Performance of a polymer electrolyte membrane fuel cell with thin film catalyst electrodes

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Abstract

In order to develop a kW-class polymer electrolyte membrane fuel cell (PEMFC), several electrodes have been fabricated by different catalyst layer preparation procedures and evaluated based on the cell performance. Conventional carbon paper and carbon cloth electrodes were fabricated using a ptfe-bonded Pt/C electrocatalyst by coating and rolling methods. Thin-film catalyst/ionomer composite layers were also formed on the membrane by direct coating and transfer printing techniques. The performance evaluation with catalyst layer preparation methods was carried out using a large or small electrode single cell. Conventional and thin film membrane and electrode assemblies (MEAs) with small electrode area showed a performance of 350 and 650 mA/cm^2 at 0.6 V, respectively. The performance of direct coated thin film catalyst layer with 300 cm^2 MEAs was higher than those of the conventional and transfer printing technique MEAs. The influence of some characteristic parameters of the thin film electrode on electrochemical performance was examined. Various other aspects of overall operation of PEMFC stacks were also discussed. © 1998 Elsevier Science S.A.

Keywords: Polymer electrolyte membrane fuel cell; Membrane and electrode assembly; Thin film electrocatalyst layer; Single cell; Stack

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have incorporated various electrodes containing ptfe-bonded Pt/C, Nafion impregnated Pt/C and sputter-deposited Pt [1–3]. Due to the catalyst costs, many researchers have been studying the membrane and electrode assembly (MEA) manufacturing processes that can reduce the content of Pt in the electrocatalyst layer while maintaining the performance. Recently, a thin film catalyst layer was developed and reported to have a very low Pt loading (0.12–0.16 mg Pt/cm^2) [4,5]. In this electrode structure, Nafion was used instead of ptfe to bond to the structure and the catalyst layer was applied to the membrane, rather than to the gas diffusion layer.

In this work, we report the performance evaluation on various MEAs made by using ptfe-bonded carbon paper and carbon cloth electrodes and a thin film electrode.

2. Experimental

2.1. Membrane pretreatment

Two forms of membrane were used during MEA manufacturing processes. Before being used in manufacturing MEA, the polymer electrolyte membranes, Nafion were washed in various solutions to remove trace organic and inorganic contaminants and to intentionally change its form. The pretreatment procedure involved boiling the polymer electrolyte membrane in 3 wt.% aqueous H$_2$O$_2$ solution for 60 min, followed by boiling for 60 min in pure water and subsequently boiling for a further 60 min in a fresh sample of pure water. The membrane for conventional MEA was then removed and boiled for 60 min in 0.5 M H$_2$SO$_4$ solution, followed by boiling for 60 min each in two different samples of pure water. On completing the purification procedure, the membrane specimen was stored in the last sample of washwater at room temperature prior to use.

The membrane for direct coated MEA was boiled for 60 min in 20 wt.% aqueous NaOH solution instead of sulfuric
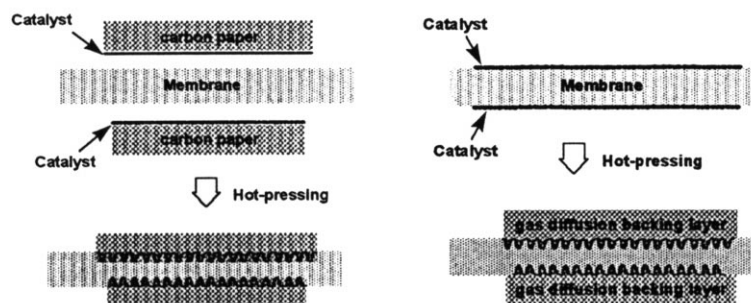
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Fig. 1. Schematic diagrams illustrating a conventional MEA and thin film MEA.

acid to get the membrane in Na$^+$ form. Then, the membrane was boiled for 60 min in pure water to remove the remaining NaOH on the surface of the membrane, followed by drying the membrane fixed with a frame in a vacuum oven at 80°C. The membrane in Na$^+$ form can be used in an electrode fabrication process based on a high temperature casting technique.

