PERFORMANCE ENHANCEMENT OF TWIN STACK DIRECT METHANOL FUEL CELLS BY COATING ACTIVE CARBON CATALYST ON FUEL CHANNELS

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In this study, a 0.09 wt% of active carbon catalyst was added onto anode and cathode channels made of PDMS (Polydimethylsiloxane) in order to promote the fuel decomposing reaction in the fuel channels, and further enhance the output of single DMFCs (Direct Methanol Fuel Cell) and twin stack DMFCs under various operating temperatures. The experimental results indicated that under the same operating conditions, the performances of the DMFCs with an active carbon catalyst added onto their channels are always superior to those of DMFCs without a catalyst added. Enhancement of 90% to 118% for DMFCs with 0.09 wt% of active carbon catalyst added onto the channels can be achieved under the operating conditions investigated. In this study, it was also found that, in the cases of DMFCs with the same added catalyst percentage, higher maximum power density increments usually could be obtained under lower operating temperatures, because lower temperatures can retard the crossover effect in DMFCs.

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1. Introduction

Direct methanol fuel cell (DMFC), which utilizes the methanol solution as a fuel, has been considered as a promising power source for portable electronic devices. Methanol has high energy density and specific, superior chemical stability, which are important for transport and storage.

Thus, compared with other fuel cell systems, the DMFC is a simple and compact system and also a potential power source for portable applications. However, the major drawbacks of DMFC including high production cost, catalyst and methanol crossover poisoning have motivated researchers and industry engineers all over the world to study the DMFC. Finding and prepare suitable catalysts to enhance the performance of DMFC and methanol tolerance is a crucial issue for the development of DMFC.

For the studies of catalyst in DMFC, Wei et al. [1] developed a new electrode structure includes a hydrophilic thin film and a traditional catalyst layer for direct methanol fuel cells. Their results showed that the performance of a cell with the hydrophilic thin film was obviously enhanced and the stability of the cell in a short-term life operation was also increased. Baranton et

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al. [2] developed new electron conductive polymers stable under oxidative environment and with a high doping capacity for using platinum alternative cathode catalysts in DMFC technology. Qiao et al. [3] developed a new plating process for the formation of the cathode catalyst of a micro tubular direct methanol fuel cell. By using this method, a thin porous layer of Pt electrocatalyst was firstly bonded onto a tubular polymer electrolyte membrane by chemical reduction of Pt complex impregnated in the membrane. Guo et al. [4] investigated the structural and surface features and electrocatalytic properties of bimetallic PtRu/OCNF and PtRu/RCNF. The OCNF supported catalysts give better performance than commercial catalysts when current density is higher than 50 mA/cm² in spite of low methanol oxidation peak current density. Baglio et al. [5] used a low temperature preparation procedure to modify the Pt catalyst with transition metals (Fe, Cu and Co). Through adsorbed methanolic residues stripping analysis, the case of the Pt–Fe system presented a better methanol tolerance and an enhanced activity towards oxygen reduction. An improvement of the DMFC single cell performance was also observed in the presence of Pt–Fe catalysts. Wang et al. [6] used Ketjen Black EC 300J as an additive in the cathode catalyst layer to improve the DMFC performance. The cathode catalyst layer with Ketjen Black EC 300J additive showed a greater single cell performance than the cathode catalyst layer without any additive, especially in the air-breathing mode. Choi et al. [7] developed a new type of Se/Ru catalyst called Se/Ru(aq) and studied the methanol tolerance and the performance of the direct methanol fuel cell for the catalyst. They indicated that the catalyst of Se/Ru(aq) was highly tolerant to methanol crossing through the membrane (from the anode side) up to a feed concentration of 17 M. Compared to Pt cathodes, the performance of Se/Ru(aq) is significantly better at high methanol concentrations. Yao et al. [8] used a magnetron sputtering (MS) and metal-plasma ion implantation (MPII) technique to prepare Pt–M/C catalyst. They indicated that the membrane electrode assembly for Pt–Ni/C, Pt–Fe/C and Pt–Cr/C catalysts can enhance DMFC cell performance, compared with traditional Pt/C and Pt–Ru/C. Luo et al. [9-10] investigated the performance of the DMFCs with different hydrophobic anode channel. They found that the performance of the DMFCs made of PDMS with high hydrophobic particles can be greatly enhanced and the hydrophobic property of the particles can be unaffected by different operation conditions. Luo et al. [11] investigated the effect of the anode channel width on the performance of the DMFCs and found that the performance of DMFCs with smaller anode channels can be enhanced due to the uniform distribution of fuel on the anode collectors and the longer retention period of the fuel within the anode channels. However, when the width of the anode channel was less than 600 μm, the hydro-resistance from the CO₂ bubbles produced within the anode channels seriously increased. Consequently, the output of the DMFCs showed an obvious decrease.

