

Effects of MEA preparation on the performance of a direct methanol fuel cell

Jian Zhang, Geping Yin*, Zhenbo Wang, Yuyan Shao

Laboratory of Electrochemistry, Department of Applied Chemistry, Harbin Institute of Technology, P.O. Box 411#, Harbin 150001, PR China

Received 11 January 2006; received in revised form 11 February 2006; accepted 13 February 2006

Available online 17 April 2006

Abstract

The effects of membrane electrode assemblies (MEAs) fabrication methods (spraying and scraping methods) and the hot-pressing pretreatment of anode electrodes on the performance of direct methanol fuel cells (DMFCs) were investigated. The MEA prepared with scraped anode catalyst layer without the hot-pressing pretreatment showed the highest power density of 67 mW cm^{-2} at 80°C and ambient pressure. The scraping method proved to be a little more profitable for improving the cell performance than the spraying method. Atomic force microscopy (AFM) analysis revealed relatively smooth surface of the scraped anode catalyst layer compared with that of sprayed anode catalyst layer. Scanning electron microscopy (SEM) images showed that a suitable number of cracks which were uniformly distributed on the surface of scraped catalyst layer formed a porous structure. It was demonstrated that the surface structure and roughness of the anode catalyst layer had less effect on the performance of the anode electrode in a DMFC. The hot-pressing pretreatment of the anode electrode decreased the performance of the MEA due to the difficulty for electrons and mass transport in the anode electrode, namely the increase of internal cell resistance.

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Keywords: Direct methanol fuel cell (DMFC); Membrane electrode assemblies (MEAs); Fabrication; AFM images

1. Introduction

The direct methanol fuel cell (DMFC) has been receiving increasing attention due to its advantages of easy transportation and storage of the fuel, reduced system weight and size, high energy efficiency and low exhaustion [1–3]. The key component of a DMFC is the membrane electrode assembly (MEA), which comprises a polymer electrolyte membrane, anode electrode (consist of anode catalyst layer and anode gas diffusion layer) and cathode electrode (consist of cathode catalyst layer and cathode gas diffusion layer) [4]. Today, two main methods are widely used to fabricate the MEA [5,6]: the gas diffusion layer (GDL)-based method [7,8] and the membrane-based method [9–12]. The GDL-based method usually consists of spraying or painting the catalyst ink directly onto the GDLs and then hot-pressing with the membrane. For the membrane-based

method, the catalyst ink is directly applied onto a polymer membrane by the spraying method, brushing method or decal method [11,12], and then followed by a hot-pressing step with the GDLs.

The GDL-based method is widely used due to the advantage that the catalyst loading can be adjusted very precisely by simply weighing the GDL before and after the coating process [5]. Based on the GDL-based method, the brushing, scraping and spraying fabrication methods are used to apply the catalyst ink onto the GDL. It is expected that different structures of the electrodes resulted from different fabrication methods would cause the differences in the performance of them. The anode electrode of the DMFC usually contains more platinum than that of $\text{H}_2\text{-O}_2$ PEMFC because of the low activity of methanol electro-oxidation [3]. Thus, the catalyst layer of the DMFC electrode is much thicker than that of the $\text{H}_2\text{-O}_2$ PEMFC electrode. It would be difficult to produce a perfectly homogeneous catalyst layer with an unsuitable preparation method due to such a thick catalyst layer.

The purpose of this work is to investigate the differences in the structures and the performance of anode electrodes resulted

* Corresponding author. Tel.: +86 451 86413721; fax: +86 451 86413720.

E-mail addresses: zhangjianhit@yahoo.com.cn (J. Zhang), yingphit@hit.edu.cn (G. Yin).

from different fabrication procedures by the GDL-based method and to identify the effect of the surface structure and roughness of the anode catalyst layer on the performance of a DMFC. The surface morphologies and roughnesses of the catalyst layers were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The internal resistances and the performance of MEAs were characterized by electrochemical impedance spectra (EIS) and polarization curves, respectively.

