Enhanced Cell Performance and Improved Catalyst Utilization for a Direct Methanol Fuel Cell with an In-Plane Gradient Loading Catalyst Electrode

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Abstract: Direct methanol fuel cells (DMFCs) offer high energy density, simple liquid fuel storage, and the ability to operate at ambient temperature. They may be used in a variety of portable mobile power supplies, small civilian power supplies, and automotive power supplies. However, in the process of electrochemical reaction inside a DMFC, because the reactants and products are distributed unevenly, the in-plane concentration of reactants and reaction rate are different; thus, the current density generated in the active area shows a high degree of non-uniformity. The high local current density can easily lead to the acceleration of DMFC aging. As a result, the operating cost of the DMFC is increased and the service life is shortened, which limits the commercial application of DMFCs. In this work, we develop an in-plane gradient loading catalyst. The loading on both the anode and cathode catalysts was lower near the inlet and higher close to the outlet. The experimental results of the single-cell test show that the performance of the gradient loading catalyst electrode was enhanced by up to 19.8% compared with the uniform loading catalyst at 60 °C for the same catalyst loading, especially under high current densities. In addition, the catalyst utilization was improved for the gradient loading catalyst electrode. Hence, the proposed approach shows potential for reducing the cost and increasing the service life of DMFCs.

Keywords: direct methanol fuel cell; in-plane distribution; gradient loading catalyst; cell performance

1. Introduction

Humans’ survival and development have been severely harmed as a result of climate change, which is closely related to the use of fossil fuel [1]. For this reason, people are looking for clean fuels. In recent years, methanol has come into people’s field of vision. Due to its wide range of sources, ease to carry, convenient storage and replenishment, and safe handling at standard temperature and pressure, it is widely used in many aspects [2–4]. DMFCs provide one way of generating electricity from methanol [5]. A DMFC is a device that converts chemical energy into electrical energy using electrochemical methods [6,7]. The advantages of DMFCs include high energy conversion efficiency, minimal pollution, convenient liquid fuel storage, and the ability to operate at ambient temperature. They may be used in a variety of portable mobile power supplies, small civilian power supplies, and automotive power supplies [8–10].

The most often used DMFC components include the membrane electrode assembly (MEA), bipolar plates, gaskets, current collectors, and endplates [11,12]. The MEA is the core of a DMFC, and its microstructure directly affects the performance of the MEA, which
in turn affects the overall performance of the DMFC. The diffusion layer (DL), catalytic layer (CL), and proton exchange membrane (PEM) make up the main structure of an MEA [13-15]. Among them, one of the most important aspects of the MEA is the CL. It is the place for electrochemical reactions as well as the transmission channel of reactants and products, the proton conduction channel, and the electron conduction channel [16,17]. As the place where electrochemical reactions occur, the CL carries out heterogeneous reactions involving many components, and it is also accompanied by complicated heat and mass transfer processes [18]. Methanol oxidation reactions (MOR) occur on the anode CL (ACL), and oxygen reduction reactions (ORRs) occur on the cathode CL (CCL) [19,20]. Only a continuous and stable electrochemical reaction between the two can produce electricity continuously. Therefore, the CL should have good proton and electron conductivity, unobstructed reaction gas diffusion channels, and an excellent drainage performance based on ensuring the high activity of the catalyst.