2.2. Conventional MEA fabrication

An electrocatalyst slurry and an electrode support are prepared in separate ways. For electrode support, a sheet of carbon paper was soaked in a waterproofing solution mixed with water for 30 min. and dried in the air for a day. Then, the carbon paper was subjected to sintering at 370°C for 20 min. The electrocatalyst slurry was obtained by two mixing steps. In the first mixing step, platinum-dispersed carbon powder with a platinum content of 20 wt.% (Johnson-Matthey) was mechanically stirred for 30 min in a solvent to give a homogeneous mixture. Subsequently, in the second step, ptfe emulsion was added to the mixture and stirred by ultrasound. The ptfe comprised about 30 wt.% of the resulting electrocatalyst layer. After adding a bridge-builder and a peptization agent, further mechanical stirring was carried out for 30 min to give an electrocatalyst slurry. In another mixing method, the bridge-builder and peptization agent were mixed with the ptfe emulsion by mechanical stirring before adding the ptfe into the mixture of Pt/C and solvent.

Using a coating apparatus, this slurry was coated upon the electrode support fixed on a flat die of the coating apparatus and dried for a day in air and then, for about 30 min in an inert atmosphere at 225°C. Then, the dried electrode was transferred to a rolling apparatus, allowed to pass between two rotating rolls, and subjected to sintering in an inert atmosphere for 30 min at 350°C.

Portions of 5 wt.% Nafion solution (Aldrich) were brush-coated onto the electrocatalyst layer. Then, the Nafion-impregnated electrodes were placed in an oven at 80°C and allowed to dry for 60 min in an air atmosphere. The amount of Nafion loading in the final dried electrode was controlled at a value of 2 mg/cm^2. Nafion-impregnated electrodes were bonded onto both sides of the purified H$^+$ form polymer electrolyte membranes by hot-pressing at 145°C

for 3 min with a pressure of 193 atm. The schematic diagram illustrating the conventional MEA is given in Fig. 1.

2.3. Thin film MEA fabrication

To increase the contact area between the polymer electrolyte and the platinum clusters, an electrocatalyst slurry was made, in which Nafion solution replaced the ptfe emulsion. The Nafion/Pt-C/glycerol slurry was prepared by first thoroughly mixing together in a small vial the 5 wt.% Nafion solution and the 20 wt.% Pt/C (Johnson-Matthey) or 40 wt.% Pt/C (Tanaka K.K.) using a magnetic stirrer. The ratio of supported Pt catalyst to Nafion for the catalyst layer is typically 3/1 (in weight of solids) [5].

The protonated form of Nafion within the slurry was converted to the TBA$^+$ (tetra-butyl ammonium cation) form by the addition of 1 M TBAOH (tetra-butyl ammonium hydroxide) in methanol. Since the addition of alkaline solutions directly to the solubilized Nafion results in some coagulation, the TBAOH solution was not added until the catalyst and Nafion solution were extremely well mixed (typically a few hours). The paintability of the slurry was improved by the addition of glycerol, in the approximate ratio of 1/1 or 3/1 (wt.%) with 5% Nafion solution, whose primary function was to enable higher temperature film casting.
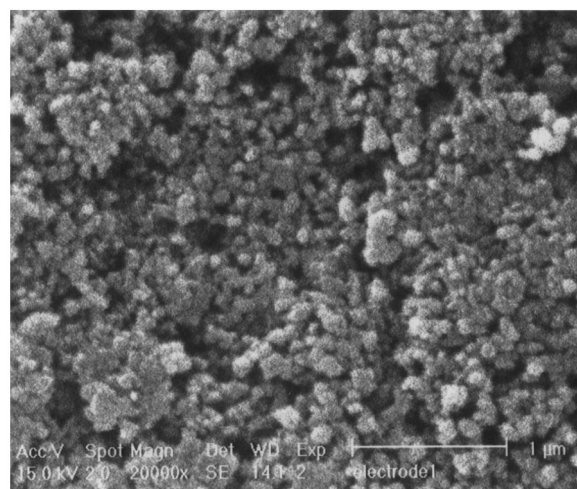

