DEVELOPMENT AND CHARACTERIZATION OF A NOVEL AIR-BREATHING MICRO DIRECT METHANOL FUEL CELL STACK

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Abstract: In this paper, a novel air-breathing micro direct methanol fuel cell (μDMFC) stack with four different anode feeding patterns was designed, fabricated, and tested. With the help of the micro stamping technology, the current collectors of each individual cell were microfabricated of the stainless steel with a thickness of 300μm. The stainless steel mesh (SSM) and TiN layer were employed to decrease the internal resistance and avoid the electrochemical corrosion. Experiment results show the μDMFC stack with pattern B generated the highest maximum power output of about 141mW, and the phenomena of polarity reversal was also studied.

Keywords: air-breathing; μDMFC stack; micro stamping; current collector; polarity reversal

INTRODUCTION
Possessing a lot of unique advantages, such as high power density, low emission, high energy conversion and ease in managing the fuels, micro direct methanol fuel cells (μDMFCs) have been considered as the most promising candidate for the conventional micro power sources of cell phones, laptop computers, PDAs, RF radios and other mobile devices. Over the past few years, numerous human and material resources have been invested to study almost every aspect of the μDMFC. Basically, the structure of a μDMFC consists of two current collectors (anode and cathode) with flow fields, and a membrane electrode assembly (MEA) in between. In the electrochemical process, the methanol and oxygen make an oxidation-reduction reaction together and generate carbon dioxide and water, which is described by:

\[ \text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \] (1)

At present, most μDMFCs were developed based on MEMS technology. Jiang et al.\cite{1} reported an air-breathing μDMFC microfabricated on silicon substrates, with a maximum power density of 2.31mW/cm². Lu et al.\cite{2} developed a 1.625cm² μDMFC fabricated on thin stainless steel plates by photochemical etching technology. Cha et al.\cite{3} fabricated an all polymer μDMFC using UV-sensitive resist, the maximum power density could reach 8mW/cm² at 37mA/cm². To date, there are three major types of materials being investigated for the current collectors, including silicon, metal and polymer.\cite{4}. Comparing to the other materials, metal has much higher electronic conductivity and mechanical strength for assembly, it can also offer a high potential to reduce fabrication difficulty and costs. However, most of the previous research concerning metallic μDMFCs were focus on individual cells. To satisfy the application requirements of various mobile devices, an integrated μDMFC system with high voltage and power output is urgently needed. Therefore, the development of the metallic μDMFC stack is imperative.

In this paper, a metallic 10-cell μDMFC stack with four different anode feeding patterns was designed, fabricated and tested. The current collectors were fabricated using micro stamping technology, which was a fast-turnaround and low-cost method for metal machining. The performance of both the individual μDMFC and the stack were tested and compared, and the effect of different anode feeding patterns on the μDMFC stack was also investigated.

DESIGN AND FABRICATION
The basic structure of the 10-cell air-breathing μDMFC stack which is connected in serial-connection is illustrated in Fig. 1. The stack is composed of one distribution plate, ten individual cells, two anode fixer plates, two cathode fixer plates and gasket layers.

![Fig. 1: Configuration of the μDMFC stack.](image_url)

Current Collector
The current collector is the key component of the μDMFC, which not only provide the flow field for the
reactants transport, but also offer the structural sustainment for the weak MEA and collect current. In this study, both the anode and cathode current collector have the same configuration with two portions, the flow field area and the interconnection area, which are detailed in Fig. 2. The flow field area plays the role of transporting reactants to the MEA, while the interconnection area acts as the electrical connector for the adjacent two μDMFCs. In order to enhance the electronic conductivity and mechanical strength for assembly, stainless steel plate with a thickness of 300 μm was adopted as the substrate of the current collector, and the flow field area was formed by the micro stamping technology. To avoid the electrochemical corrosion and cover the cracks caused by the stamping process, a 0.5 μm-thick TiN layer was deposited onto the surface of the stamped plate, the comparison is shown in Fig. 3. Fig. 4 shows the picture of the TiN-plated cathode current collectors with the active area of 0.64 cm², the airflow holes were manufactured by laser beam.

**Membrane Electrode Assembly**

A piece of catalyst coated membrane (CCM) which was composed of a Nafion117 membrane, an anode catalyst layer of Pt-Ru back (4.0 mg/cm²) and a cathode catalyst layer of Pt back (2.0 mg/cm²) was employed in this work. The CCM was sandwiched between two traditional carbon cloth, and hot pressed under the condition of 135°C, 5 Mpa for 180s to form the MEA. And then, stainless steel mesh with a thickness of 100 μm were also hot pressed on both sides of the MEA to reduce the connect resistance.

**Distribution Plate**

With the designed channels and holes, the distribution plate could provide the methanol to each unit cell in four different feeding patterns, which is illustrated in Fig. 5. The structure was micromachined on a 5 mm-thick polymethyl methacrylate (PMMA) plate, and cut by carbon dioxide laser. Considering the uniform distribution of fuels and convenient removal of products, channels were fabricated with 2 mm width and 1 mm depth. In addition, two gasket layers made of silicon rubber were employed between the distribution plate and the anode fixer plates to keep the stack from liquid leakage and sustain the other plates for package.