For platinum-based catalysts, the Pt particles in the CL must be reasonably distributed to ensure high catalytic activity and good conductivity [21]. In response, many researchers have optimized the electrode structure to ensure high catalytic activity and good electrical conductivity to improve catalyst utilization. For example, Suo et al. [22] suggested a double-layer anode structure. The mass transfer and proton and electron conductivity were all excellent in the double-layer anode. As a result, the performance improved. Nakashima et al. [23] developed a multi-layer anode catalyst loading. The suggested multi-layer CL exhibited good cell performance due to excellent contact at the CL/membrane interface and reduced mass transfer resistance. The stratified gradient of the CL at the anode could improve the cell performance. Some researchers have also conducted a layered study on the CCL. Wang et al. [24] developed a new double-layer catalyst cathode electrode. The double-layer catalyst cathode electrode reduced the effect of methanol crossover, and the active position of the Pt was enhanced. When compared to the performance of a traditional cathode, the MEA with a double-layer catalyst cathode showed a significant improvement. Kim et al. [25] also reported a method for grading the CCL. Methanol crossover has a negative influence on cathode performance, which can be mitigated by using a graded CCL, thus enhancing the utilization of the catalyst. Deng et al. [26] created a new trilaminar-catalytic layer structure for DMFCs. The new trilaminar-catalytic layer reduced methanol crossover and increased oxygen transfer. Recently, Jiang et al. [27] presented a gradient order-structured CCL and developed a 2D two-phase gradient model for DMFCs. Higher catalyst loading near the membrane was discovered to increase cell performance significantly. Similarly, the stratified gradient of the CL at the cathode could also enhance the DMFC’s performance. Therefore, the stratified gradient of the CL plays an active role in enhancing catalyst utilization.

The above researchers mostly concentrated on electrode optimization in the through-plane direction, while few articles have been reported on electrode optimization in the in-plane. For traditional electrodes, it is common knowledge that the catalyst is uniformly distributed in the in-plane. However, when a DMFC discharges, despite the catalyst’s uniform distribution, the concentration and reaction rate of reactants differ in-plane, resulting in a non-uniform current density distribution in the in-plane [28]. As a result, the catalyst utilization may be inconsistent, resulting in lower overall catalyst utilization. Until now, little research has been conducted on PEMFC catalyst in-plane gradient loading electrodes. Santis et al. [29] simulated a cathode gradient loading catalyst electrode. The loading on this electrode was lower at the inlet and higher near the outlet. At 0.5 V, the cell performance improved by 20%. To enhance catalyst utilization while reducing Pt consumption without losing cell performance, Prasanna et al. [30] prepared gradient electrodes with increasing amounts of catalyst in the cathode from the inlet to the outlet. This electrode increased the local reaction rate and enhanced the cell performance. Recently, Xing et al. [31] constructed a segmented fuel cell model with different Pt loadings and temperatures applied in the direction of gas flow. The goals of saving Pt use and improving cell performance and uniformity in current density were achieved. Chen et al. [32] researched the progress of CL
and inter-layer interface structures in the MEA for PEMFCs and found that the structure of the CL in the MEA is evolving from a traditional CL to a gradient and ordered CL. For PEMFCs, a gradient loading catalyst on the cathode electrode in-plane alone is sufficient. However, in DMFCs, the reaction kinetics of both MORs and ORRs is relatively slow. Therefore, the anode and cathode of DMFCs can have an in-plane gradient loading catalyst at the same time.

To reasonably reduce the amount of catalyst and enhance catalyst utilization in the in-plane, some studies on the distribution of reactants, products, and current density in fuel cells have been conducted [33]. Jung et al. [34] used a multi-dimensional DMFC model to complete a basic investigation of two-phase water and methanol transfer in a DMFC. It was found that the concentration distribution of methanol in the CL was higher at the inlet than at the outlet. Yang et al. [35] investigated the behavior of the CO$_2$ bubble in the anode flow field and discovered that CO$_2$ behavior varied with current density. Takanohashi et al. [36] created a novel visualization cell to view the partial pressure of oxygen and current density distributions within an operational PEFC. Studies have shown that the partial pressure of oxygen is higher at the inlet than at the outlet, and the higher the average current density is, the higher the current density is at the inlet than at the outlet. From the above distribution of reactants, products, and current density in the CL, it is clear that the concentration of reactants reduces and the product concentration increases in the direction of flow from the inlet to the outlet. Hence, we focus on a gradient loading catalyst in the in-plane.