2. Experimental

2.1. Preparations of MEAs

All the electrocatalysts used in this work were prepared in-house by chemical reduction with formaldehyde of H_2PtCl_6 and RuCl_3 as precursors [13]. The anode catalyst is 40 wt.% Pt–Ru (with an atomic ration of 1:1)/C and the cathode catalyst is 40 wt.% Pt/C.

The homemade MEA is a seven-layer structure. The GDL for the anode (cathode) catalyst layer was wet-proofed Toray carbon paper coated with the hydrophilic (hydrophobic) diffusion layer. The hydrophilic diffusion layer for the anode comprised Vulcan XC-72 carbon black and 10 wt.% of Nafion ionomer, and the hydrophobic diffusion layer for the cathode comprised Vulcan XC-72 carbon black and 20 wt.% of PTFE. The loading of carbon black is 2 mg cm^{-2} for both the anode and the cathode.

The catalyst powder and 5 wt.% Nafion ionomer solution were ultrasonically mixed in isopropyl alcohol to form a homogeneous catalyst ink. The Nafion content in both the anode and the cathode catalyst layers were 20 wt.%. The cathode catalyst ink was scraped onto the hydrophobic diffusion layers to form the cathode electrodes. Then the cathode electrodes were dried for 2 h in the vacuum oven at 80°C . The Pt metal loading was 3 mg cm^{-2} for the cathode electrode.

Four kinds of anode catalyst layers were fabricated. The first one (designated E1) was fabricated by spraying the catalyst ink onto the hydrophilic diffusion layer. Then the anode electrode was hot-pressing pretreated under a specific load of 80 kgf cm^{-2} for 3 min at 110°C , and then it was dried for 2 h in the vacuum oven at 80°C . The anode electrode hot-pressing pretreatment involved before hot-pressing the electrodes and membrane to form the MEA was used to reduce the cracks on the surface of anode catalyst layer. The second one (designated E2) was fabricated by scraping method, followed a hot-pressing pretreatment (like E1). The third one (designated E3) was fabricated by spraying the catalyst ink onto the hydrophilic diffusion layer, without the hot-pressing pretreatment. The fourth one (designated E4) was fabricated by scraping method, without the hot-pressing pretreatment. The PtRu metal loading was 3 mg cm^{-2} for the anode electrode.

Nafion 117 polymer membranes from DuPont were used to fabricate MEAs. Before being applied to the electrodes, the membranes were pretreated in four steps to remove the organic and inorganic contaminants [14]. First, the membranes were boiled in 3 wt.% H_2O_2 solution followed by washing in ultra-pure water. Then, the membranes were boiled in 0.5 mol l^{-1}

H_2SO_4 solution. Finally, the membranes were boiled again in ultra-pure water. Each step took about 2 h.

The pretreated Nafion membranes sandwiched between the anode electrodes and the cathode electrodes assemblies and then the assemblies were hot-pressed under a specific load of 100 kgf cm^{-2} for 3 min at 135°C .

2.2. Single-cell test

Polarization curves were obtained by the Fuel Cell Testing System (Arbin Instrument Corp.) using a commercial single cell (ElectroChem Corp.) with a working area of 5 cm^2 . A solution of 2 mol l^{-1} aqueous methanol was fed to the anode side at a flow rate of 3 ml min^{-1} . Oxygen was supplied to the cathode side at a flow rate of 500 ml min^{-1} under ambient pressure. The single cell was operated at 80°C .

Electrochemical impedance spectra were measured under open circuit voltage at 23°C using an electrochemical analysis instrument (Model CHI 604b) in a frequency range from 1 kHz to 0.1 Hz with 6–12 points per decade. The amplitude of the ac-voltage was 5 mV.

2.3. Physical characterizations of the catalyst layer

The surface morphologies and structures of the catalyst layers were observed by scanning electron microscopy (Hitachi S-4700).

The atomic force microscopy measurements were carried out using an atomic scanning probe microscope Explorer Solver P47 (Russia, NT-MDT Corp.) in a non-contact mode.

