ANODE FLOW FIELDS STRUCTURES OF MICRO DIRECT METHANOL FUEL CELLS

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Abstract:
To improve the low mass transfer efficiency and poor performance of micro direct methanol fuel cells (µDMFCs), a detailed study on the micro direct methanol fuel cell flow field structure is developed in this paper. Since the flow field structure plays an important role in increasing the performance of cells. Silicon-based self-breathing µDMFCs with the grid, parallel, single serpentine, double serpentine and tapered single serpentine anode flow fields are fabricated using MEMS technology. First of all, compared to the grid and parallel and double serpentine structures, single serpentine has been proved to perform a best result. However, Owing to the mass transport shadow region of an under-rib diffusion layer from the channel to the electrode, it results in the fall of methanol transport efficiency. A new tapered single serpentine has been fabricated and tested to prove its superiority. The results show that the cell performance with tapered single serpentine flow field is better than conventional single serpentine. And the maximum output power density is 15.41mW/cm² with the increment of 35%, which contributed to further development of portable micro power sources systems.

Keywords: µDMFC, flow field, tapered single serpentine

INTRODUCTION
In recent years, the use of portable and mobile electronic devices, such as laptops or cellular phones, has spread rapidly due to remarkable progress in technology and the information demand of our society. Therefore, the need for more compact power sources with higher power density has increased rapidly. Fuel cells employ hydrogen as fuel to generate power and meet portable requirements. They possess high efficiency and are clean and quiet. Applied electrochemical and new energy source developments have also focused on fuel cells. In particular, micro-electro-mechanical systems (MEMS) technology based on micro direct methanol fuel cells (µDMFCs) has been recognized as a leading candidate to supply power to portable electronics. Considering the potential of µDMFC to overturn the use of conventional power sources, many researchers have paid increasing attention to various aspects concerning µDMFC technology [1-4]. Above all, the anode flow field configuration is a crucial factor for µDMFC applications [5, 6].

Basically, a µDMFC is composed of two current collectors (the anode and the cathode) with flow fields sandwiched around a membrane electrode assembly (MEA). In the oxidation process at the anode and deoxidization process at the cathode, the electric power is exported continually [7]. The anode current collector not only supplies a passage for the transport of reactants (methanol) and resultants (CO₂), but it also provides structural support for the weak MEA and collects current. At present, studies of anode flow fields mainly focus on parameter optimizations and new configuration designs. Yang et al. [8] investigated the effects of different anode flow fields and parameters on the performance of DMFCs, and the experiments indicated that the single serpentine flow fields performed better than parallel ones. Similarly, Zhao et al. [6] fabricated a µDMFC with an active 1.0 cm × 1.0 cm area to study the effects of flow field structures on cell performance and reached the same conclusions. Furthermore, channel depths of the serpentine flow field were optimized experimentally. Oliveira et al. [5] studied the effects of three different serpentine anode flow fields (single serpentine (SFF), multi-serpentine (MSFF) and mixed parallel and serpentine (MFF) on the performance of DMFCs, and the experimental results showed that the use of MSFF or MFF as anode flow fields yielded a better performance. Moreover, new anode flow fields were also presented to improve the performance of DMFCs [5, 7, 10].

First of all, the structures of convention flow fields are showed in Fig. 1. Single serpentine flow fields have a better performance than grid, parallel structures and double serpentine, are generally applied in the anode configurations of efficiency to reduce the cell performance. In fact, the pressure difference between adjacent flow channels of the ribs determines the convection and diffusion of the methanol molecules in the electrode. If the transport velocity of molecules increases with increment of the pressure difference, the methanol transport efficiency to the catalyst layer is improved and the resultant (CO₂) is also exhausted from the flow channels more quickly. Secondly, based on the above considerations, we presented a new tapered single serpentine flow field for the anode of a self-breathing µDMFC, as illustrated in Fig. 2(b).Fig. 2(a) and (b) present the different structure between
conventional single serpentine and new tapered single serpentine. The experimental results showed that the pressure difference could be enhanced effectively with the same channel areas and channel length of conventional single serpentine flow fields. Using silicon-based MEMS technology, the self-breathing μDMFC was fabricated and tested to prove the superiority of this new flow field.

