A High Catalyst-Utilization Electrode for Direct Methanol Fuel Cells

G. Zhao, T.S. Zhao *, X.H. Yan, L. Zeng

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay Kowloon, Hong Kong SAR, China

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ABSTRACT

In this study, a simple method is devised to investigate the local current distribution of the anode of a direct methanol fuel cell (DMFC). It is shown that the local current decreases along the methanol flow direction as a result of the decreased methanol concentration along the same direction during discharge. This finding suggests that the catalyst loading along the flow direction needs to be distributed by following the same trend as the distribution of methanol concentration to achieve high catalyst utilization. In line with this idea, we propose and fabricate a novel anode structure that enables the catalyst loading to be reduced along the methanol flow direction. The fuel cell performance characterization demonstrates that the new anode with uneven catalyst loading matches the performance of the conventional anode involving an evenly distributed catalyst, but the total amount of catalyst loaded in the new anode is substantially reduced.

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1. Introduction

In recent years, direct methanol fuel cells (DMFCs) have attracted significant attention due to their high energy densities; however, the high cost of DMFCs hinders their widespread commercialization [1–4]. This high cost is the result of DMFCs’ expensive components, such as Nafion membranes, catalysts for anodes and cathodes, carbon paper and bipolar plates, etc. Among these materials, the largest portion of the cost is attributed to the catalysts.

In DMFCs, noble metals of Pt and PtRu are conventionally used as catalysts for cathodes and anodes, due to the sluggish kinetics of oxygen reduction reaction and methanol oxidation reaction. Although the literature shows that non-noble metal compounds such as ferric, cobalt, nickel, and carbonaceous materials can potentially act as substitutes for Pt [5–7], much more research needs to be done to completely replace noble metals by non-noble metal compounds as catalysts. Thus, noble metals currently remain as the most dominant materials for DMFCs’ catalysts.

Hence, a promising way to cut down the cost is to improve the utilization of the noble metal catalyst. There are two methods to achieve this: the first method is to develop advanced supporting materials such as carbon nanotubes [8–11], carbon nanofibers [12–14], mesoporous carbon [15–18] and other types of materials [19–22]; the second method is to optimize the electrode structure to improve the utilization of the catalyst. For example, Liu [23] prepared novel anode catalyst layer by ultrasonic-spray process which combines directly spray method and catalyst-coated membrane switchover method. Results show that the anode outer catalyst layer with pores and mesh work structure has increased the electrochemical active surface area and retained the transfer of protons and electrons, and the anode inner catalyst layer with compact structure has prevented methanol crossover. The peak power density increased from 116.8 mW cm⁻¹ of traditional MEA to 202.6 mW cm⁻¹ of novel MEA. Suo [24] also proposed a novel anode structure composed of a hydrophilic inner catalyst layer with PtRu black and an outer catalyst layer with PtRu/C. In the double-layer structured anode, there existed a catalyst concentration gradient and porosity gradient, resulting in good mass transfer, proton and electron conducting. Therefore, the performance got enhanced. Nakashima [25] designed the multi-layer anode with localized catalyst loading prepared by the sputtering method. The designed multi-layer electrode showed a high cell performance and mass activity because of the good contact at the interface between the catalyst and the electrolyte membrane and low mass transfer resistance. The ultra-low catalyst loading electrode preparing by the sputtering method was a very effective method for reducing the catalyst amount and enhancing the mass activity.

The above researchers mainly focused on the optimization of electrode in the through-plane direction, while few papers were published about the optimization of electrode in the in-plane
direction. It is well known that the catalyst is evenly distributed in the in-plane direction for the conventional electrodes. However, when a DMFC discharges, the concentration of reactants decreases and the concentration of products increase along the flow direction from inlet to outlet. As a result, this concentration disparity will lead to an uneven local current distribution in the in-plane direction, despite the even catalyst distribution. The part with large local current definitely contributes more to the total performance than that with small local current contributes. Therefore, catalyst utilization may not be consistent, varying according to the position along the flow direction and consequently causing the total utilization of the catalyst to be lowered.

