Influence of electrode structure on the performance of a direct methanol fuel cell

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Abstract

Direct methanol fuel cells (DMFCs) consisting of multi-layer electrodes provide higher performance than those with the traditional electrode. The new electrode structure includes a hydrophilic thin film and a traditional catalyst layer. A decal transfer method was used to apply the thin film to the Nafion® membrane. Results show that the performance of a cell with the hydrophilic thin film is obviously enhanced. A cell with the optimal thin film electrode structure operating at 1 M CH_3OH, 2 atm oxygen and 90 °C yields a current density of 100 mA/cm^2 at 0.53 V cell voltage. The peak power density is 120 mW/cm^2. The performance stability of a cell in a short-term life operation was also increased when the hydrophilic thin film was employed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrode; Fuel cell; Current density

1. Introduction

The liquid feed direct methanol fuel cell (DMFC) based on a solid polymer electrolyte (SPE) is seen as a potential power source in static and portable applications due to its inherent simplicity of operation [1–5]. Significant improvement in the field of DMFC has been obtained using the manufacturing technology of SPE fuel cells, especially the membrane-electrode assembly (MEA) preparation [6]. A widely used technology consists of the preparation of a gas-diffusion electrode having suitable polytetrafluoroethylene (PTFE) contents in both the diffusion and catalyst layers. Nafion® ionomer is spread on the catalyst layer surface followed by MEA by a hot-pressing procedure [7]. The anode of DMFC is different from that of a H_2–O_2 PEMFC. It must be hydrophilic to facilitate the mass transfer of methanol. The fabrication of the anode usually involves a procedure of direct mixing of the Nafion® with the catalyst, and only a small mount of PTFE is added. As far as DMFC are concerned, there are two major obstacles inhibiting the application of DMFC due to using liquid methanol solution as feed: the low activity of methanol electro-oxidation catalysts and the methanol crossover through the polymer electrolyte membrane from the anode to cathode side. Furthermore, the delamination of the electrode catalyst from the membrane caused by the "wetting" state of the methanol anode must be solved before the widespread commercial application of DMFC.

Many efforts have been made to find some new membrane or to modify the Nafion® membrane to inhibit or to reduce methanol crossover [8–10] and search for some new catalyst with a high activity for methanol electro-oxidation [11–13].

In this work, our general approach in developing the high performance DMFC is to maximize the performance of "off-the-shelf" membrane and catalysts. Accordingly, we did not utilize any special approach to minimize methanol crossover or develop cell components or hardware that was any different from that typically used for DMFC. Instead, the key factor that was responsible for our increased performance was the optimization of the electrode structure. Improved techniques for multi-layer electrode fabrication or MEA were applied. The results show that the crossover of methanol and the delamination of the electrode catalyst from the membrane have been reduced to a certain extent.

2. Experimental

2.1. Membrane/electrode assemblies

The methanol anode and oxygen cathode consist of a traditional electrode and a hydrophilic thin film respectively. The protocol for forming the hydrophilic thin film described here is somewhat different from that for the H_2/air cells [14]. The primary difference is that isopropanol is used as solvent instead of glycerol and some pore former has been used [16]. The thin film was sprayed from the inks consisting of Pt–Ru/C (20 wt.% Pt, 10 wt.% Ru, supplied by Johnson Matthey), 5 wt.% solubilized Nafion® (supplied by DuPont Company), deionized (DI) water, $(NH_4)_2C_2O_4$ (pore forming additive) and isopropanol (for anode, some PTFE is added). The ratio of supported Pt–Ru/C catalyst to Nafion® is 3:1. This ink was uniformly applied to Teflon decal blanks. After the applied inks were dried, the thin film was transferred from the teflon decal blank to the Na^+ form of Nafion® 115 membrane by hot-pressing at 160–200 °C and 5–9 MPa for 150 s. After the decal blanks were removed, the hydrophilic film/Nafion® membrane assemblies were ion-exchanged to the protonated form by immersing them in lightly boiling 0.5 M H_2SO_4 solution for about 1 h. The thickness of the thin film for the anode or the cathode is <5 μm.

