

Short communication

A comparative study of CCM and hot-pressed MEAs for PEM fuel cells

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Abstract

A comparative investigation was performed on PEM fuel cells made with conventional hot-pressed MEAs and catalyst-coated membranes (CCM) under identical conditions of Pt electrocatalyst loadings. The results showed that cells with a CCM exhibit significantly higher electrochemical performance and power density than those prepared with conventional hot-pressed MEAs. Cyclic voltammetric and impedance studies showed that the MEAs prepared by the CCM method have a higher electrochemical surface area, low cell ohmic resistance and low charge transfer resistance as compared to those prepared with hot-pressed MEAs and the same Pt loading. The results demonstrate that a CCM can enhance the utilization efficiency and improve the catalyst layer and membrane interface of PEM fuel cells.

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1. Introduction

Proton exchange or polymer electrolyte membrane fuel cells (PEMFC) are considered to be the most promising power sources for portable and transportation applications since they electrochemically convert the chemical energy of hydrogen fuel into electrical energy with high efficiency and very low greenhouse gas emissions [1–4]. Due to the fact that PEMFCs need precious metals as the electrocatalyst, decreasing the amount of precious metal without sacrificing the performance is necessary [5,6]. The key to reducing the loading of precious metals and maintaining the performance is to increase the catalyst utilization of the membrane electrode assemblies (MEA) of a PEM fuel cell. The MEA comprises a polymer electrolyte membrane and catalyst electrodes for hydrogen oxidation (anode) and oxygen reduction (cathode).

In a fuel cell system, the electrochemical reaction can only occur at “triple-phase boundaries”, where the electrolyte, reaction material, and electrically connected catalyst particles contact together in a MEA [7,8]. The triple-phase-boundary area in turn depends significantly on the fabrication procedure of

MEA in addition to other important parameters such as catalyst loading and ionomer loading [9–11]. Primarily two fabrication methods may be used to prepare MEAs, hot-press and catalyst-coated membrane or CCM method. In the case of MEA by hot-press method, the Pt/C catalyst mixing with a PTFE suspension is spread onto the porous carbon paper or cloth support, and sintered to produce the electrodes. The electrodes are sandwiched between a proton exchange membrane and then hot pressed to form a MEA [12,13]. On the other hand, MEA can also be prepared by a catalyst coated membrane (CCM) method [14–16]. In the CCM method, the Nafion containing catalyst ink is spread on a Teflon support and then transferred to the proton exchange membrane by hot pressing. The Teflon support is then peeled away and the catalyst coated membrane is sandwiched between porous carbon paper or cloth supports. It is reported that the MEA prepared by the CCM method provides better power density due to an extended catalyst/ionomer interface and improvement of catalyst utilization [17]. Thus it is important to investigate the performance and electrochemical activity of the MEA by the hot-press and CCM methods under identical experimental conditions. The results in the present study clearly show that the MEAs prepared by the CCM method not only have high catalyst utilization, but also have a smaller contact resistance and charge-transfer resistance which makes the fuel cells have a promising power output.

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2. Experimental

2.1. Preparation of membrane electrode assemblies (MEA)

Prior to fabricating the electrodes, a homogeneous suspension composed of PTFE and carbon powder was sprayed onto carbon paper (TGP-060, Toray Inc.) to form the gas diffusion layer (GDL) with a sublayer [18]. The proton exchange membranes (PEM, Nafion 112, DuPont) were treated according to the standard procedure of 30 min in 5 wt.% H_2O_2 solution at 80°C , 30 min in distilled water at 80°C , 30 min in 8 wt.% H_2SO_4 solution at 80°C and finally 30 min in distilled water at 80°C again.

The catalyst slurry was prepared before the MEA and CCM fabrications. During the preparation, 1 g Pt/C catalysts (60 wt.% Pt/C, Johnson Matthey) were mixed with 13 mL deionized water under vigorous stirring. Then 6.7 mL Nafion solution (DE 520, 5 wt.%, EW 1000, DuPont) was added to the mixture, followed by ultrasonic treatment for 30 min and a high-speed homogenizer (20,000 rpm) for 1 h to form catalyst slurry.