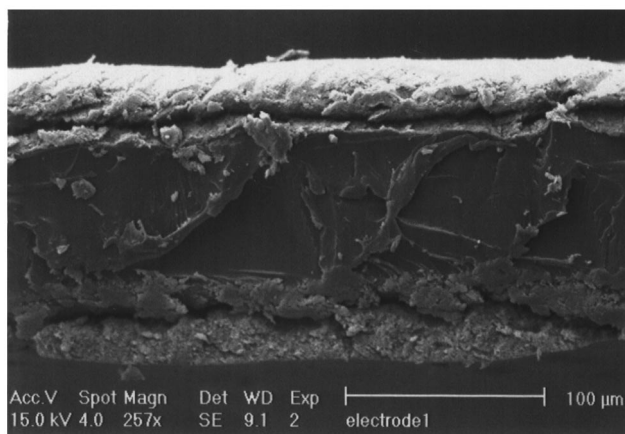Fig. 2. Scanning electron micrograph of the electrocatalyst layer of a thin film MEA.

Fig. 3. Scanning electron micrograph of the cross section of a thin film MEA.

In the direct coating method [5], by using the screen printer, the slurry was applied to one side of a membrane in Na^+ form held in place on a vacuum table. Then, the coated layer was dried for 60 min on the vacuum table at 140°C. The table was cooled, the membrane was turned over, and the process was repeated on the other side of the membrane. This assembly was also hot-pressed for 1.5 min at 195°C with a pressure of 77 atm to compact and strengthen the catalyst layer.

In the transfer printing technique [4], the slurry was applied on Kapton polyimide film (Chemical Fabrics) by the same process as in the direct coating method. Then the coated layer was dried for 120 min at 135°C in a vacuum oven. The coated blank, membrane and counter electrode were hot-pressed together for 1.5 min at 195°C with a pressure of 77 atm. The membrane/catalyst assembly was removed from the press and allowed to cool, then the Kapton film was peeled away from the membrane, leaving the thin film catalyst layer adhering to the membrane.

Finally, the catalyzed membrane was rehydrated and ion-exchanged to the H^+ form by immersing it in lightly boiling 0.5 M sulfuric acid for 60 min, followed by rinsing it in de-ionized water. A separate Teflon-coated carbon cloth was used as a backing for the thin film MEA to provide support and to provide a hydrophobic distribution network for the gases. The carbon cloth backing was made by coating the slurry containing carbon black powder and ptfe emulsion on the carbon cloth. The process of making the slurry and the drying and sintering process are similar to that of making the conventional catalyst layer. The schematic diagram illustrating the direct coated MEA is also given in Fig. 1.

Fig. 2 shows a typical scanning electron micrograph (SEM) of the electrocatalyst layer of the thin film MEA. The porous structures of Pt/C agglomerates were uniformly distributed in the electrocatalyst layer and were evenly closely contacted, similar to the ptfe-bonded Pt/C electrocatalyst. Fig. 3 shows a SEM picture of the cross-section of the thin film MEA. The catalyst layers are on the top and

bottom sides, the membrane is in the centre. The thickness of the catalyst layer and membrane are approximately 25 and 100 μm, respectively.

3. Results and discussion

3.1. Performance of small electrode single cells

A fuel cell test fixture was fabricated using machined graphite blocks, having rib-channel patterns on one side, which facilitated the distribution of humidified gases to the porous gas-diffusion electrodes, as well as providing current collection from the electrodes. The blocks became gas tight and waterproof due to the impregnation treatment of phenol resin. The active cell areas, represented by the rib-channel patterns, were 25 and 50 cm^2. Teflon-coated fiberglass gasket materials, placed on both sides of the membrane, provided sealing on bolting the cell components together. Copper endplates enabled test cell fixtures to be bolted together, and electrical cartridge heaters inserted into the walls of the copper plates allowed various operating cell temperatures to be selected.