3. Results and discussion

3.1. SEM surface morphologies of the catalyst layer

Fig. 1 presents SEM images of the surfaces of catalyst layers fabricated by four different preparation procedures: the sprayed anode catalyst layer with an additional hot-pressing pretreatment (Fig. 1a, E1), the scraped anode catalyst layer with the hot-pressing pretreatment (Fig. 1b, E2), the sprayed anode catalyst layer without the hot-pressing pretreatment (Fig. 1c, E3) and the scraped anode catalyst layer without the hot-pressing pretreatment (Fig. 1d, E4). Some cracks are found on the surfaces of the catalyst layers. It is believed that the cracks are caused by the residual stress between the catalyst layers and the gas diffusion layers during the fabrication process. The number and the width of the crack gaps on the surfaces of the hot-pressed catalyst layers (Fig. 1a and b) are decreased due to the hot-pressing pretreatment which would result in compact catalyst layers. There are fewer cracks on the surface of the scraped catalyst layer (Fig. 1c) than that of the sprayed catalyst layer (Fig. 1d). The widths of the crack gaps on the surface of the scraped catalyst layer and those of the sprayed catalyst layer are estimated to be 10–20 and 50–60 μm , respectively. Apparently, the scraping method is helpful to alleviate the catalyst layer cracking.