A 5-layered MEA with an active area of 0.8 cm × 0.8 cm fabricated by the catalyst coated membrane (CCM) method was employed for the silicon-based μDMFCs. The hydrophilic catalyst layer was prepared utilizing the decal transfer method. First, the Nafton@117 membrane (DuPont TM, 175 μm) was ion-exchanged to its Na⁺ form by boiling in 0.5 M NaOH solution at 80 °C for 1 h and then in deionized water at 80 °C for 1 h. The confected catalyst ink (Pt-Ru/Pt black, 5 wt.% solubilized Nafton®, isopropanol, alcohol, glycerol, and deionized water) was uniformly sprayed onto the poly tetra fluoro ethylene (PTFE) sheets using a spray gun, with the catalyst loadings of 4.0 mg cm⁻² (anode) and 2.0 mg cm⁻² (cathode). The thin films were then transferred from the PTFE sheets to both sides of the membrane by hot pressing at 160 °C and 5 MPa for 90 s, thus forming the CCM. Afterward, carbon paper (TGPH-090, Toray, Inc.) was prepared with a hydrophobic (10 wt.% PTFE for the anode and 30 wt.% PTFE for the cathode) and pore-forming (NH₄HCO₃) pretreatment to form the gas diffusion layer (GDL). In the end, the 5-layered MEA was achieved with two GDLs hot pressed on both sides of the CCM at 130 °C and 4 MPa for 120 s.

Utilizing the polydimethylsiloxane (PDMS) packaging process, the MEA was sandwiched between the anode and cathode current collectors to realize a self-breathing μDMFC with an active area of 0.8 cm × 0.8 cm. For performance evaluation of the μDMFCs, an electronic load (N3300A&N3302A, Agilent Technologies) was employed to measure the polarization curves and power density curves.

**FABRICATION AND ASSEMBLY**

The anode current collectors were fabricated using normal silicon-based MEMS technology. Two anode flow fields had the same active area (0.8 cm × 0.8 cm), the same open ratio (47.3%) and the same total length of the single channel (63.50 mm). Two 480±10 μm silicon wafers with <100> crystal orientation were employed as anode current collectors, including grid, parallel, conventional single serpentine and tapered single serpentine. First, a 0.8-μm-thick Si₃N₄ layer was deposited on the Si wafers using low pressure chemical vapor deposition (LPCVD). To achieve the selected etching, photolithography was applied to pattern microchannels on the Si₃N₄ layer. The serpentine channels were etched with the depth of 240 μm using an anisotropic etching process, which was performed using a 40% KOH solution at 40°C. Considering their application for portability, the cathode current collectors with common perforated structure were employed with the same active areas. To fashion the self-breathing openings, circular holes with a radius of 0.3 mm were inserted on the silicon wafer using a laser process. To collect current and minimize contact resistance between the MEA and the silicon wafer, a Ti/Au (0.05 μm /1.0 μm) layer was sputtered on the current collectors.

**RESULT AND DISCUSSION**

The working conditions of the silicon-based self-breathing μDMFCs were room temperature, fed with 1.0 M methanol solution with the flow rate of 1.0 mL /min. It was mainly considered that the different anode flow field patterns had great effects on the cell performance using the same perforated cathode structures. First of all, silicon-based self-breathing μDMFCs with the gird, parallel, single serpentine and double serpentine have been studied. Then, we will compare the performance of conventional single serpentine to that of tapered single serpentine.

The performances of the μDMFCs with different anode flow field structures were shown in the Fig. 3. It could be seen that the cell performance using the single serpentine flow field was the best with the maximum power density of 11.39 mW/cm². On the contrary, the maximum power density of the cell with the grid flow field is only 6.23 mW/cm². The good and bad of the cell mainly came from the differences of flow field patterns as the four flow fields had the same channel areas and channel length of the single channel (63.50 mm). Two 480±10 μm silicon wafers with <100> crystal orientation were employed with the same active areas. Considering their application for portability, the μDMFC was fabricated and tested to prove the superiority of this new flow field.