In this work, we develop an in-plane gradient loading catalyst. The loading on both the anode and cathode catalysts is lower near the inlet and higher near the outlet. The depletion of reactants in the CL can be countered with this design so that the in-plane reaction rate area inside the CL can be uniform. The utilization of the catalyst is enhanced. To consider the effect of gradient loading catalyst electrodes on the electrochemical properties of DMFCs, single-cell performance was evaluated and compared.

2. Materials and Methods

2.1. Catalyst and Electrode Preparation

Anode catalyst ink was made by combining 60 wt.% PtRu/C (Hesen, Shanghai, China) and isopropyl alcohol (Baker Analyzed HPLC Reagent) and Nafion solution (EW1100, 5 wt.%, DuPont Inc., Newark, DE, USA). To make cathode catalyst ink, 40 wt.% Pt/C (Hesen, China) was mixed with isopropyl alcohol (Baker Analyzed HPLC Reagent) and Nafion (EW1100, 5 wt.%, DuPont Inc.) solution. The catalyst ink was sonicated for 1 h. Finally, the catalyst ink was sprayed on a treated diffusion layer electrode with an area of 4 cm$^2$.

To prepare MEAs with the gradient loading catalyst electrode, different amounts of catalyst ink were sprayed. When using an average Pt loading of 2 mg cm$^{-2}$, 1 mg cm$^{-2}$ of Pt was first loaded over the whole area, then 1/4 part of the Pt loading of 1 mg cm$^{-2}$ was covered with a piece of tarpaper and the rest of the area was sprayed with 1 mg cm$^{-2}$ Pt loading. The last 3/4 part was then covered with a piece of tarpaper and the remaining 0.5 cm for the exit part of the area was sprayed with 1 mg cm$^{-2}$ Pt loading, and anode electrodes with gradient loading of catalyst were obtained. The cathode with the gradient loading catalyst was obtained by the same method as for the anode.

2.2. Single Cell Assembly

The prepared anode electrode, cathode electrode, and treated Nafion117 membrane were combined to form an MEA [37]. The MEA was sandwiched between stainless steel serpentine flow field plates. The gradient electrodes corresponded well to the flow channel inlet and outlet and had the same torque to assemble the single cell. Methanol was delivered to the anode side with a peristaltic pump (BT100-1F, Longer), and a flow meter was used to regulate the flow of oxygen into the cathode side. During the experiments, the single cell was heated with a heater, and the working temperature was monitored with a thermocouple.
2.3. Single-Cell Test

In this study, the Arbin BT-I battery tester (Arbin Instrument Inc., College Station, TX, USA) was used in connection with a computer to measure cell function. During the performance evaluation, methanol was delivered to a single cell anode at a rate of 2 mL min⁻¹, while oxygen was fed to the cathode at a rate of 0.2 NL min⁻¹.

2.4. Electrode Characterization

The cross-sectional thicknesses of gradient electrodes with different catalyst loadings were observed by scanning electron microscopy (SEM, JEOL S-7800F, Tokyo, Japan). Detection of the electrical impedance spectrum (EIS) of a 0.3-volt DMFC was realized by using an electrochemical workstation (CHI600, Chenhua Company, Shanghai, China) [38]. During the EIS test, the anode received 2 M methanol while the cathode received dry oxygen, both at 60 °C.

3. Results and Discussion

To analyze the influence of gradient loading catalyst electrodes on DMFC performance, three distinct types of MEAs were developed. Figure 1 shows the types of catalyst loading. The average Pt loading of MEA-I and MEA-II was 2 mg cm⁻². In the case of MEA-II, the Pt loading gradually increased from 1 to 3 mg cm⁻² from the inlet to the outlet. The first part had a Pt loading of 1 mg cm⁻² at the inlet, representing 1/4 of the total area. The second part had a regional Pt loading of 2 mg cm⁻², representing 1/2 of the total area. The third part had a regional Pt loading of 3 mg cm⁻² at the outlet, representing 1/4 of the total area. The average Pt loading of MEA-III was 1.5 mg cm⁻², with the Pt loading gradually increasing from 1 to 2 mg cm⁻² from the inlet to the outlet.