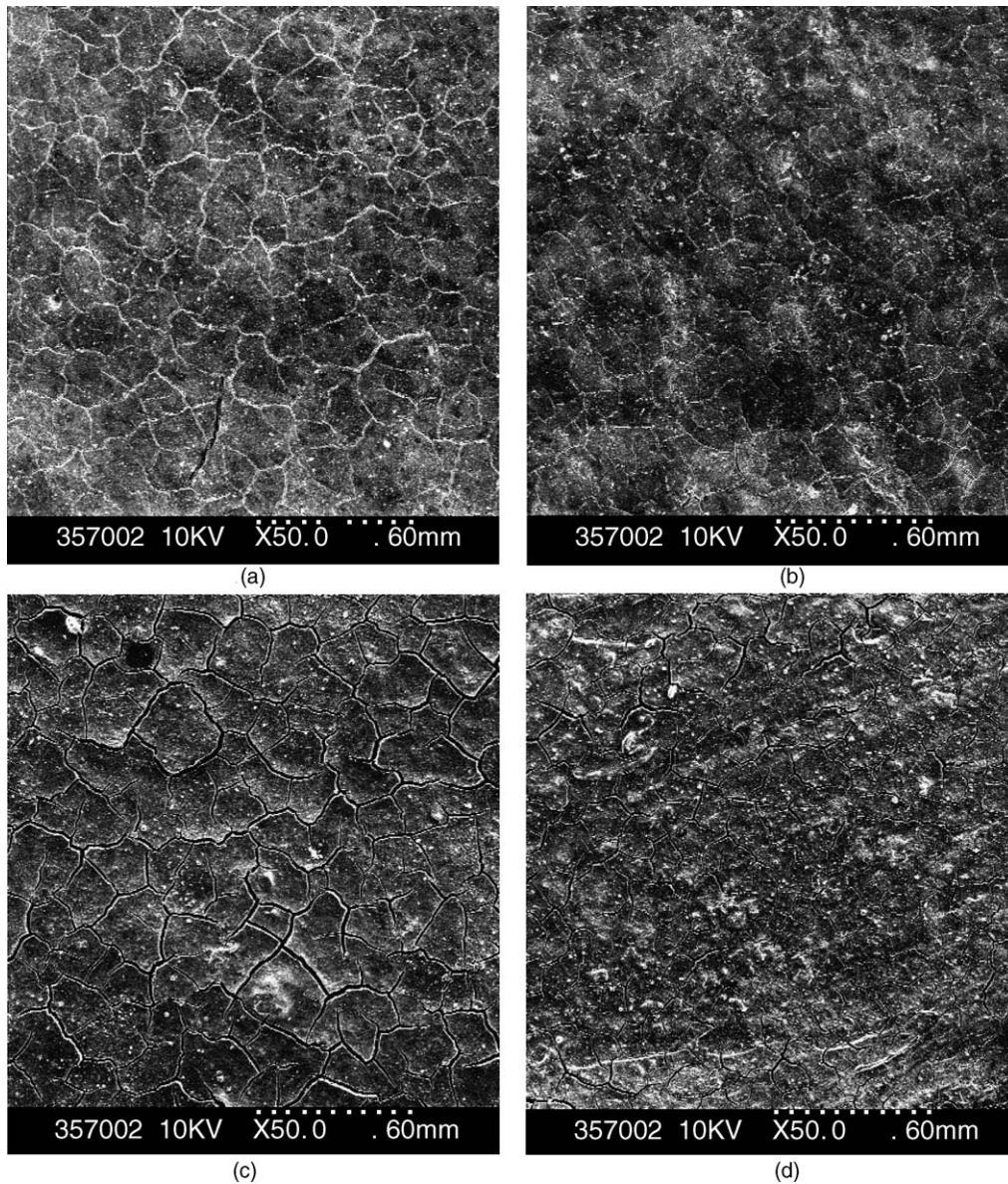


Fig. 1. SEM images of the surfaces of anode catalyst layers: (a) sprayed, hot-pressing pretreatment; (b) scraped, hot-pressing pretreatment; (c) sprayed; (d) scraped.

3.2. AFM surface analyses of the catalyst layer

Fig. 2 shows the 2D and 3D AFM images ($4\ \mu\text{m} \times 4\ \mu\text{m}$ area) of the surface of the sprayed anode catalyst layer without hot-pressing pretreatment (E3), revealing the coarse and grainy structures of the electrode surface. It is commonly said that carbon particles cohere together and form the agglomerate structures [15]. It can be easily seen that there are some unregulated “mountains” on the surface of sprayed catalyst layer. Fig. 3 shows the 2D and 3D images ($4\ \mu\text{m} \times 4\ \mu\text{m}$ area) of the surface of scraped anode catalyst layer without the hot-pressing pretreatment (E4). It can be seen that the surface of scraped catalyst layer is homogeneous with only a few surface agglomerates.

The surface structures of the electrodes are greatly dependent on the fabrication methods. For the spraying method, the catalyst ink would prefer to load on the “mountains” on the gas diffusion layer substrate and form a fluctuant catalyst layer. Moreover, the

cracks on the surface of catalyst layer would be easily formed because of the poor adhesion between the catalyst powders. For the scraping method, the adhesion between the catalyst layer and the gas diffusion layer substrate is enhanced by using the spatula. Overall, the surface of the scraped catalyst layer is more homogeneous and flat with less roughness value.

To quantitatively characterize the surface roughnesses of these four different catalyst layers, the Ra roughnesses of the catalyst layers were evaluated by analyses of the 3D AFM images. Ra roughness is an average roughness of the surface, and it is defined as:

$$\text{Ra} = \frac{1}{N_x N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \left| z_{ij} - \frac{1}{N_x N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} z_{ij} \right|$$

where N_x and N_y are the number of points along axes x and y , respectively.