The fuel cell test station used in this investigation had several temperature controllers and flow meters, which control the temperatures and flow rates of the hydrogen and oxygen gases entering the fuel cell and also control the temperatures of humidification vessels. An electronic load with a maximum capability of 1 kW (Scribner Associates) was used to obtain the performance of the single cells.

The single cell was operated at various temperature of 60–90°C on H_2/O_2. Humidification of the anode/cathode gas streams is accomplished by diverting the streams
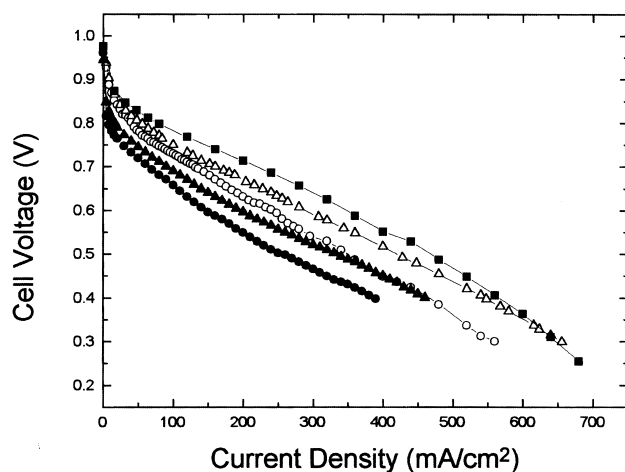

Fig. 4. Comparison of cell voltage against current density performances for H_2O_2 cells with a carbon paper electrode (0.3 mg Pt/cm^2) and a carbon cloth electrode (0.4 mg Pt/cm^2). Conditions: Nafion 117 membrane; electrode area = 25 cm^2; conventional MEA (1.2 mg Nafion/cm^2); H_2/O_2 = 1:1 atm; H_2 = 7.5 l/min; O_2 = 2.25 l/min; (○), carbon cloth electrode at 60°C; (△), carbon cloth electrode at 90°C; (●), carbon paper electrode at 60°C; (▲), carbon paper electrode at 90°C; (■), carbon paper electrode with different mixing conditions at 90°C.
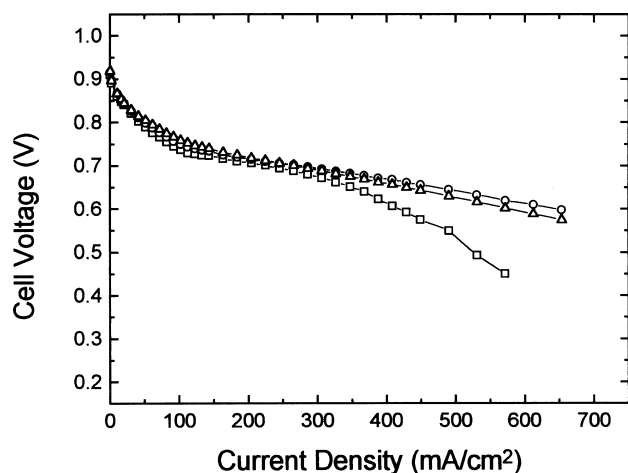
Fig. 5. Polarization curves for transfer printing technique thin film MEA (0.1 mg Pt/cm^2) with Nafion 115 membrane. Conditions: electrode area = 50 cm^2; H$_2$/O$_2$ = 1:1 atm; H$_2$ = 7.5 l/min; O$_2$ = 2.25 l/min; (○), low glycerol at 80°C; (△), low glycerol at 70°C; (□), high glycerol at 70°C.

through heated water-filled sparger bottles that are usually kept at 90 and 80°C for H$_2$ and O$_2$, respectively.

Fig. 4 shows the performance of the conventional MEA with an electrode area of 25 cm^2, made from a Nafion 117 membrane and commercial carbon cloth electrode (E-TEK) or carbon paper electrode. As the cell temperature increases from 60 to 90°C, the cell performance slightly increases. The improvement in the mixing of the slurry enhances significantly the performance of the conventional MEA. This indicates that the uniform distribution of ptfe in the electrocatalyst layer can greatly affect the performance of the MEA. The performance of the carbon paper MEA was 0.6 V, 350 mA/cm^2. This result indicates that the technique of the conventional MEA manufacturing process could not be acceptable for applying stack fabrication [1].