To investigate the local current distribution of a DMFC to figure out the contributions of different parts, we divided the anode into upstream and downstream two parts along the flow direction. This anode structure can be simulated by applying two single cells with anodes connected by series. By measuring the currents of these two single cells, we are able to determine the local currents at the upstream and the downstream parts, as well as their contributions to the total performance. Based on the results of the local current distribution, we propose and fabricate a novel anode structure, in which the catalyst is unequally loaded at the upstream and downstream parts. With this new anode structure, the total amount of catalyst loaded at the anode decreases significantly, while the performance is barely influenced. Hence, the catalyst utilization remarkably increases.

2. Experimental

2.1. Preparation of the membrane electrode assembly (MEA) for DMFCs

The MEA studied in this work was fabricated according to the following method [26,27]. For the anode, a diffusion layer comprising of Vulcan XC-72 carbon powder and PTFE was brushed onto a PTFE-treated carbon paper (Toray), followed by the catalyst layer consisting of PtRu/black (Johnson Matthey), PTFE, and Nafion ionomer. The amount of cathode catalyst loaded was 2 mg cm\(^{-2}\).

In the conventional anode structure, the loadings of catalyst at the upstream part and the downstream part were the same (6 mg cm\(^{-2}\)), denoted as A6 + 6. While in the new anode structure, the catalyst was unevenly distributed: 6 mg cm\(^{-2}\) was loaded at the upstream part and 4 mg cm\(^{-2}\) and 2 mg cm\(^{-2}\), denoted as A6 + 4, and A6 + 2, respectively, was loaded at the downstream part.

The MEA was obtained by hot-pressing the anode and cathode on each side of a pretreated Nafion 115 membrane. This pretreatment included boiling the membrane for 1 hour in 5 vol.% H\(_2\)O\(_2\) at 80°C and another 1 hour in 0.5 M H\(_2\)SO\(_4\) at 80°C before washing it in boiling DI water.

2.2. Single cell test

The MEA was sandwiched between two stainless steel plates with a single serpentine flow field on each plate. It was noted that when assembling the new structured MEA, the upstream portion should be installed close to the inlet, and the downstream portion

![Fig. 1. Scheme diagram of the local current measurement. (a) Local current measurement of a single cell; (b) the setup with two cells simulated as a cell.](image)

![Fig. 2. I-V performance of the anode with evenly distributed catalyst at the anode flow rates of 0.5 mL min\(^{-1}\), 1.0 mL min\(^{-1}\), 1.5 mL min\(^{-1}\), and 2.0 mL min\(^{-1}\).](image)
should be installed to the outlet according to the anode flow direction. Gaskets between MEA and the plates were used for sealing. 1 M aqueous methanol solution was pumped into the anode flow field at a constant rate. Oxygen was supplied to the cathode chamber from the cylinder at a flow rate of 100 mL min⁻¹. Arbin instrument was used as the electric load. The test temperature was set at 75 °C.

2.3. Local current distribution measurement

In this experiment, we simply divided the anode into two parts along the anode flow direction as Fig. 1(a) depicted: the upstream portion and the downstream portion. I_u, I_d and I_total stood for the currents at the upstream, the downstream, and the total cell, obtaining I_total = I_u + I_d.

We constructed a setup comprising of two cells to simulate the above cell in order to measure the I_u and I_d as shown in Fig. 1(b). The methanol solution flowed through two cells by series and the two cells were electrically connected by parallel. The currents of the two cells were taken as I_u and I_d, and the I_total could be reached by the sum of I_u and I_d. This means that the local current of a single cell can be converted to measure the currents of the two separated cells. The contributions are calculated by $I_u/I_{total}$ and $I_d/I_{total}$.

It should be noted that the route of the anode flow between the two single cells must be short enough to avoid the influence of retention time.