The traditional methanol anode and oxygen cathode studied in this work were made in the following manner. For the anode, a diffusion-layer comprising XC-72 carbon and 13 wt.% Nafion® was first brushed onto a teflonized carbon paper support (Teflon 13 wt.%), followed by the catalyst layer consisting of the Pt–Ru/C (20 wt.% Pt, 10 wt.% Ru, Johnson Matthey) and 10 wt.% Nafion®. Total metal loading on the anode is 2 mg/cm². The cathode was constructed by using a similar method to that of the anode. A diffusion layer and a catalyst layer comprises XC-72 carbon, Pt/C (Johnson Matthey, Pt 20 wt.%) and PTFE (10 wt.%), respectively. Total metal loading on the cathode is 1 mg/cm².

The MEAs were obtained by hot-pressing the normal anode and cathode on the each side of the hydrophilic film-membrane-film assembly, respectively, at 135 °C and 3 MPa for 150 s.

2.2. Single cell test

Single cell tests on the DMFC were performed on a cell with a cross-sectional area of 9 cm². The MEA was sandwiched between two stainless steel plates with dotted flow field for reactants and products to enter and exit the cell. The insulation rubber gaskets were used to prevent the cell from leaking. The cell was heated to the desired temperature by an electrical heater placed in the hole of the stainless steel plates. Aqueous methanol solution preheated at a certain temperature by an electrical heater was pumped through the anode flow-field at a constant rate. O_2 was supplied to the cathode chamber from cylinders at ambient temperature.

For all the cells, 1.0 M methanol solution was supplied to the anode chamber at the rate of 1.0 ml/min. The pressure of O_2 was kept at 2 atm.

3. Results

The MEA of multi-layer electrode with thin film is shown in Fig. 1. It is composed of five layers: a traditional anode, an anode thin film, a Nafion® membrane, a cathode thin film and a traditional cathode. The main difference between the anode thin film and the cathode film is in the content of Nafion® or Teflon. In the cathode thin film the Nafion® content was higher than that of the anode thin film. For the latter, a definite amount of Teflon was added.

Fig. 2 shows polarization curves of the DMFCs operated at 75 °C and 2 atm oxygen pressure. The results show that the performance of the cell with the thin film is obviously improved. For the cell with the thin film, voltage 0.50 V was obtained at 100 mA/cm²; while for the cell without the thin film, only 0.45 V was obtained.

The effect of PTFE content in the hydrophilic thin film on the performance of the DMFC was examined. Fig. 3 depicts the performances of the DMFC as a function of the content of PTFE in the anode thin film. The open-circuit potential was increased slightly with the content of PTFE increasing in the anode thin film. The best performance was obtained on the cell with 20% PTFE in the anode thin film.

Fig. 4 shows the influence of the pore forming additive in the anode thin film on the performance of the DMFC. It is clear that the addition of pore former $(NH_4)_2C_2O_4$ improved the performance of the DMFC. The difference in the performance for the two cells becomes much larger at high current density.

The performance of the cell with the optimal thin film structure as a function of cell temperatures is shown in Fig. 5.
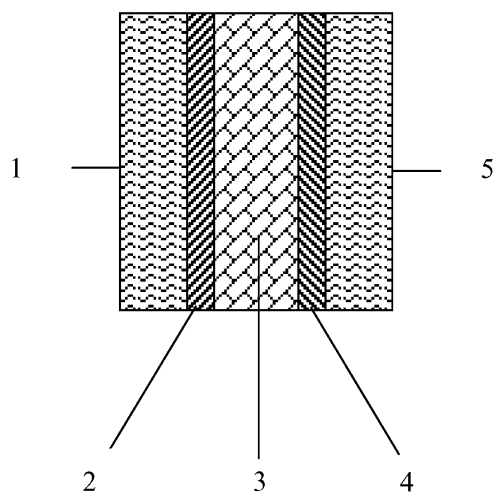