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also the CO\textsubscript{2} could be ensured to exclude from the anode more effectively. So the cell with the single-serpentine flow field could reach the best performance than the other three. Moreover, it was illustrated that the concentration polarizations for grid and parallel flow fields appeared earlier than that for the others. It was resulted from the flow dead zones in two anode flow fields. More resultants (CO\textsubscript{2}) were produced with increment of the current density. So some CO\textsubscript{2} bubbles might enter the dead zones through the diffusion layer not to be excluded out hardly. As a result, the anode effective mass transport would be reduced to intensify the concentration polarization.

Fig. 3 The effect of the anode flow field structures on the \(\mu\)DMFC performance.

Fig. 4 compares the performances of \(\mu\)DMFCs with single-serpentine flow fields for the different opening ratios. It could be seen that the cell performances were reduced sequenctly according to 47.3\%, 60.6\%, 73.0\% and 29.1\%. The correspond maximum power densities were 16.83, 15.13, 11.39 and 10.83 mW/cm\textsuperscript{2}, respectively. It seemed a little different from the simulation results not to be explained. In fact, the opening ratio mainly depends on the flow channel widths if the flow channel lengths is determined. The flow channels with the opening ratio of 47.3\% were wider than that with 29.1\%. On one hand, the wider flow channels can increase the contact areas between the flow channel and the diffusion layer so that the anode mass transport efficiency is improved. On the other hand, it would reduce the probability that the CO\textsubscript{2} bubbles block the flow channel, and it would enhance the flow stability of methanol solutions in the anode. The flow channels with the opening ratio of 47.3\% is narrower than those with 60.6\% and 73.0\%, however, the supporting ridge widths were increased. So the contact resistance between the current collector and the diffusion layer was reduced. On the other hand, it could weaken the methanol crossover due to the decline in the contact areas between the methanol and the diffusion layer. In a word, the opening ratio was a complex but important parameter. It could balance the influences of the above referred facts only as the optimum value was achieved. According to the test results, the optimum opening ratio is 47.3\% in this work.

As shown in Fig. 5, it illustrates that the different flow channel lengths had effects on the performance of the \(\mu\)DMFCs with the same opening ratios. It could be seen that the flow channel length obviously influenced the cell performances. The peak power density is 16.83 mW/cm\textsuperscript{2} with the length of 63.50 mm. The cell performances would drop no matter what the lengths increases or decreases.

Fig. 5 The effect of the channel lengths of the anode flow field on the \(\mu\)DMFC performance.

Furthermore, in order to find a better structure, conventional single serpentine and new tapered single serpentine flow fields were also studied and compared. For the new tapered single serpentine flow field, the methanol content on the surface could be obviously increased and distributed more uniformly. Thus, the cell performance could be enhanced, and the concentration polarization could be avoided to a certain extent.

To ensure that the mass transport limitation was caused by the transport of methanol at the anode in different serpentine flow channels only, all the tests in this work were operated synchronously using the same conditions, including the cathode structure and environment. From the measured polarization curves illustrated in Fig. 6, the open circuit voltage (521.1 mV) of the \(\mu\)DMFC with the tapered single serpentine flow field was a little lower than that of its conventional counterpart (535.7 mV). However, the new tapered flow field (15.4 mW/cm\textsuperscript{2}) yielded a substantial (35.3\%) increase in peak power density over the conventional design.
μDMFC with the single serpentine flow field yielded a maximum power density of 16.83 mW/cm² with 1 M methanol concentration and 1 ml/min flow rates at room temperature. For the single serpentine flow channel, the opening ratio of 47.3% and the flow channel length of 63.50 mm are optimum parameters. And then, a self-breathing μDMFC with a new tapered single serpentine anode flow field and other structure were presented and compared. Compared with its conventional counterpart, the new flow field was able to enhance the pressure difference between any of the adjacent flow channels and thus improve the mass transport efficiency and the exhaust resultant rate utilizing the simulation analysis. Due to the increase in methanol mass transport efficiency from the channel to the electrode, the μDMFC with the new single serpentine flow field yielded a maximum power density of 15.4 mW/cm² at room temperature. From the results obtained in this work, it can be concluded that the tapered single serpentine flow field demonstrated in the μDMFC is also applicable to the greater DMFCs or the PEMFCs running on the anode.

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