As shown in Figure 2, the Pt loading was confirmed by SEM images of the MEAs, and the thickness of the CL was proportional to the catalyst loading.

![Figure 1](image-url)  
**Figure 1.** Catalyst loading types in both cathode and anode. I is a uniform electrode with an average Pt loading of 2 mg cm⁻², II is a gradient electrode with an average Pt loading of 2 mg cm⁻², III is a gradient electrode with an average Pt loading of 1.5 mg cm⁻².
To investigate the impact of gradient loading catalyst electrodes on the DMFCs’ performance, the uniform and gradient electrodes were tested at different temperatures. Figure 3 shows the polarization and power density curves for MEA-I, MEA-II, and MEA-III at 40 °C. Other than that, the operating conditions remained the same. As shown in Figure 3 under the conditions of a methanol concentration of 2 M, the peak current densities of...
MEA-I, MEA-II, and MEA-III were 109.9, 129.6, and 89.7 mA cm$^{-2}$, and the maximum power densities were 14.2, 15.9, and 11.5 mW cm$^{-2}$, respectively. Compared with MEA-I, the peak current density of MEA-II increased by 17.9%, and the maximum power density increased by 12.0%, while compared with MEA-I and MEA-III, the peak current density and maximum power density decreased by 18.4% and 18.9%, respectively. Figure 4 shows the voltages corresponding to each cell at different current densities. It can be seen that at a current density of 50 mA cm$^{-2}$, the voltages of MEA-I, MEA-II, and MEA-III were 0.26, 0.27, and 0.23 V, respectively. From 50 to 80 mA cm$^{-2}$, the voltages dropped to 0.17, 0.20, and 0.12 V, respectively. In contrast, the MEA-II electrode had the smallest voltage drop rate. When the test temperature was 60 °C, all other operating conditions were the same. Figure 5 shows the polarization and power density curves for the three types of electrodes. As shown in Figures 5 and 6, MEA-I, MEA-II, and MEA-III achieved peak current densities of 159.8, 199.8, and 139.8 mA cm$^{-2}$ and maximum power densities of 25.8, 30.9, and 17.0 mW cm$^{-2}$, respectively. Compared with MEA-I, MEA-II’s peak current density and maximum power density increased by 25.0% and 19.6%, respectively. Meanwhile, compared with MEA-I, MEA-III’s peak current density and maximum power density decreased by 12.5% and 34.0%, respectively. In the region of medium current density, which was dominated by ohmic loss, for MEA-I and MEA-II the rate of voltage decrease was comparable, from 0.36 and 0.38 V to 0.25 and 0.28 V, respectively. In the region of high current density, MEA-I’s voltage dropped faster than those of MEA-II and MEA-III. In the high current density region, the voltage of MEA-I dropped faster than those of MEA-II and MEA-III, and only MEA-II remained over 0.20 V, showing excellent performance. The reason is that due to the consumption of fuel, the reactant concentration near the outlet is lower than that of the inlet region, while the larger catalyst loading increases the local electrochemical reaction rate, making the overall overpotential become smaller as shown in MEA-II and MEA-III.

Therefore, it can be concluded that at the same catalyst loading, at both 40 and 60 °C, the gradient loading catalyst shows better performance; especially at a high current density, the advantage of the gradient loading catalyst is more obvious. While decreasing the catalyst loading, the electrochemical reaction of the cell using the gradient loading catalyst decreased due to lower less catalyst loading, so the performance of the cell was poorer. At a high current density, however, this rate of performance decline was mitigated.

![Figure 3](image_url)

**Figure 3.** Comparison of the performance of DMFCs with different catalyst loading electrodes. (a) Polarization curves; (b) power density curves.
Figure 4. Voltage values corresponding to several current density points in the above polarization curves at 40 °C.