Fig. 1. Schematic structure of a multi-layer electrode MEA: (1) traditional anode; (2) anode thin film; (3) Nafion® membrane; (4) cathode thin film; (5) traditional cathode.
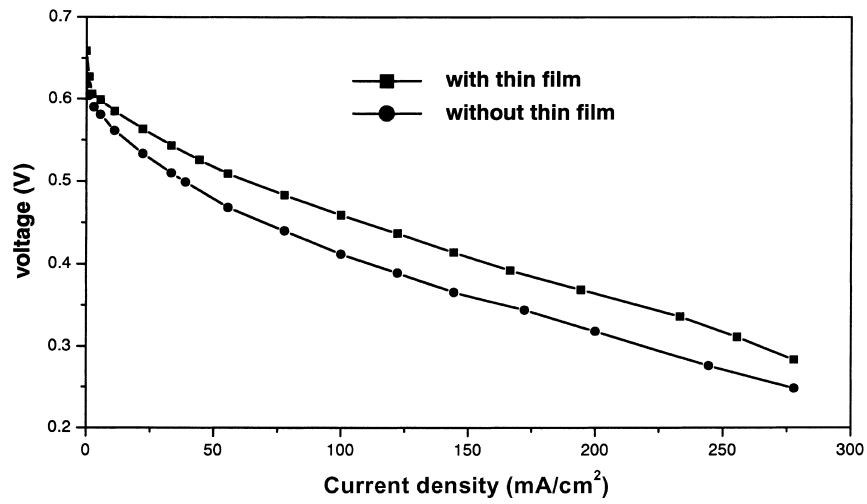
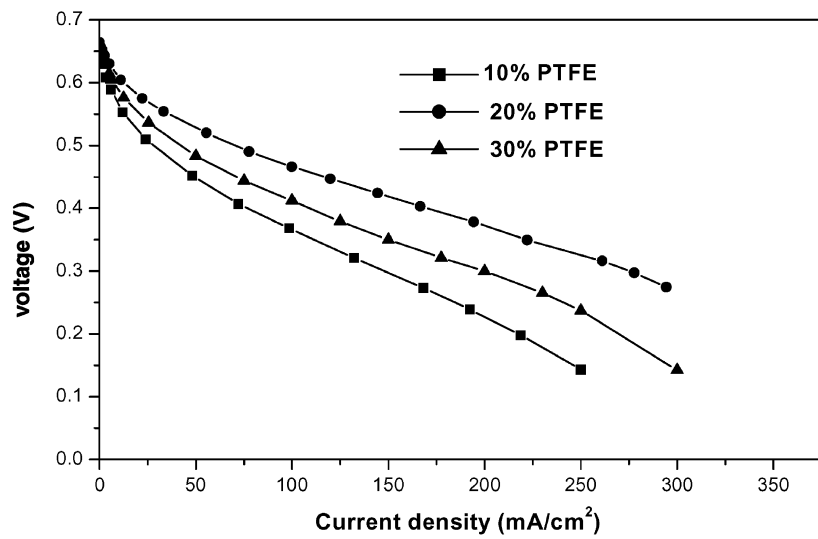Fig. 2. Polarization curves of DMFC ($T = 75\,^{\circ}$C, $P_{O_2} = 2$ atm, CH_3OH 1.0 M, 1.0 ml/min).