Fig. 5 shows the performance of the thin film MEA with an electrode area of 50 cm^2, made by the transfer printing technique with a Nafion 115 membrane. As the cell temperature increases from 70 to 80°C, the cell performance slightly increases. The content of glycerol in the slurry affects the performance of the thin film MEA in the high current region. The glycerol improves the paintability of the slurry ink, but could reduce the contact area of the Pt electrocatalyst and Nafion powder and the charge transfer. The performance of 0.6 V, 650 mA/cm^2 of the thin film MEA indicates that the thin film MEA manufacturing processes are well established and can be acceptable for applying stack fabrication [1].

3.2. Performance of large electrode single cells

The large electrode single cell was designed and fabricated with internal humidifiers and water cooling channels. The single cell has a gas flow field area of 300 cm^2 which is a parallel rib-channel pattern. The functions of the internal humidifiers and the gas flow field pattern were checked

during the single cell tests. Then, the concept of the single cell design was expanded to make stacks.

Fig. 6 shows the performances of home made MEAs and a commercial MEA, both tested in this laboratory. The conventional MEA shows a lower performance compared with the thin film MEAs and commercial MEA which show a performance of 0.6 V, 400 mA/cm^2. However, the performance of the direct coated thin film MEA was still lower than that of the commercial MEAs reported in literature [6]. In order to improve the performance of the direct coated MEA, the optimization of the manufacturing processes and parameters for MEA has been carried out through the single cell tests. The higher performance of the direct coated thin film MEA compared with that of the transfer printing technique thin film MEA seems to be related to the formation of a more intimate membrane/electrode interface.

The proton penetration and gas accessibility may define the active reaction region in the electrocatalyst layer. As the current density increases, the active reaction region narrows and closes to the interface of membrane and electrode. The transfer printing technique thin film MEA made from a 40 wt.% Pt/C electrocatalyst has a higher density of the electrocatalyst in the active reaction region and shows higher performance in the high current region as shown in Fig. 6, compared with the MEA made from 20 wt.% Pt/C.

3.3. Performance of small stacks

Two small stacks with electrode areas of 50 and 300 cm^2 were designed and fabricated to have separate active electrode and humidifier sections. The active section includes the plurality of MEAs, fluid flow field plates, coolant flow plates, electrical connections between the individual cells, as well as control circuitry to generate electric power. The
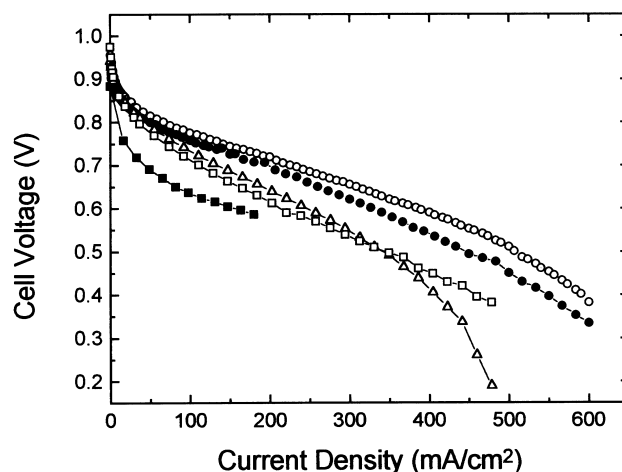