3. Results and discussion

3.1. Measurement of a conventional DMFC with evenly distributed catalyst at anode

3.1.1. I-V performance test

Fig. 2 depicts the I-V performances of a conventional DMFC with the catalyst evenly distributed on the anode at different anode flow rates. When the anode flow rate increases from 0.5 mL min⁻¹ to 2.0 mL min⁻¹, the performance improves continuously. In addition, the peak power density improves with the increased anode flow rate, which rises from 0.116 W cm⁻² to 0.158 W cm⁻². This phenomenon can be attributed to the fact that the increased anode flow rate greatly alleviates the transportation polarization and enlarges the limiting transportation current.

3.1.2. Measurement of local current distribution

To investigate the contributions of different parts to the total performance, measurement of local current distribution is used in this work. Figs. 3–6 show the results of the local current and

![Fig. 3. Local currents of $I_u$, $I_d$ (a) and their contributions (b) to the $I_{total}$ when methanol solution flows at 0.5 mL min⁻¹.](image)

![Fig. 4. Local currents of $I_u$, $I_d$ (a) and their contributions (b) to the $I_{total}$ when methanol solution flows at 1.0 mL min⁻¹.](image)
part becomes increasingly lower until transportation polarization happens, causing a peak current of $I_d$. After $I_d$ reaches the maximum value, the decreasing methanol concentration trend continues, resulting in the limiting transportation current of $I_d$ to also fall.

Fig. 3(b) illustrates the contributions of $I_u$ and $I_d$ to $I_{total}$. Based on the local current measurements, it shows that $I_u$ and $I_d$ contribute the same percentage (about 50%) when discharging at a small current. With an increase in $I_{total}$, $I_u$ contributes more to $I_{total}$ than $I_d$. When $I_{total}$ reaches a current above 1.4 A, 80% of $I_{total}$ comes from $I_u$, while only 20% comes from $I_d$.

When the anode flow rate rises to 1.0 mL min$^{-1}$, 1.5 mL min$^{-1}$, and 2.0 mL min$^{-1}$, similar trend can be observed, shown in Figs. 4–6. As the anode flow rate increases, the transportation polarization is greatly alleviated, resulting in the peak limiting transportation current of $I_d$ to disappear and the contribution of $I_d$ to improve.

### 3.2. Measurement of the DMFC with novel structure MEA

#### 3.2.1. Performance test of new anode structure

Based on the findings in 3.1, we fabricate a new anode structure with an unevenly distributed catalyst at the upstream and downstream parts to the total performance at different anode flow rates.

When the anode flow rate is 0.5 mL min$^{-1}$, the local currents of upstream part ($I_u$) and downstream part ($I_d$) can be seen in Fig. 3(a). $I_u$ and $I_d$ are virtually the same during small current discharge ($I_{total}$ is small). With the discharge current ($I_{total}$) increases, both $I_u$ and $I_d$ increase; but $I_u$ increases faster than $I_d$. A disparity in the speed of increase between $I_u$ and $I_d$ causes $I_d$ to become outweighed by $I_u$. The disparity becomes larger as a result of an increase in $I_{total}$. It is, therefore, not surprising that $I_u$ follows the same growing trend of $I_{total}$, but $I_d$ manifests a strange tendency: after reaching a current peak, $I_d$ begins to fall with the increase of $I_u$ and $I_{total}$.

The aforementioned phenomenon can be explained by the methanol concentration difference during discharge. When discharging at a small current, methanol consumption is so small that it is negligible compared with the methanol supply rate. Therefore, the methanol concentrations at the upstream and the downstream parts are almost the same, thus $I_u$ and $I_d$ are similar in value. With an increase in the current, methanol consumption becomes large enough to be accounted for; the methanol concentration at the upstream part is higher than that at the downstream part, which enables the upstream part to contribute more current than the downstream part. The methanol concentration at the downstream part becomes increasingly lower until transportation polarization happens, causing a peak current of $I_u$. After $I_d$ reaches the maximum value, the decreasing methanol concentration trend continues, resulting in the limiting transportation current of $I_d$ to also fall.