This study aimed to investigate the output efficiency of DMFCs by coating different catalysts on the fuel channels in order to promote the fuel decomposing reaction within the channels and further enhance the output of the DMFCs. At present, the platinum is often used as catalyst in MEA, but it is still expensive. In order to reduce the cost, this study used the catalyst of active carbon as the substitute added onto fuel channels, which have the similar effect and lower price. The effect of adding proportions of the catalysts on the output efficiency of DMFCs was investigated under different operating temperatures.

2. Experiment

2.1 Channel fabrication

In this study, the channel for DMFCs uses PDMS as substrate. The related injection molding processes are described below [12-15]:

(1) PDMS preparation: the silicone resin (Agent A) and hardener (Agent B) are mixed in a weight ratio of 10:1, and then, the mixture is uniformly mixed with different weight ratios of catalysts; the total weight is 35 g. The PDMS is mixed with catalysts at different concentrations. For the weight proportions of 0.03%, 0.06%, 0.09%, 0.29% and 0.34%, the additive weight accounts for 0.01 g, 0.02 g, 0.03 g, 0.1 g and 0.12 g of the total weight, respectively.
(2) Vacuum treatment: since the mixing of A and B agents in the previous step produces a large amount of bubbles, the mixed PDMS is placed in a vacuum chamber for vacuum treatment to completely eliminate the bubbles.

(3) Injection mold solidification and catalyst coating: the master mold is placed on a balanced stage, and then, the vacuumized PDMS is injected into the master mold (8cm x 8cm). The channel area (3.5cm x 3.5cm) of the master mold is isolated by a self-made square glass plate before injection, and then the PDMS with the catalyst is injected into it. The PDMS without a catalyst fills up the exterior of the mold, and then the glass plate is taken out, placed on a hot plate and baked at 70°C for 30-40 minutes, so as to complete the solidification of the PDMS.

4) Turning mold: the solidified PDMS is removed from the master mold, as shown in Fig. 1. The fabrication channels of active carbon catalyst at different concentrations are shown in Fig. 2.

Fig. 1 Injection molding processes of the fuel channels

Fig. 2 Channels of catalysts at different concentrations

2.2 Transparent cell
Fig. 3 shows the exploded view of the transparent single DMFC test fixture designed and fabricated for the visualization study in this paper. The MEA, which is detailed in the subsequent paragraph, was sandwiched between two bipolar plates with a gasket on either side of the MEA.
This assembly, including the bipolar plates and MEA, was clamped between two enclosure plates by using eight M8 screw joints (each having a torque of about 12 KGF-CM). The active area of the MEA adopted in this paper was 3.5cm×3.5cm, which consisted of two single-sided ELAT electrodes from E-TEK and a Nafion® membrane 117. Both anode and cathode electrodes used carbon cloth (E-TEK, Type A) as the backing support layer with a 30% PTFE wet-proofing treatment. The catalyst loading on the anode side was 4.0 mg/cm² with unsupported [Pt:Ru] Ox (1:1 a/o), while the catalyst loading on the cathode side was 2.0 mg/cm² with 40% Pt on Vulcan XC-72. Furthermore, 0.8 mg/cm² Nafion® was applied to the surface of each electrode. The bipolar plates (shown in Fig. 3) were made of 316 stainless steel plates with a thickness of 2.0mm in order to avoid corrosion. As shown in Fig. 3, the rectangular bipolar plate consisted of two portions: the channel area and the extension area. The channel area acted as the distributor for supplying fuel and oxidant to the MEA. The parallel serpentine channels, having an area of 2.0mm×2.0mm, were machined using the wire-cut technology. The width of the ribs was 2 mm. The serpentine channel comprised a total length of 676 mm. The extension area of the bipolar plates served as a current collector. For the purpose of visualization, the two enclosure plates (2.0 cm thick) were made of transparent Lucite. The twin stack fuel cell tested in this study was composed of two single cells possessing a common cathode flow board with cathode fuel channels on each side of the board, as shown in the schematic diagram of Fig. 4.