To prepare the MEA by the hot-press method, the catalyst slurry was screen-printed onto the GDL to form the electrode layer. The electrode layer was dried at 60°C for 10 min followed with at 90°C in N_2 atmosphere for 3 min. The pretreated membrane and electrode layers were bonded together by hot pressing under 10 MPa for 90 s, maintaining the temperature at 125°C . The Pt loading was controlled by weight and the value for both the anode and cathode was 0.2 mg cm^{-2} .

For the preparation of MEA by the CCM method, the same catalyst slurry was applied to PTFE thin film by spraying. After dried at 60°C for 10 min followed with at 90°C in N_2 atmosphere for 3 min, the catalyst layer was then transferred onto the membrane at 125°C and 10 MPa by the decal method to form the catalyst-coated membrane (CCM). The GDL was placed on the anode and cathode side of the CCM to form the MEA. The Pt loading was controlled by weight and the value for both the anode and cathode catalyst layer was 0.2 mg cm^{-2} .

2.2. Single cell tests

Single cells were assembled with the prepared MEAs and graphite flow field plates under the assembly pressure of 10 MPa. The active area of the cell was $5\text{ cm} \times 5\text{ cm}$. The experiments were operated in a fuel cell mode. For H_2/O_2 and H_2/air test, the flow rate of pure hydrogen, oxygen and air are controlled at a stoichiometry of $1.2\times$, $2\times$ and $3\times$, respectively. The gases were not humidified before being fed into the cell. The test was carried out at ambient temperature with zero back pressure. Performance of the single cell was evaluated by measuring the I – V curves using a fuel cell test station (G50, GreenLight).

Polarization resistance of the single cells was investigated by electrochemical impedance spectroscopy (EIS). The impedance spectra were recorded in the 10 mHz to 100 kHz frequency range with a sinusoidal amplitude of 10 mV using IM6 (Zahner). The oxygen (air) and hydrogen gas were supplied into the cathode and anode, respectively. Due to the much faster reaction kinetics of the H_2 oxidation reaction on the Pt/C electrocatalysts as com-

pared to that of the O_2 reduction reaction [19], the cell impedance would be mainly dominated by the cathode impedance. The anode at which hydrogen oxidation takes place was used as the reference and also as the counter electrode of the AC measurements (the cathode was used as the working electrode). The electrochemical active surface area or activity of the cell was estimated from cyclic voltammograms measured at scan rate of 20 mV s^{-1} and at ambient temperatures. During the measurement, dry hydrogen at a flow rate of 10 sccm was fed to the anode (which served as the counter and reference electrodes) and argon to the cathode at 100 sccm, which served as working electrode. The potential was scanned between 0.05 and 1.2 V versus the cathode (working electrode). Relative electrochemical active surface areas were obtained by comparing the area of hydrogen oxidation peaks from the cyclic voltammograms.

3. Results and discussion

Current density–voltage and current density–power density curves for the CCM hot-pressed MEA under H_2/O_2 and H_2/air are shown in Fig. 1. The cell performance of the CCM is clearly better than the hot-pressed MEA under identical test condition of H_2/O_2 and H_2/air . Under H_2/O_2 , the peak power of the cell made by CCM is 718 mW cm^{-2} , higher than 651 mW cm^{-2} measured on the cell made by hot-pressed MEA. Under test conditions of H_2/air , the peak power is 450 and 352 mW cm^{-2} for the cell made by CCM and hot-pressed MEA, respectively. This indicates that the CCM effectively improves the performance of the PEM fuel cell without the increase in the Pt electrocatalyst loading. In the case of H_2 as fuel and air as oxidant, the cell made from CCM reached the limiting region at a current density of $\sim 1400\text{ mA cm}^{-2}$, which almost doubled $\sim 760\text{ mA cm}^{-2}$ for the cell made from conventional hot-pressed MEA. This suggests that the cell with CCM must have high utilization of Pt electrocatalyst and better contact between the Pt catalysts and the ionomer, probably due to the reduced catalyst loss into the gas diffusion layer. In the resistance-controlled region, the slope of