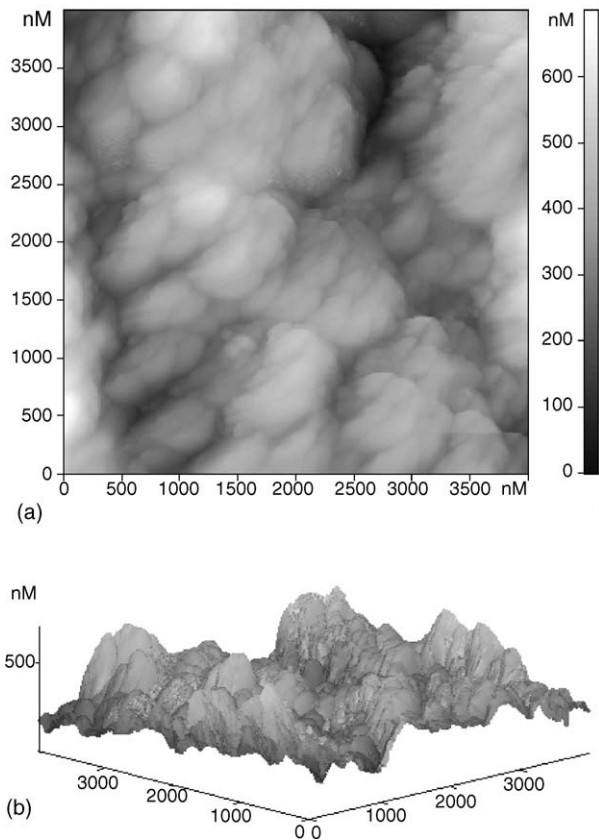


Fig. 2. 2D (a) and 3D (b) AFM images ($4\ \mu\text{m} \times 4\ \mu\text{m}$ area) of the surfaces of the sprayed anode catalyst layer without an additional hot-pressing pretreatment (E3).

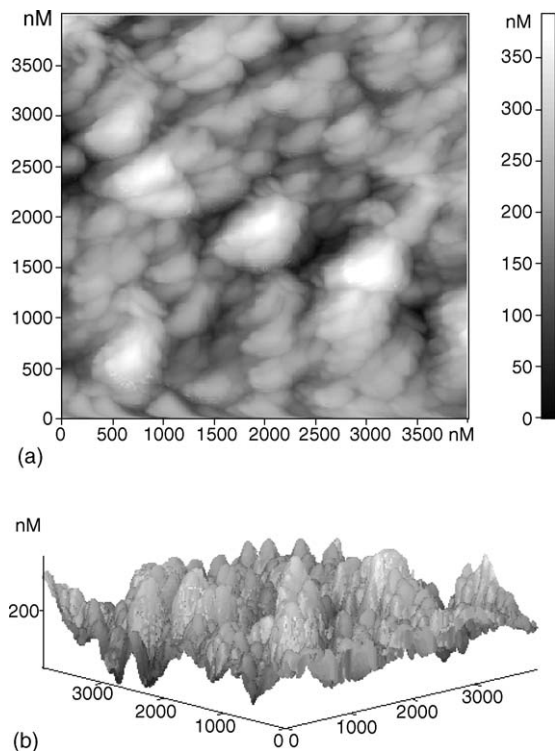


Fig. 3. 2D (a) and 3D (b) AFM images ($4\ \mu\text{m} \times 4\ \mu\text{m}$ area) of the surfaces of the scraped anode catalyst layer without an additional hot-pressing pretreatment (E4).

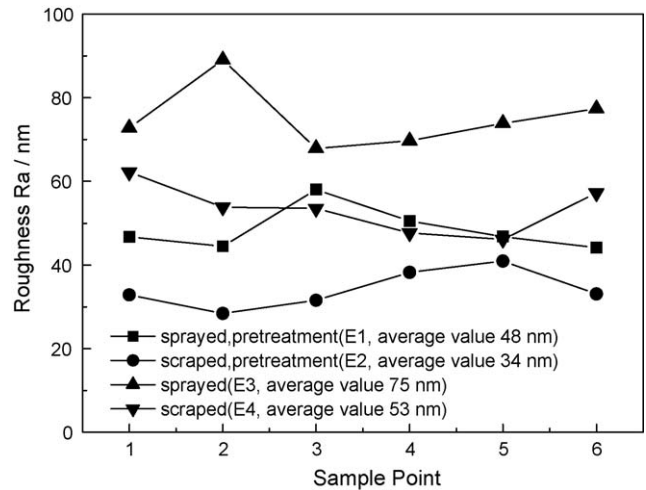


Fig. 4. The Ra surface roughness of the different anode catalyst layers performed at six different random positions ($4\ \mu\text{m} \times 4\ \mu\text{m}$ area) for each sample: (E1) sprayed, hot-pressing pretreatment; (E2) scraped, hot-pressing pretreatment; (E3) sprayed; (E4) scraped.