Fig. 3 Exploded view of the transparent test fixture of the single DMFC

Fig. 4 Exploded view of the transparent test fixture of the twin stack DMFC
2.3 Experimental procedure

The schematic of the experimental setup for a single DMFC is shown in Fig. 5. The methanol solution was driven by a squirr pump, which can precisely control the liquid flow rate from 3 to 20 ml/min with an error of 2%. Before entering the cell, methanol solution was preheated to a desired temperature by placing the methanol solution tank in a temperature controllable water bath. The mixture of CO$_2$ gas and unreacted methanol solution was drained from the cell and cooled down when passing through the cooling system. The gas (CO$_2$) produced at the anode was separated from the methanol solution tank and released to the atmosphere, while the unreacted methanol solution was re-collected into a chemical liquid tank. Simultaneously, the ambient air, with almost 80% oxygen as the oxidant, was provided to the cathode side of the cell without humidification. The flow rate of oxygen was controlled by an air mass flow regulator, which has an error of 5% of the full scale. Fig. 6 illustrates the schematic experimental apparatuses for twin stack DMFC. The volume of methanol solution driven by a squirr pump was evenly distributed into two anode fuel channels through a 3-way valve in an anode fuel transmission loop. Through another 3-way valve in an air transmission loop, even air flow rate from ambient air can be supplied to each cathode channel on the cathode board simultaneously by an air regulator. The tested twin stack DMFC was composed of two single fuel cells which were connected to an electric load with a parallel circuit.

As shown in Figs. 5 and 6, when the MEA was activated, the electronic DC loader was connected to the fuel cell by connecting the anode to the negative terminal and connecting the cathode to the positive terminal. The 0.6V~0.2V load was given in constant voltage mode, the time for each interval of 0.05 V was several minutes and the voltage and current were recorded. The I-P curve and I-V curve were drawn, and the current density and power density distribution curves were worked out. All the measurements of the DMFCs investigated were tested in an experimental chamber in which the temperature and humidity could be controlled.
3. Results and discussion

In the experiments, 10% of the methanol-water fluid concentration was injected into the fuel channels of DMFCs with a flow rate of 10 cc/min. 0.09 wt% of active carbon catalyst were added onto the PDMS channels of 2 cm widths, and the performance of DMFC was tested under different operating temperatures (30°C, 40°C, 50°C, 60°C, 70°C), respectively.

3.1 Performance of DMFCs without active carbon catalyst added onto fuel channels

Table 1 indicates the maximum generating powers and corresponding maximum power densities of the DMFCs without a catalyst being added under different operating temperatures. From the table, it can be seen that the maximum power densities and maximum generating powers of the single fuel cell and the twin stack fuel cell increase with the increase in the operating temperature due to the activity enhancement of the reactants by the operating temperature. The maximum power density of the twin stack fuel cell is a little less than that of the single fuel cell at the same operating temperature. At the operating temperature of 70°C, the maximum power density of a single fuel cell can reach a value of 10.4 mW/cm², but the maximum output power of a twin stack fuel cell is 9.96 mW/cm². However, the transverse areas of the twin stack and the single cell are the same, and the effective reaction area of the twin stack fuel cell is twice that of the single cell. Therefore, under the same operating conditions and power densities, the generating power of the twin stack fuel cell should be, theoretically, twice that of the single cell. From the table, it can be seen that, at the operating temperature of 70°C, the maximum output power of the single fuel cell is 127.4 mW, but the maximum output power of the twin stack fuel cell can reach a value of 244.2 mW. Because the power density of the twin stack fuel cell is a little less than that of single fuel cell, the generating powers of the twin stack fuel cell are also a little less than the corresponding theoretical value of the output powers. Figures 7 and 8 show the generating electric powers of the single and twin stack cells without an active carbon catalyst added onto the channels at various operating temperatures. The tested twin stack DMFC was composed of two single fuel cells which were connected to the electric load with a parallel circuit. Under the same output electric potentials, the generating currents of the twin stack fuel cell are much greater than those of the single fuel cell but also, a little less than twice those of the single fuel cell at different operating temperatures. This phenomenon also causes the generating powers of the twin stack fuel cell to be a little less than the theoretical values.
Table 1. Maximum generating powers and corresponding maximum power densities of DMFCs without active carbon catalyst added onto channels at different temperatures