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When the anode flow rate rises to 1.0 mL min$^{-1}$, 1.5 mL min$^{-1}$, and 2.0 mL min$^{-1}$, similar trend can be observed, shown in Figs. 4–6. As the anode flow rate increases, the transportation polarization is greatly alleviated, resulting in the peak limiting transportation current of $I_d$ to disappear and the contribution of $I_d$ to improve.
Fig. 7. Performances comparison when the anode flow rates are 0.5 mL min\(^{-1}\) (a), 1.0 mL min\(^{-1}\) (b), 1.5 mL min\(^{-1}\) (c), and 2.0 mL min\(^{-1}\) (d).

Fig. 8. Specific activity of the anode catalyst at the flow rates of 0.5 mL min\(^{-1}\) (a), 1.0 mL min\(^{-1}\) (b), 1.5 mL min\(^{-1}\) (c), and 2.0 mL min\(^{-1}\) (d).
downstream parts. Fig. 7 shows the I-V performance comparisons between the conventional anode structure (evenly distributed catalyst) and our improved structure. I-V curves show similar performances of the three samples although less total catalyst is used for the novel structure. It can be concluded that the influence of the reduced amount of anode catalyst on the performance is negligible. When methanol solution flows at the rate of 0.5 mL min⁻¹ (shown in Fig. 7a), it can be seen that the new anode structured MEAs of the A6+4 and A6+2 bear the same performance as the conventional one of the A6+6. As the methanol solution flow rate increases to 1.0 mL min⁻¹ (Fig. 7b), 1.5 mL min⁻¹ (Fig. 7c), and 2.0 mL min⁻¹ (Fig. 7d), performances follow the same trend, with only a slight difference observed in the transportation polarization region.

3.2.2. Utilization analysis of the DMFC anode catalyst

Although the I-V test demonstrates that the new anode and the conventional anode structured MEA show similar performances, it is noted that the total amount of the newly structured anode becomes significantly reduced. These results suggest that the anode catalyst is better utilized. When the anode fuel flows at 0.5 mL min⁻¹ (Fig. 8a), the anode catalyst reaches a peak activity of 19.4 mW mg⁻¹ in the conventional anode structure (A6+6), while in the novel structure, it reaches 23.2 mW mg⁻¹ (A6+4) and 28.6 mW mg⁻¹ (A6+2) respectively, improving the efficiency by 20% and 47% in each case. When the anode fuel flows at 1.0 mL min⁻¹ (Fig. 8b), 1.5 mL min⁻¹ (Fig. 8c), and 2.0 mL min⁻¹ (Fig. 8d), the same trend can be observed. The peak activity of the anode catalyst becomes significantly enhanced with the novel anode structure in which the catalyst is unevenly distributed, compared with the conventional anode structure.

Fig. 9 lists the peak anode catalyst activities of both the conventional anode structure and the new anode structure at the four anode flow rates. It can be seen that the activity of the anode catalyst becomes greatly strengthened at each flow rate. This is, in fact, achieved by reducing the amount of catalyst at the downstream part without any ill-effects on the DMFC’s performance, thus increasing the utilization efficiency of the anode catalyst at the downstream part. In other words, the total anode catalyst’s utilization is enhanced.

4. Conclusions

The local current distribution of a conventional DMFC with an evenly distributed catalyst on the anode is studied. Although the anode catalyst was evenly loaded on the anode electrode, different parts of the anode contributed differently to the entire DMFC’s performance along the anode flow direction. The upstream portion contributed more toward the entire cell performance than did the downstream portion. This was explained by an apparent disparity of methanol concentration at the upstream part and downstream part during discharge. Based on this discovery, a new structure anode was proposed, in which the catalyst was unevenly loaded on the anode electrode along the flow direction. The conventional amount of catalyst is used at the upstream part; however, less catalyst is loaded at the downstream part. By using this new anode structured MEA, the overall cell performance is slightly influenced, but most importantly, the amount of catalyst used is greatly reduced. With a decrease in the use of catalyst, the effective cost of manufacturing such a DMFC will be significantly lowered, potentially allowing commercialization to become a closer reality.

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References