Fig. 3. The effect of PTFE content in the anode thin film on the performance of DMFC ($T = 75\,^{\circ}$C, $P_{O_2} = 2$ atm, CH_3OH 1.0 M, 1.0 ml/min).
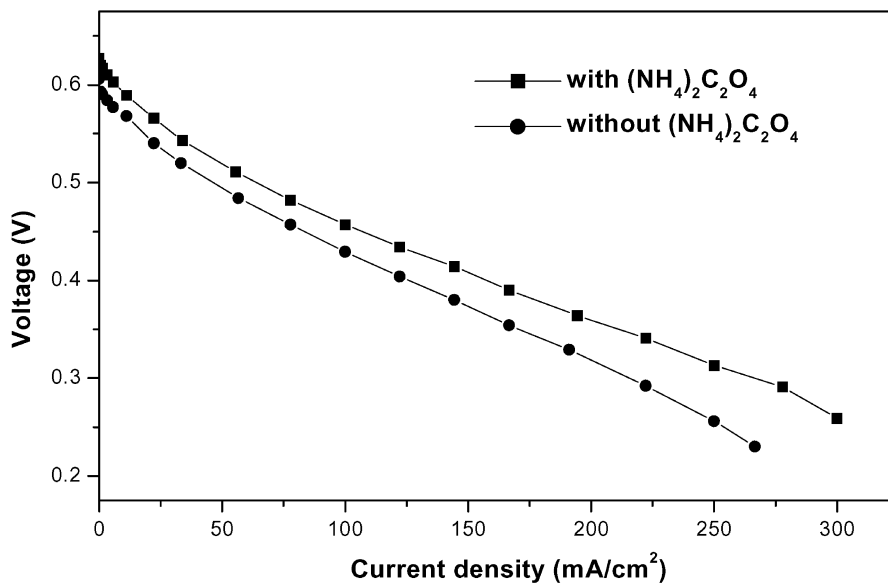

Fig. 4. The effect of pore forming additive in the anode film on the performance of DMFC ($T = 75\,^{\circ}$C, $P_{O_2} = 2$ atm, CH_3OH 1.0 M, 1.0 ml/min).
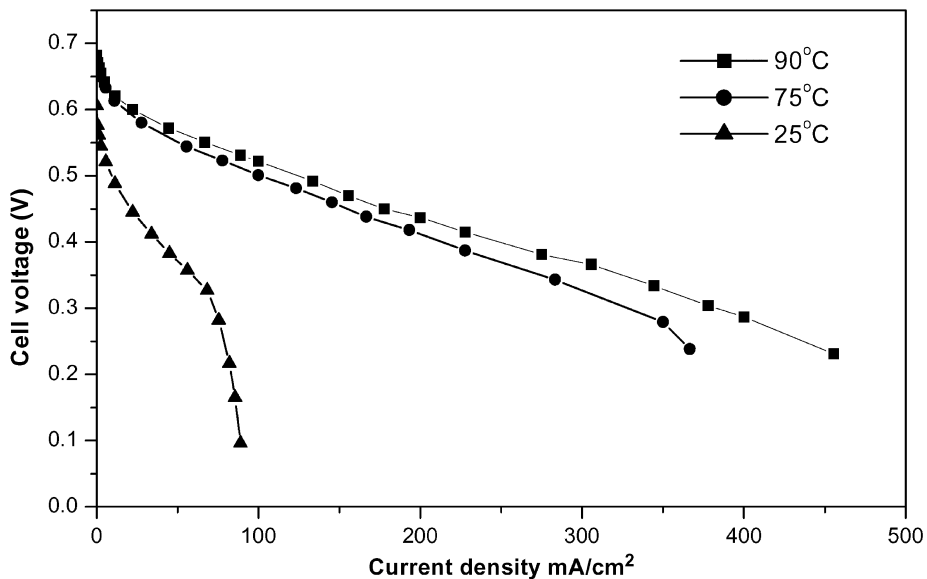
Fig. 5. Current–voltage curves of the cell with the thin film at various temperatures (P_{O_2} = 2 atm, CH_3OH 1.0 M, 1.0 ml/min).
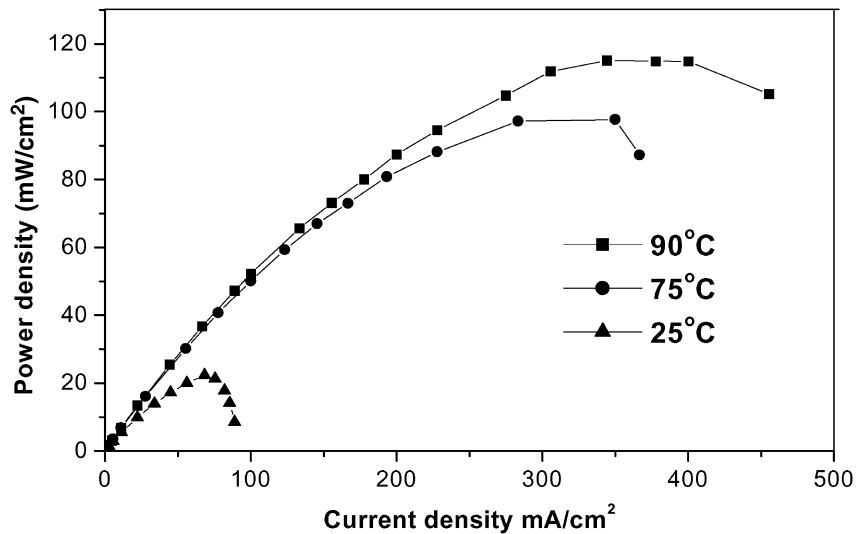