<table>
<thead>
<tr>
<th>Output</th>
<th>Temperature</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single fuel cell</td>
<td>Maximum power density (mW · cm⁻²)</td>
<td>6.36</td>
<td>7.48</td>
<td>8.35</td>
<td>9.36</td>
<td>10.40</td>
</tr>
<tr>
<td></td>
<td>Maximum generating power (mW)</td>
<td>77.9</td>
<td>91.6</td>
<td>102.3</td>
<td>114.7</td>
<td>127.4</td>
</tr>
<tr>
<td>Twin stack fuel cell</td>
<td>Maximum power density (mW · cm⁻²)</td>
<td>5.99</td>
<td>6.96</td>
<td>8.06</td>
<td>8.94</td>
<td>9.96</td>
</tr>
<tr>
<td></td>
<td>Maximum generating power (mW)</td>
<td>146.8</td>
<td>170.6</td>
<td>197.5</td>
<td>219.1</td>
<td>244.2</td>
</tr>
</tbody>
</table>

Fig. 7 Generating electric power of a single fuel cell without active carbon catalyst added onto channels at various operating temperatures
3.2 Performances of DMFCs with 0.09 wt% of active carbon catalyst added onto fuel channels

In the case of 0.09 wt% of active carbon catalyst added onto fuel channels, as shown in Table 2, the maximum power densities and generating powers of DMFCs also increase with the increase in the operating temperature. As shown in Table 2, the maximum power densities of a single fuel cell and twin stack fuel cell can reach values of 19.93 mW/cm² and 19.43 mW/cm² at 70°C, respectively. The maximum generating powers of a single fuel cell and twin stack fuel cell can reach values of 244.1 mW and 476.2 mW at 70°C, respectively. In the case of 0.09 wt% of active carbon catalyst added, due to promotion of the fuel decomposing reaction by the added catalyst on the channels, the performances of DMFCs with active carbon added are improved greatly compared with those without a catalyst added on the channels, as shown in Table 1, at the same operating temperature. Because the effective reaction area of the twin stack fuel cell was twice that of the single cell, and the power densities of the twin stack fuel cell were a little less than those of the single fuel cell at the same operating temperatures, the generating powers of the twin stack fuel cell were also a little less than the corresponding theoretical values of the output powers. Figures 9 and 10 illustrate the generating electric powers of the single fuel cell and the twin stack fuel cell with active carbon catalyst added onto channels at various operating temperatures, respectively. The tested twin stack DMFC was composed of two single fuel cells which were connected to an electric load with a parallel circuit. Under the same output electric potentials, the generating currents of the twin stack fuel cell are also much greater than those of the single fuel cell. This phenomenon also causes the generating powers of the twin stack fuel cell to be much greater than those of the single fuel cell but still a little less than the theoretical values. Figure 11 illustrates the comparison of output powers of the single fuel and the twin stack fuel cell with 0.09 wt% of catalyst added on the fuel channels at an operating temperature of 70°C. It can be seen that the generating currents and output powers of the twin stack fuel cell are greatly enhanced. Table 3 indicates the increment percentages of maximum output powers of DMFCs with 0.09 wt% of active carbon catalyst added onto the channels at different temperatures. In the case of the single fuel cell, a maximum generating power increment of 118.7% can be attained with 0.09 wt% of catalyst at the operating temperature of 30°C. With the increase in the operating temperature, the generating power increment gradually decreases because higher operating temperatures may make the methanol solution exceed the tolerance of its membrane and lead to
the effect of performance deterioration of the fuel cell. However, the minimum generating power increment of 91.6% can also be reached at an operating temperature of 70°C. In the case of the twin stack fuel cell, a maximum generating power increment of 118.7% can be attained at an operating temperature of 30°C, and a minimum generating power increment of 95.2% can also be reached at an operating temperature of 70°C.