Figure 5. Comparison of the performance of DMFCs with different catalyst loading electrodes. (a) Polarization curves; (b) power density curves.

In order to interpret the polarization behaviors of differently structured electrodes, the electrical impedance spectra of MEA-I, MEA-II, and MEA-III at 0.3 V are shown in Figure 7. The ohmic resistance (R1) is the point where the high-frequency region intersects the X-axis. It is composed of the contact resistance between each interface in the whole electrode [39]. The MEA-I, MEA-II, and MEA-III electrodes’ R1 values were 0.18, 0.32, and 0.81 Ω cm², respectively. The MEA-II electrode’s R1 was slightly larger than that of MEA-I, probably due to the non-uniform thickness of the CL, which thus increased the contact resistance. The length of the intersection of tall and low frequencies on the X-axis can be credited to the whole charge transfer resistance, called the electrode reaction resistance (R2) [40]. MEA-I, MEA-II, and MEA-III exhibited R2 values of 3.09, 2.42, and 4.57 Ω cm², respectively. This relates to their performance; the lower the electrode response resistance is, the higher the cell performance is. The value for MEA-II is probably due to the lower
reaction rate at the anode inlet; the CO₂ produced will not easily form a gas plug to adhere to the catalyst surface, which is conducive to the contact of methanol with the catalyst and reduces the reaction resistance. At the same time, at the cathode, liquid water will not accumulate along the direction of gas flow, which is conducive to gas transmission and reduces transfer resistance. Therefore, the use of gradient loading catalyst electrodes can decrease electrode response resistance.

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**Figure 6.** Voltage values corresponding to several current density points in the above polarization curves at 60 °C.

The stability test of single DMFCs is shown in Figure 8, and the curves were obtained with a continuous discharge procedure under 100 mA cm⁻² at 60 °C for 10 h. The voltage of both DMFCs slowly decreased from the beginning of the discharge test. The voltage of the gradient loading catalyst electrodes decreased more gently, while the voltage of the uniform loading catalyst electrodes decreased unsteadily. For the DMFC with uniformly
loading catalyst electrodes, the average voltage was 255 mV at the initial time point and was 180 mV after 10 h of the stability test; the decay rate of the cell voltage was 7.5 mV h\(^{-1}\), and the cell voltage decreased by 29.4%. For the DMFC with gradient loading catalyst electrodes, the average voltage was 293 mV at the initial starting time and was 233 mV after 10 h of the stability test; the decay rate of the cell voltage was 6.0 mV h\(^{-1}\), and the cell voltage decreased by 20.5%. Therefore, compared with the DMFC with the uniformly loading catalyst electrodes, the DMFC with the gradient loading catalyst electrodes has an advantage in terms of stability during long-term operation.

Figure 7. Impedance spectra at 0.3 V for DMFCs with different MEAs (methanol concentration 2 M, temperature 60 °C).

Figure 8. Stability testing curves of DMFCs. Testing condition of the DMFCs: methanol concentration, 2 M; temperature, 60 °C; discharging current density, 100 mA cm\(^{-2}\).

4. Conclusions

This work shows that using a gradient loading catalyst MEA can effectively increase the performance of a DMFC. The MEA includes both cathode and anode catalysts with gradient loading. At the in-plane, the loading on both the anode and cathode catalysts is lower near the inlet and higher near the outlet. With an average Pt loading of 2 mg cm\(^{-2}\), the gradient loading catalyst MEA performs better than the uniform loading catalyst MEA; the advantage of gradient loading catalyst electrodes is more obvious, especially at high current density. Based on this study, the gradient loading catalyst electrodes not only enhance cell performance but also improve catalyst utilization. In addition, the stability of the gradient loading catalyst MEA was slightly better after 10 h continuous discharging. The proposed method provides ideas for reducing the cost and increasing the lifetime of fuel cells.

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