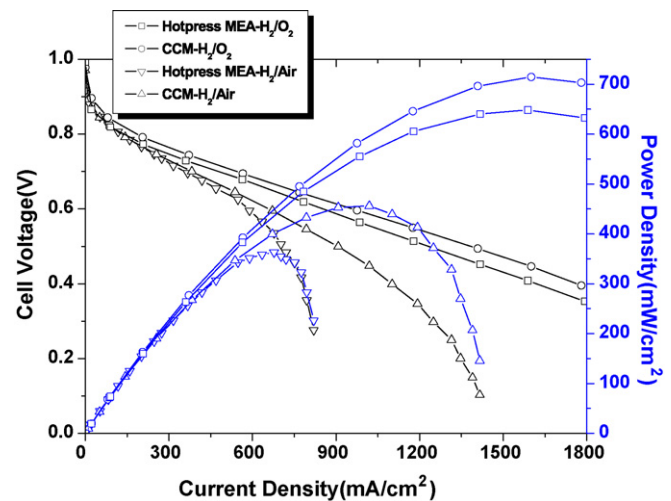


Fig. 1. Current density–voltage and current density–power density curves of single cells made from CCM and hot-pressed MEAs under H_2/O_2 and H_2/air at ambient temperature.

the CCM is also lower than that of the hot-pressed MEA, indicating that the catalyst layer has close contact with the electrolyte membrane which increases the reaction activity. The departure from linear relationship between potential and current density at high current density is predominantly due to the rapid increase in the contributions of mass transport limitations. Since the diffusion layers used in both test cells are the same, the decrease trends of hot-pressed MEA in the diffusion-controlled region of current–voltage curves is more rapid than CCM under H₂/air, which suggest that the microstructure of CCM can alleviate the influence of flooding on the cathode side of the cell. One of the reasons could be the microporous and mesoporous structure produced by the CCM method is more beneficial for the water and gas transportation in the catalyst layer [20].

The catalyst utilization or electrochemical active surface area can also be estimated from the charge of hydrogen oxidation peak observed on cyclic voltammograms. Fig. 2 shows the cyclic voltammograms of the cells made from CCM and hot-pressed MEAs. During the measurement of cyclic voltammograms, argon was fed to the working electrode (cathode) and hydrogen was fed to the counter and reference electrode (anode). Thus, the electrochemical active surface area estimated from cyclic voltammograms could be mainly associated with the cathode catalyst layer. The cyclic voltammetric studies from 0.05 to 0.4 V provides information on the hydrogen adsorption and desorption which occurs on the platinum surface. The region from 0.4 to 0.5 V is regarded as the double-layer region. The area under the hydrogen desorption peak at 0.2 V versus SHE is proportional to electrochemical surface area. As can be seen, the cell made from CCM exhibit significantly larger hydrogen desorption peak than that prepared by the hot-pressed MEA. This shows that CCM has higher electrochemical surface area than that MEA prepared by the conventional hot-press method. The cyclic voltammetric results confirm the higher electrochemical performance of the PEM fuel cells made by the CCM (Fig. 1).

