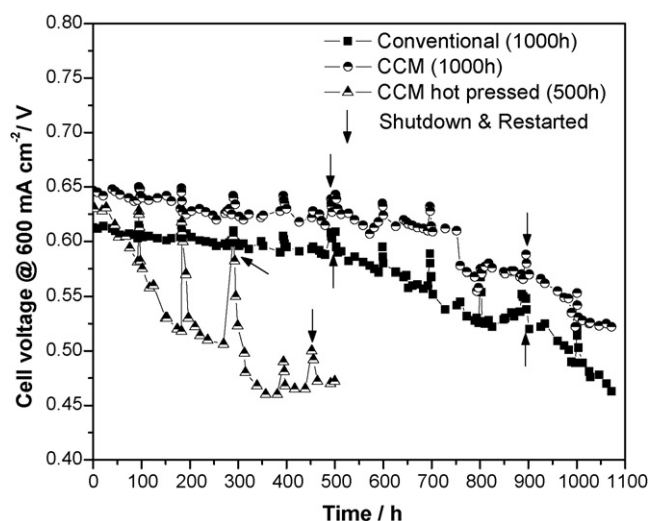


Fig. 1. Effects of MEA fabrication method on voltage degradation of the single cells operated at 600 mA cm<sup>-2</sup>.

Those results show that, among the MEAs prepared in this study, the CCM MEA had the best performance and durability.

It should be noted that, for all the prepared single cells, slight increases in the cell voltage were observed after the electrochemical analyses taken about every 100 h. These increases could be associated with water distribution in the single cells. During continuous operation of a single cell, water can accumulate in the gas diffusion media and the catalytic layers since water is produced by the electrochemical reactions in proportion to an applied load. However, for the electrochemical analyses, the load was removed from the cell without changing the gas supply to allow the cell to reach an equilibrium state (open circuit voltage). It is therefore possible that some of the accumulated water in the cell was removed from the cell with the gas flow, resulting in a performance improvement. The increase in cell performance was temporary and the cell voltage returned to the previous state, probably due to re-accumulation of water in the gas diffusion media and the catalytic layers. The abrupt increases and decreases in cell voltage at 500 and 900 h for the conventional MEA and the CCM MEA and at 300 and 450 h for the CCM-hot pressed MEA were caused by shutdown and restart of the single cells due to electricity interruption; these changes could also have been caused by redistribution of water in the gas diffusion media and catalytic layers.

Up to 300 h, whenever the cell voltage of the CCM-hot pressed MEA temporarily increased, it reached almost the same value as that of the conventional MEA or the CCM MEA. Hence, the fast degradation of the CCM-hot pressed MEA seems to be related to accumulation of water in the gas diffusion media and the catalytic layers. In other words, the fast voltage drop of the CCM-hot pressed MEA was not mainly caused by irreversible degradation of the MEA such as catalyst loss, membrane degradation, etc., but by reversible phenomena such as water accumulation in the gas diffusion media and the catalytic layers. After 300 h, the cell voltage of the CCM-hot pressed MEA did not recover to as high a value as that of the conventional MEA or the CCM MEA, suggesting that irreversible degradation occurred or that the accumulated water was not completely removed from the gas diffusion media and catalytic layers.

The reason that the water accumulation was more severe in the CCM-hot pressed MEA than in the conventional MEA and the CCM MEA can be found in the fabrication process. It is straightforward that the catalytic layers of the CCM-hot pressed MEA have lower porosity than the CCM MEA since it was made by hot pressing a CCM MEA. Fig. 2 shows the cumulative pore area of the catalytic layers

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