Fig. 6. Power density curves of the cell with the thin film at various temperatures (P_{O_2} = 2 atm, CH_3OH 1.0 M, 1.0 ml/min).
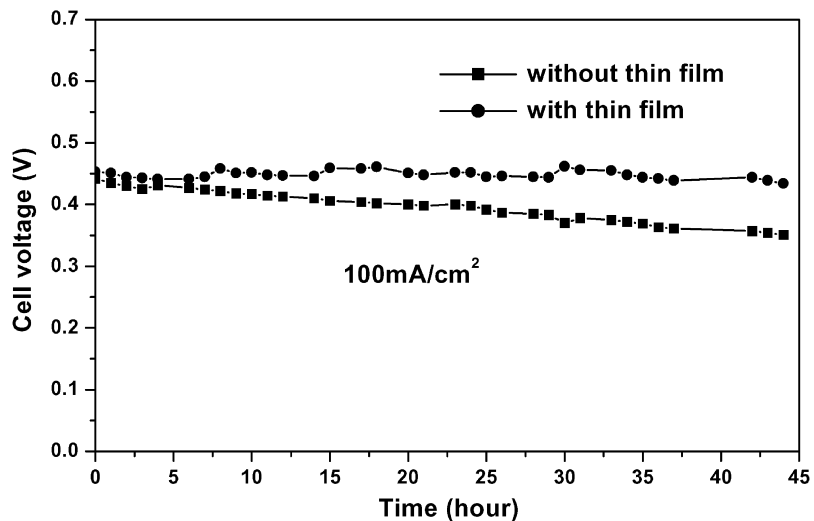

Fig. 7. Performance of DMFC at 100 mA/cm^2 (T = 75 °C, P_{O_2} = 2 atm, CH_3OH 1.0 M, 1.0 ml/min).

When the cell temperatures increased, the performance of the DMFC is obviously enhanced. The power density of the cell was also increased at higher temperature, as shown in Fig. 6. A power density of almost 120 mW/cm^2 from the cell operating at 90 °C can be reached, and for the cell without the thin film, only 90 mW/cm^2 can be obtained at the same operating conditions.

The stability of the cell performance in a short-term life was examined and the results are shown in Fig. 7. The cell was operated at a current density of 100 mA/cm^2. It is demonstrated that the performance of the cell with the thin film was almost unchanged during a 45 h period, but for the cell without the thin film, its performance declined seriously during the operating time.