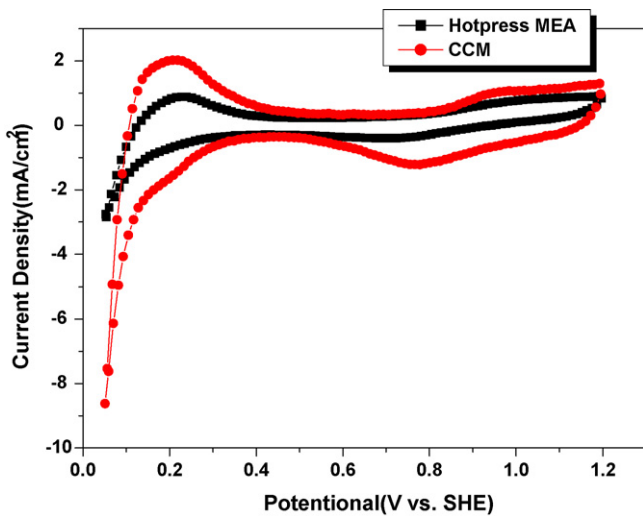


Fig. 2. Cyclic voltammograms of the single cells made from CCM and hot-pressed MEAs. During the measurement of cyclic voltammograms, argon was fed to the working electrode (cathode) and hydrogen was fed to the counter and reference electrode (anode).

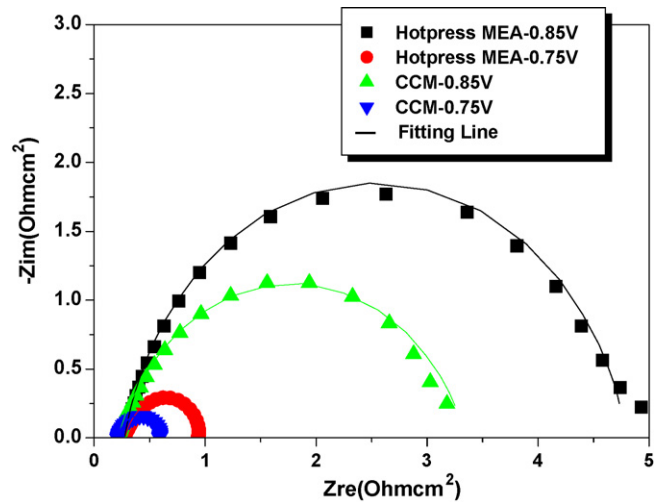


Fig. 3. Impedance curves of the single cells with hot-pressed MEA and CCM, measured at 0.85 and 0.75 V under H₂/O₂.

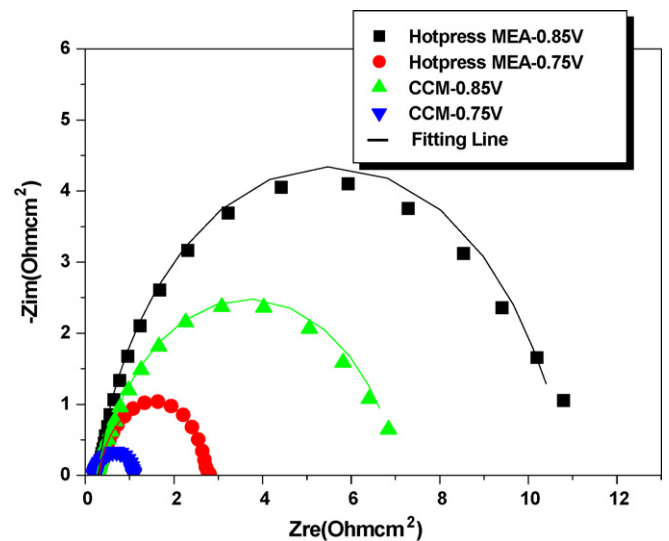


Fig. 4. Impedance curves of the single cells with hot-pressed MEA and CCM, measured at 0.85 and 0.75 V under H₂/air.

Fig. 3 is the impedance responses of the single cells prepared by CCM and hot-pressed MEA under H₂/O₂ and Fig. 4 is the corresponding impedance curves under H₂/air at cell potential of 0.85 and 0.75 V, respectively. In the figure, the symbols are the experimental results and lines are the fitted data using the equivalent circuit (Fig. 5). In the equivalent circuit, R₁ represents the total ohmic resistance of the cell which includes ohmic resistances of various cell components and also the end plates and the contacts between them. R₂ is usually associated with the charge transfer resistance across the catalyst/electrolyte interface, and CPE1 is a constant phase element related to the double-layer