**Fig. 2: Geometry of the current collector.**

**Fig. 3: SEM photographs of the surface of the current collectors: (a) without the TiN layer, and (b) with the TiN layer.**

**Fig. 4: Picture of the TiN-plated cathode current collectors.**

**Fig. 5: Schematics of four anode feeding patterns: (a) pattern A, (b) pattern B, (c) pattern C, and (d) pattern D.**
**Fixer Plate**

Anode fixer plate and cathode fixer plate were both made of 2mm-thick PMMA plates. Each anode fixer plate had five micromachined chambers to mount the anode current collectors, and five windows were cut on each cathode fixer plate by carbon dioxide laser to make the cathode open to the air.

**ASSEMBLY**

Fig. 6 shows the assembly drawing of the μDMFC stack. First, two current collectors (anode and cathode) with a MEA in between were pressed for 8h, and epoxy resin was used around the edges of the MEA and current collectors as a sealant, thus an individual μDMFC was formed. And then, every five cells were mounted into the chambers of each anode fixer plate, epoxy resin was also used to fill in the void space to fasten the cells and prevent the liquid leakage. Third, the individual cells were electrical connected by bolts and nuts one by one, as sketched in Fig. 1. Finally, the anode fixer plates with ten unit cells, the distribution plate and the cathode fixer plates were clamped by twelve M2 screw joints. The photograph of the assembled stack is shown in Fig. 7, the total size is about 95mm × 15mm × 23mm.

![Assembly drawing of the μDMFC stack.](image)

**RESULTS AND DISCUSSION**

Each MEA of the individual cells was activated before the assembly. First, to activate the PEM, fed 90°C hot deionized water to the anode side and saturated oxygen (80°C, ambient pressure) to the cathode side, and maintained the cell at 80°C for 1h. Second, with the cell maintained at 0.2V and 80°C for 4h, fed 2M methanol with a flow rate of 5mL/min to the anode and saturated oxygen with a flow rate of 720mL/min at 25psig. Thus, the MEA had been activated.

The performance of an individual cell at room temperature is described in Fig. 8, and 1M dilute methanol solutions was used with a flow rate of 1mL/min. The open circuit voltage was 0.622V, and the maximum power density could reach to 24.2mW/cm² at the current density of 137.5mA/cm².

![Performance curves of the individual cell using 1M dilute methanol solutions with a flow rate of 1ml min⁻¹ at room temperature.](image)

Fig. 9 shows the performance of μDMFC stack that operated at different anode feeding patterns from pattern A to D and room temperature, and with 1M dilute methanol solutions fed at 2mL/min. It can be seen from the figure that anode feeding patterns have a significant influence on the stack performance, including the maximum power density and current density. Comparing to the other patterns, pattern B led to the highest maximum power output of the stack of about 141mW at the same flow rate, while the maximum power density was 22.03mW/cm² which was 91.03% of that of an individual cell. In other words, the stack with pattern B could perform better at the same consumption of methanol. The above results indicate that there exists an optimal anode feeding pattern for the μDMFC stack, this performance variation behavior can be explained as follows. The methanol flow rate of each individual cell with pattern B was 0.4mL/min, which was doubled the methanol flow rate (0.2mL/min) of each individual cell with pattern A. Previous study has shown that the cell performance with 0.4mL/min is better than the cell performance with 0.2mL/min. Meanwhile, because the active area was only 0.64cm²,
methanol concentrations of every two cells with one feeding channel of the stack with pattern B were almost the same, so the stack performance with pattern B was much better. On the other hand, although the distributed methanol flow rate to each individual cell was much higher in the stack with pattern C or D, the methanol concentrations of the individual cells were quite inhomogeneous, which could reduce the stack performance. In addition, we also found that the performance of the stack with pattern D had a large decline at high current densities. It was mainly caused by the phenomenon of polarity reversal, which often happened in the μDMFC stack because of the insufficiency of methanol. Therefore, we also tested the open circuit voltage of each individual cell of the stack with pattern D after the operation with 1M dilute methanol solutions at 2mL/min, as shown in Fig. 10. As a result, the open circuit voltages of cell 5 to 10 all declined to different extents, the open circuit voltage of cell 10 was almost 0.1V especially. It indicated that the MEAs of cell 5 to 10 were devastated by the stack polarity reversal, which could validate our foregoing analysis.

Fig. 9: Performance curves of the stack with different anode feeding patterns.

Fig. 10: Open circuit voltage of each unit cell of the stack with pattern D after the operation with 1M dilute methanol solutions at 2mL/min

CONCLUSION
A novel air-breathing μDMFC stack consists of ten individual cells has been developed. Micro stamping technology was adopted to manufacture both the anode and cathode current collectors on 300μm-thick stainless steel plates, and TiN layer was deposited onto the surface of the current collectors to prevent electrochemical corrosion. By employing the distribution plates with different structures, four anode feeding patterns to each individual cell were achieved. The assembly method by using epoxy resin and PMMA fixer plates are employed to keep the stack from leakage and mount the individual cells. Experiment results show that the air-breathing stack with pattern B generated the highest maximum power output of about 141mW at the same operating conditions, while the corresponding maximum power density was 22.03mW/cm² which was 91.03% of that of an individual cell. This performance variation behavior suggests that there exists an optimal anode feeding pattern for the μDMFC stack performance, which is significative for the future applications.

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REFERENCES