The roughness measurements were performed at six different random regions ($4\ \mu\text{m} \times 4\ \mu\text{m}$ area) for each catalyst layer. The results are shown in Fig. 4. The average values of the Ra roughness of the sprayed and hot-pressed anode catalyst layer (E1), the scraped and hot-pressed one (E2), the sprayed one (E3) and the scraped one (E4) are 48, 34, 75 and 53 nm, respectively. It can be seen from these values that the roughnesses decrease as the hot-press pretreatment involved. The roughness of the scraped catalyst layer is much less than that of the sprayed one.

3.3. Electrochemical characteristics of MEAs

Electrochemical impedance spectra were measured in order to determine the internal resistances of the four MEAs with different anode catalyst layers [16,17]. The resistance was determined by the high frequency intercept of the electrochemical impedance spectra response on the real axis of the Nyquist plot. The Nyquist diagrams under open circuit conditions at $23\ ^\circ\text{C}$ are shown in Fig. 5. The typical resistance values under these conditions are listed in Table 1. The resistance values of the MEA with sprayed anode electrode with and without the hot-pressing pretreatment are $0.65\ \Omega$ (E1) and $0.40\ \Omega$ (E3), respectively. In the case of scraped anode electrode, the corresponding values are $0.63\ \Omega$ (E2) and $0.37\ \Omega$ (E4), respectively. It is obvious that the internal resistances of the MEAs (E1 and E2) were higher than those of MEAs (E3 and E4). Fig. 6 shows the SEM images of the carbon paper before (Fig. 6a) and after (Fig. 6b) the hot-pressing pretreatment. It can be seen that the long carbon fibers are crushed into pieces after the hot-pressing pretreatment. So the resistance of MEA is increased due to the breaking of the carbon fibers which are used as the electron transport supports in the carbon paper. The resistance of the MEA with scraped anode electrode ($0.37\ \Omega$, E4) is slightly less than that of MEA with the sprayed anode electrode ($0.40\ \Omega$, E3).

The polarization curves and the power density curves of the MEAs with different anode catalyst layers are presented in

Table 1

Comparison of the resistances of the MEAs fabricated by spraying or scraping method with or without the hot-pressing pretreatment operated under open circuit conditions at 23 °C

	E1 (spraying, pretreatment)	E2 (scraping, pretreatment)	E3 (spraying)	E4 (scraping)
Resistance (Ω)	0.65	0.63	0.40	0.37

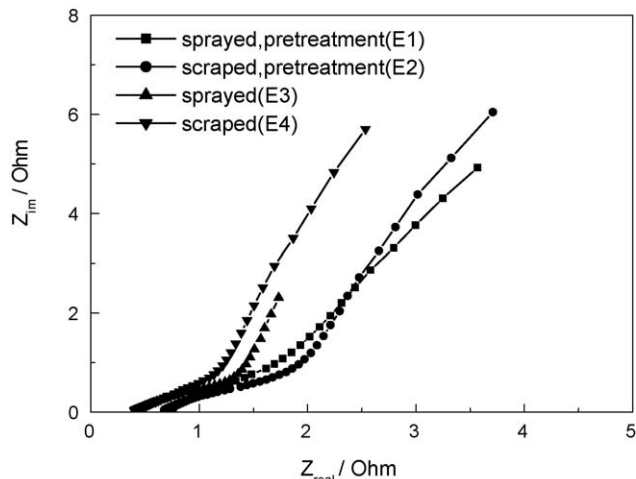


Fig. 5. Nyquist diagrams of the MEAs with different anode catalyst layers: (E1) sprayed, hot-pressing pretreatment; (E2) scraped, hot-pressing pretreatment; (E3) sprayed; (E4) scraped, under open circuit voltage at 23 °C.