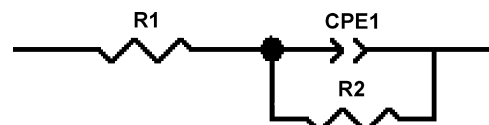


Fig. 5. Equivalent circuit used for the impedance analysis.

capacitance of the porous electrode. The impedance responses were characterized by a semi-circle at low overpotentials (i.e., at a cell potential of 0.85 V). However, as the cell potential decreased to 0.75 (i.e., the increase of overpotentials), a low frequency loop was observed. Nevertheless, as expected, the impedance arc for the reaction on the cell made from CCM is much smaller than that observed on the cell made from hot-pressed MEA. As the cell impedance is kinetically dominated by the oxygen reduction at the cathode [18], the much smaller impedance arc for the cell prepared by the CCM demonstrates that the oxygen reduction reaction on the catalyst layer of the CCM is significantly faster than that of the hot-pressed MEA. This is consistent with that of the cyclic voltammetric studies.

The fit between the observed and calculated data was reasonable, indicating that the equivalent circuit may be applicable though the real reaction pathways could be very complicated. The fitting results are given in Table 1. The ohmic resistance R_1 for each test cell is relatively constant. In general, the cell with the CCM has a smaller R_1 than the cell with the hot-pressed MEA at the same voltage under the same test conditions. As the gas diffusion layer, membrane and assembly pressure were equal for cells with either CCM or hot-pressed MEA, the differences in R_1 appear to show that the catalyst layer made by the CCM method has much better contact with the polymer electrolyte membrane than that of the hot-pressed MEA. The much smaller charge transfer resistance, R_2 , indicates a faster charge-transfer reaction for the oxygen reduction at the electrode and electrolyte

Table 1

Fitted impedance parameters of the single cells made from hot-pressed MEA and CCM

Test condition	MEA	Voltage (V)	R_1 ($\Omega \text{ cm}^2$)	R_2 ($\Omega \text{ cm}^2$)
H_2/O_2	Hot-pressed MEA	0.85	0.28	4.52
		0.75	0.27	0.687
	CCM	0.85	0.22	3.14
		0.75	0.21	0.38
H_2/air	Hot-pressed MEA	0.85	0.31	10.51
		0.75	0.28	2.48
	CCM	0.85	0.25	6.87
		0.75	0.21	0.88

The impedance curves were measured under H_2/O_2 and H_2/air at cell voltages of 0.85 and 0.75 V, respectively.

interface of the cell with CCM. This again shows that CCM have a much more efficient electrochemical active layer than that of the hot-pressed MEA.

Morphology analysis was investigated in this comparative study to give a direct comparison between these two MEAs. Fig. 6 shows SEM micrographs and the corresponding Pt EDAX mapping of cross-section MEA prepared by the CCM method and the hot-press method. The result reveals very different microstructures in the membrane–electrode interface. For the MEA prepared with CCM method, the catalyst electrode has been integrated with the Nafion membrane due to the close