Fig. 6. Comparison of cell voltage against current density performances at 90°C for H$_2$O$_2$ cells with commercial MEA (●), conventional MEA of carbon paper electrode (■) and thin film MEAs (○, △, □). Conditions: Nafion 115 membrane; electrode area = 300 cm^2; H$_2$/O$_2$ = 1:1 atm; H$_2$ = 8.5 l/min; O$_2$ = 3.8 l/min; (○), direct coated thin film MEA, 20% Pt/C; (△), transfer printing technique thin film MEA, 20% Pt/C; (□), transfer printing technique thin film MEA, 40% Pt/C.
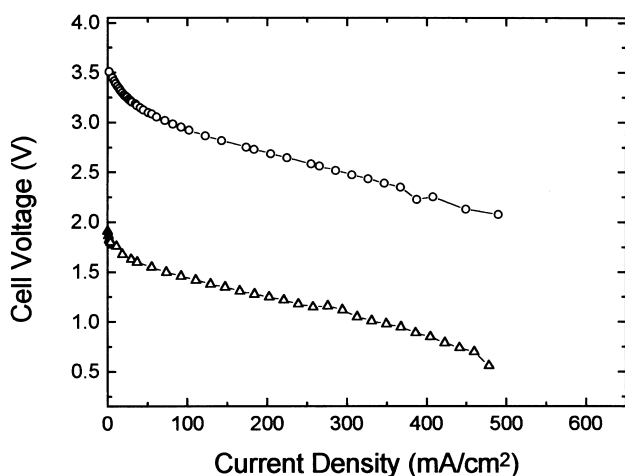
Fig. 7. Comparison of cell voltage against current density performances for a 4-cell stack with electrode area of 50 cm^2 (○) and a 2-cell stack with electrode area of 300 cm^2 (△). Conditions: Nafion 115 membrane; transfer printing technique thin film MEA; H$_2$/O$_2$ = 1:1 atm; H$_2$ = 8.5 l/min; O$_2$ = 3.8 l/min.

humidification section includes a plurality of membrane humidification cells which intoduce water to the respective inlet hydrogen and inlet oxygen streams. The inlet hydrogen stream entering the fuel cell stack is humidified in the humidification section and then directed to the plurality of individual MEAs in the active section. The pure water was pumped into the reaction side to cool the each cell and then passed through the humidifier section to humidify the reaction gases. In the humidifier section, the hydrogen and oxygen gases are humidified by flowing each gas on one side of a water permeable membrane and by flowing the pure water on the opposite side of the membrane. The water is transferred across the membrane to the hydrogen and oxygen gases. A cheaper nano-filtration membrane is now being tested.

Fig. 7 shows the performance of a 4-cell stack with an electrode area of 50 cm^2 and a 2-cell stack with an electrode area of 300 cm^2. The stacks have the same stack configuration as mentioned above but a different flow path field. The lower performance of the 2-cell stack was closely related to the parallel straight rib pattern with a storage chamber at both ends in which gas distribution is not uniform on the overall electrode area. Water supply and removal could also be irregular.

4. Conclusions

In order to obtain some key technologies of MEA fabrication that can be applicable to a kW-class PEMFC, several MEAs have been fabricated by different catalyst layer preparation procedures and evaluated based on the cell performance. Conventional MEAs were fabricated using carbon paper and carbon cloth electrodes and showed a performance of 350 mA/cm^2 at 0.6 V. Thin film MEAs manufacturing processes were developed using direct coating and transfer printing techniques. The thin film MEAs showed a performance of 650 mA/cm^2 at 0.6 V in the small electrode single cell and of 400 mA/cm^2 at 0.6 V in the large electrode single cell.

References

[1] R. Mosdale and S. Srinivasan, *Electrochim. Acta, 40* (1995) 413.
[2] M. Uchida, Y. Aoyama, N. Edo and A. Ohta, *J. Electrochem. Soc., 142* (1995) 4143.
[3] J. Fournier, G. Faubert, J.Y. Tilquin, R. Cote, D. Guay and J.P. Dodelet, *J. Electrochem. Soc., 144* (1997) 145.
[4] M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem., 22* (1992) 1.
[5] M.S. Wilson, J.A. Valerio and S. Gottesfeld, *Electrochim. Acta, 40* (1995) 355.
[6] J.A. Kolde, B. Bahar, M.S. Wilson, T.A. Zawdzinski and S. Gottesfeld, in S. Gottesfeld, G. Halpert and A. Landgrebe (eds.), *Proc. 1st Int. Symp. on Proton Conducting Membrane Fuel Cells*, The Electrochemical Society, Vol. 95-23, 1995, pp. 193–201.