Table 2 Maximum generating powers and corresponding maximum power densities of DMFCs with 0.09 wt% active carbon catalyst added onto channels at different temperatures

<table>
<thead>
<tr>
<th>Output</th>
<th>Temperature</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single fuel cell</td>
<td>Maximum power density (mW cm⁻²)</td>
<td>12.74</td>
<td>15.81</td>
<td>17.54</td>
<td>18.49</td>
<td>19.93</td>
</tr>
<tr>
<td></td>
<td>Maximum output power (mW)</td>
<td>156.1</td>
<td>193.7</td>
<td>214.9</td>
<td>226.5</td>
<td>244.1</td>
</tr>
<tr>
<td>Twin stack fuel cell</td>
<td>Maximum power density (mW cm⁻²)</td>
<td>12.45</td>
<td>14.99</td>
<td>17.37</td>
<td>18.03</td>
<td>19.43</td>
</tr>
<tr>
<td></td>
<td>Maximum output power (mW)</td>
<td>305.1</td>
<td>367.3</td>
<td>425.6</td>
<td>441.8</td>
<td>476.2</td>
</tr>
</tbody>
</table>

Fig. 9 Generating electric powers of the single fuel cell with 0.09 wt% active carbon catalyst added onto channels at various operating temperatures
Fig. 10 Generating electric powers of the twin stack fuel cell with 0.09 wt% active carbon catalyst added onto channels at various operating temperatures

Fig. 11 Comparison of generating powers of a single fuel and twin stack fuel cell with 0.09 wt% catalyst added on fuel channels at operating temperature of 70°C
Table 3 Increment percentages of maximum generating powers of DMFCs with 0.09 wt% active carbon catalyst added onto channels at different temperatures

<table>
<thead>
<tr>
<th>Fuel cell</th>
<th>Temperature</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single fuel cell</td>
<td></td>
<td>118.7%</td>
<td>111.3%</td>
<td>110.3%</td>
<td>95.4%</td>
<td>91.6%</td>
</tr>
<tr>
<td>Twin stack fuel cell</td>
<td></td>
<td>107.8%</td>
<td>115.4%</td>
<td>115.5%</td>
<td>101.6%</td>
<td>95.2%</td>
</tr>
</tbody>
</table>

Maximum generating power increment is defined as \( \frac{(E_X - E_P)}{E_P} \times 100 \% \), where \( E_X \) is the maximum output power of a DMFC with 0.09 wt% catalyst added onto channels, \( E_P \) is the maximum output power without additive catalyst on channels at the same operating temperature.

4. Conclusions

This study investigated the enhancement effect of the output performance of a single fuel cell and a twin stack fuel cell by adding 0.09wt% active carbon catalyst onto fuel channels under different operating temperatures, respectively. It is found that the performances of the DMFCs can be greatly enhanced by adding appropriate percentages of catalysts on the channels due to promotion of the fuel decomposing reaction within the channels. In this study, the highest maximum power density of 19.93 mW/cm² can be obtained for a single fuel cell with 0.09 wt% active carbon catalyst at an operating temperature of 70°C. In comparison to the maximum generating powers of the PDMS channel without a catalyst at various operating temperature, the highest maximum generating power increment of 118.7% can be attained in the case of a single fuel cell with an active carbon catalyst added on the channels at an operating temperature of 30°C. In this study, the maximum generating power of 476.2 mW can be obtained in the case of a twin stack fuel cell with a catalyst added on the channels at an operating temperature of 70°C. In this study, it is also found that, in the cases of DMFCs with the same added catalyst percentages, higher maximum power density increments usually can be obtained under lower operating temperatures because lower temperatures can retard the crossover effect in the DMFCs. The experimental results suggested that adding an appropriate percentage of catalyst on the channel is helpful to increase the efficiency of DMFC. At present, the platinum catalyst is still expensive. In order to reduce the cost, a catalyst with the same effect but at a lower price can be used as a substitute.

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