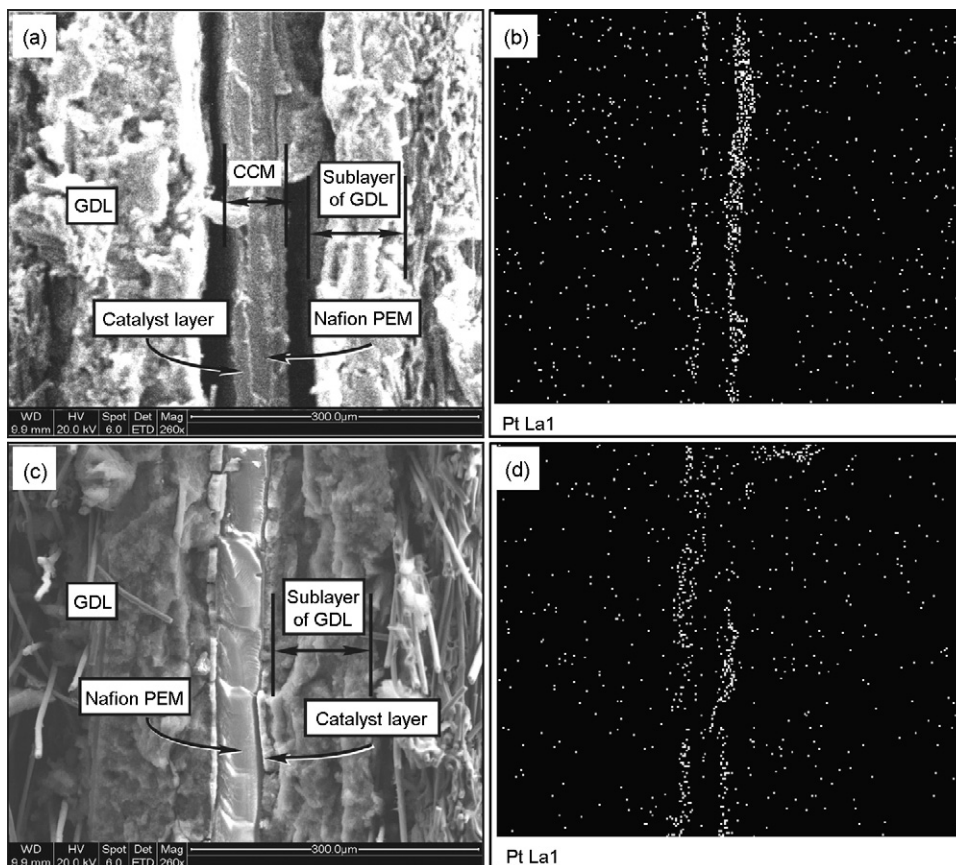


Fig. 6. SEM micrographs and Pt mapping of cross-section membrane electrode assembly prepared by CCM method (a and b) and hot-press method (c and d).

contact between the catalyst layer and the membrane (6a). In contrast, the interface between the catalyst electrode and the Nafion membrane is clearly visible and most region of the catalyst layer has not been directly contacted with the membrane in the hot-pressed MEA (6c). The Pt mapping of the cross section also indicates that the catalyst is uniformly distributed in CCM (6b), while the Pt distribution is scattered in the hot-pressed MEA (6d). The uniformly disperse and close contact of the catalyst layer on the membrane is reasonably beneficial to fuel cell performance since the catalyst layer the most important region of the electrochemical reaction. However, things are reversed for the GDL-catalyst layer interface. Because of the hot-pressed step in the MEA preparing procedure, the hot-pressed MEA have better GDL-catalyst layer interface than that of the MEA prepared by CCM method. Nevertheless, the membrane-electrode interface is more important than the GDL-catalyst interface for the electrochemical reaction since the former is in charge of conducting proton, while the latter is in charge of conducting electron. In a typical fuel cell MEA, the proton conductivity in catalyst layer and proton exchange membrane is about 2.5×10^{-3} – $1 \times 10^{-3} \text{ S cm}^{-1}$ and $0.001 \sim 0.1 \text{ S cm}^{-1}$, respectively [21,22]. However, the electron conductivity in the catalyst layer and GDL are about $1 \sim 100 \text{ S cm}^{-1}$ [21–23]. As a result, the proton conductance is the control process for the fuel cell conductance.

4. Conclusions

A comparative investigation was performed on PEM fuel cells made with conventional hot-pressed MEAs and CCMs and tested under identical experimental conditions and Pt electrocatalyst loadings. The results showed that the cell with the CCM exhibited significantly higher electrochemical performance than that prepared with the conventional hot-pressed MEA. The cyclic voltammetric studies showed that the electrochemical surface area of the MEA by the CCM method is significantly higher than that prepared by the hot-pressed MEA at the same Pt loading. EIS results revealed that CCM had a smaller contact resistance and charge-transfer resistance as compared with hot-pressed the MEA under H_2/O_2 and H_2/air . Again, this study indicates that fabrication procedures have a major influence on the performance of PEM fuel cells.

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