4. Discussion

The performance of the DMFC was enhanced due to the application of a multi-layer electrode. The new electrode structure presented here improved upon the previous structure by adding a hydrophilic thin film. The advantage of the multi-layer electrode is that the new technology in electrode fabrication improved the bonding of the catalyst and the membrane at the membrane-electrode interface of the MEA. As described in the experimental section, the thin film and the sodium-ionized Nafion$^®$ membrane were bonded together by hot-pressing at a higher temperature 180 °C than that of traditional MEA fabrication, 150 °C. This makes good contact between the thin film and the ionomeric membrane. The catalytic layer of the electrode and the thin film are readily bonded together at a normal hot-pressing temperature. As a result, the contact resistance between the catalyst layer and Nafion$^®$ membrane is reduced, and the performance of the cell was obviously improved.

It is well known that catalyst sites on the anode and the cathode must satisfy proton access, gas access and electronic path continuity in the electrochemical reaction of the DMFC. There are two reaction zones in the new electrode, one is the thin film, and the other is the traditional electrode. For the anode reaction in the DMFC, the product CO_2 needs to be eliminated, thus proper gas access is necessary. Ammonium oxalate is believed to be the proper pore former [16]. When the thin film was transferred from the Teflon decal blank to the Na$^+$ form Nafion$^®$ membrane by hot-pressing at 180 °C, the ammonium oxalate decomposed. The addition of the proper pore former can improve the pore network for CO_2 gas removal and increase the utilization of the catalysts. For the cathode, methanol permeating from the anode usually increases the polarization of the cathode to a great degree, and results in cell performance decrease. The Pt–Ru/C catalyst in the cathode thin film can oxidize the methanol permeated from the anode, and eliminate the harmful effect of the methanol crossover on the cathode Pt/C catalyst. Therefore, the performance of the DMFC with the thin film increased greatly.

The function of the PTFE in the electrode is to provide a network for gas transport and to give structural integrity to the layer. However, hydrophobic PTFE in the anode thin film has the effect of decreasing the crossover of methanol from the anode to the cathode through the Nafion$^®$ membrane. So a suitable PTFE content added in the anode thin film improved the performance of the DMFC cell. But the presence of PTFE in the thin film increased the internal resistance of the cell. When the PTFE content was beyond 30 wt.%, the performance of the cell decreased, especially in the case of the high current density.

It is reported that delamination of the electrode catalyst layer from the membrane is the main reason for the performance decline [15]. In our experiment we also found that the catalyst layer readily broke away from the membrane when the cell with a traditional MEA was operated for several days. But for the multi-layer electrode fabricated by the new technology, the bonding of the catalyst and the membrane was improved, and the delamination of the electrode catalyst layer from the membrane was not found. As a result, the performance stability of the cell with the thin film increased.

In summary, the new electrode structure improved the performance of the cell in three ways. First, the thin film and the sodium-ionized Nafion$^®$ membrane are bonded together by using hot-pressing at a higher temperature than that of normal MEA fabrication. As a result, separation of the catalytic layer from the membrane was avoided when a cell was operated at a definite current density for a long time. Second, a suitable Teflon content added into the thin film for the anode has an obvious role in decreasing the crossover of methanol to the cathode, but otherwise does not influence the hydrophilicity of the catalytic layer at the anode. Third, Pt–Ru/C catalysts existing in the thin film for the cathode can oxidize the methanol permeated from the anode, and eliminate the harmful effect of the crossover of methanol on the cathode Pt/C catalyst to a great degree. Therefore, the performance of a single cell consisting of multi-layer electrodes is dramatically improved.

5. Conclusions

The performance of the DMFC is strongly affected by the structure of an electrode and the technology of the MEA. It was found that a methanol anode and an oxygen cathode with a hydrophilic thin film exhibited many advantages over the traditional MEA. The performance of a cell consisting of multi-layer electrodes is enhanced and the delamination of the catalytic layer from the membrane during long time operation is also solved.

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