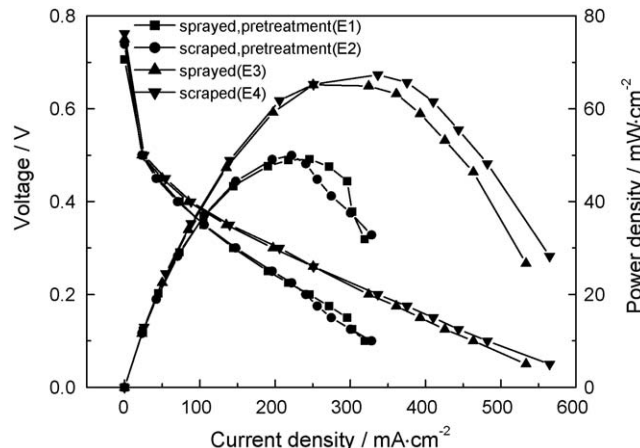


Fig. 7. The polarization curves and the power density curves of single cells with different anode catalyst layers: (E1) sprayed, hot-pressing pretreatment; (E2) scraped, hot-pressing pretreatment; (E3) sprayed; (E4) scraped, under application 2 mol l^{-1} methanol/oxygen at 80 °C.

Fig. 7. The E4 shows the highest power density of 67 mW cm^{-2} , followed by the E3 (64 mW cm^{-2}). The power densities of E1 and E2 are, respectively, 49 and 50 mW cm^{-2} .

There are about three regions in the DMFC polarization curves [18,19]: At low cell currents, the cell voltage is dominated by the electrochemical kinetics of the anode methanol oxidation. By increasing the current load, the cell voltage further decreases

due to the electric resistance of the membrane and electrode. And then, the cell voltage decreases due to the mass transport resistance of the methanol in high current region. As shown in Fig. 7, the polarization curve of the MEA (E3) with sprayed anode catalyst layer shows a slightly lower in the high current region than that of the MEA (E4) with scraped anode catalyst layer. These features are also consistent with the results of the

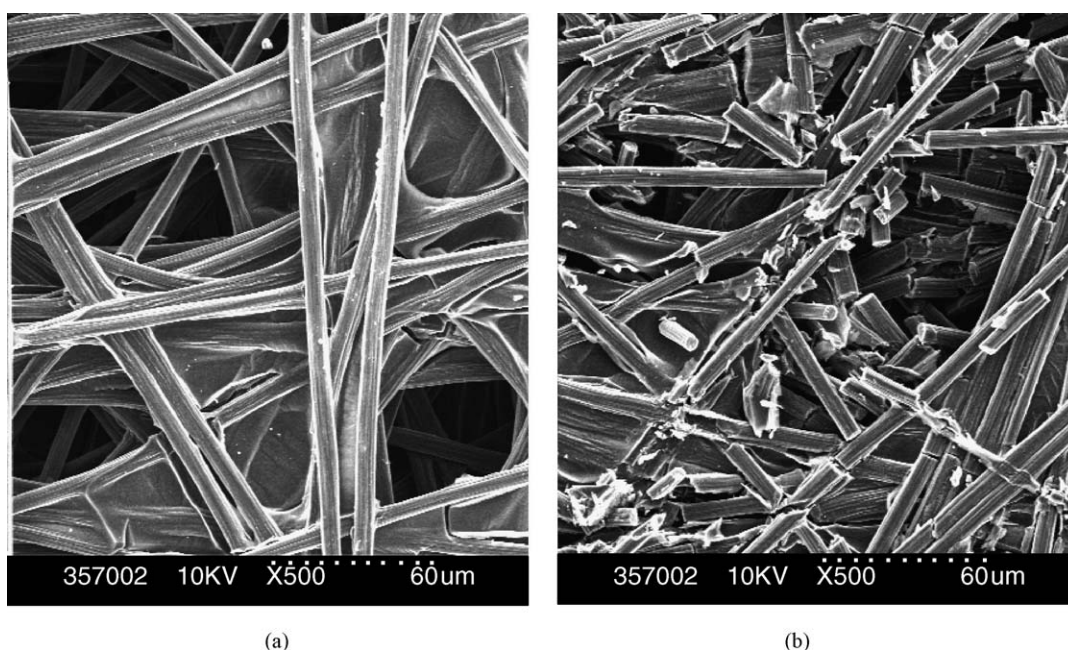


Fig. 6. SEM images of the carbon paper (a) before and (b) after hot-pressing.

EIS and the SEM and AFM images. The resistance of the MEA with scraped anode electrode (0.37Ω , E4) is slightly smaller than that of the MEA with sprayed anode electrode (0.40Ω , E3). The surface of scraped catalyst layer is more homogeneous and has fewer cracks than that of the sprayed catalyst layer. The surface roughness of the scraped catalyst layer (53 nm) is less than that of the sprayed catalyst layer (75 nm). The homogeneous and flat surface of the anode catalyst layer prepared by the scraping method is helpful for improving the mass transport property in the electrode and enhancing electrical contact between a smoother catalyst surface and membrane. However, the polarization curves show no obvious difference between the performance of these two MEAs (E3 and E4), suggesting that the surface structure and roughness of the anode catalyst layer has less effect on the performance of the anode electrode in a DMFC. It is believed that the electrochemical behavior of anode electrode in the DMFC is influenced by several other factors, including the inner structure [20,21] and electrode composition [5,22]. For future research, it is worthwhile to explore the effects of inner structure and the electrode composition on the performance of the anode electrode in the DMFC.

As shown in Fig. 7, the performances of the MEAs (E1 and E2) with the hot-pressing pretreated electrodes are lower than those of the MEAs (E3 and E4). The polarization curves of the MEAs (E1 and E2) show a decrease in the ohmic polarization region compared with those of the MEAs (E3 and E4). This also indicates that the internal resistances of the MEAs increase after hot-press pretreatment of the anode electrodes, according with the values of the EIS. The resistance of MEA is increased due to the breaking of the carbon fibers in the carbon paper. The polarization curves of the MEAs (E1 and E2) also show a decrease in the slope indicating that the change in the rates of mass and ion transport. It is indicated that the cell performance decreases due to the restricting mass transport in the anode electrode. It is well known that catalyst sites on the anode and the cathode electrodes must satisfy proton access, mass access and electron path continuity in the electrochemical reaction of DMFC. And the diffusion of methanol into the catalyst layer and the removal of carbon dioxide away from the catalytic sites require a DMFC anode with an “open” structure [23–25]. The surface of anode electrode is smooth and there are fewer cracks on it after the hot-pressing pretreatment, however, these do not favor the performance of the anode electrode in a DMFC because the surface structure and roughness of the anode catalyst layer has less effect on the performance of the anode electrode in a DMFC. And the catalyst layer is compact after the hot-press pretreatment which make it difficult for electrons and mass transport in the electrode. Overall, the performances of the MEAs (E1 and E2) decrease.

4. Conclusion

We have investigated the effects of the spraying and scraping fabrication methods (based on the GDL-based methods) and the hot-pressing pretreatment of the anode electrodes on the performance of DMFCs. It is demonstrated that the MEA (E4)

with the scraped anode catalyst layer without the hot-pressing pretreatment of the anode electrode shows the highest power density of 67 mW cm^{-2} . The scraping method is proved to be a little more profitable for improving the cell performance than the spraying method for the fabrication of the anode catalyst layer. The relatively homogeneous and smooth surface of the scraped anode catalyst layer (the Ra surface roughness is 53 nm) is helpful for improving the mass transport property in the electrode and enhancing electrical contact between a smoother catalyst surface and membrane. However, it is found that the surface structure and roughness of the anode catalyst layer has less effect on the performance of the anode electrode in a DMFC. The hot-pressing pretreatment of the anode electrode (under a specific load of 80 kgf cm^{-2} for 3 min at 110°C) does not favor the performance of it. The anode electrode is compact after the hot-press pretreatment which make it difficult for electrons and mass transport in the electrodes. The internal resistance of the MEA with hot-pressed anode electrode significantly increases due to the breaking of the carbon fibers in carbon paper.

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