

## AN AIR-BREATHING SILICON-BASED MICRO DIRECT METHANOL FUEL CELL STACK

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**Abstract:** This paper presents an air-breathing silicon-based micro direct methanol fuel cell ( $\mu$ DMFC) stack featured by an anode plate shared with two air-breathing cathode plates. Micro fabrication technology, including double-side lithography, is used to fabricate both anode and cathode silicon plates on the same wafer simultaneously. Experimental results show that the  $\mu$ DMFC stack achieves a power density of  $3.85\text{mW}/\text{cm}^2$  which is almost double that of the single cell, and an open-circuit potential of  $0.45\text{V}$ .

**Key words:**  $\mu$ DMFC stack, Air-breathing, MEMS, Micro power source

### 1. INTRODUCTION

The direct methanol fuel cell (DMFC), a galvanic device that converts the chemical energy of the methanol directly into electrical energy, has been widely considered as the next generation power source in place of conventional batteries because of its higher energy density and lower pollution exhaust [1]. In particular,  $\mu$ DMFC is a leading candidate for portable power device of the future due to its various advantages, such as large energy density, inexpensive fuel, recharge-free, easiness to carry and ability to drive at lower temperature than the other fuel cells [2]. A single DMFC generally consists of two plates, anode and cathode, sandwiched around a membrane electrode assembly (MEA). During the operation, methanol solution is fed to the anode, and protons and electrons are generated by the catalyzed reaction of the methanol and the water. The protons directly travel through the proton exchange membrane (PEM) to the cathode whereas the electrons flow to the cathode through external circuit, forming the electrical current. In the cathode, oxygen reacts with the protons and the electrons, and water is generated.

The most promising application of  $\mu$ DMFCs is to power portable electronic devices and low-power System on a Chip (SOC). In order to meet these requirements and reduce the overall cost and parasitic power loss, external pumps or other ancillary devices should be simplified or eliminated without great performance degradation. Some researchers have developed fully passive  $\mu$ DMFCs in which both the liquid methanol pump and cathode gas pump have been eliminated [3]. The access of methanol to the MEA depends on diffusion only and oxygen is directly taken from the atmosphere in those  $\mu$ DMFCs. Considering the significant effects of methanol pump

on methanol transport, removal of  $\text{CO}_2$ , and lifecycle, the air-breathing  $\mu$ DMFC, "partly passive  $\mu$ DMFC", i.e. the cathode gas pump is eliminated but the methanol pump is reserved [4], is adopted in this work.

Though great progress has been made in  $\mu$ DMFCs[5], the output power density is still not high enough to meet the requirements of practical applications. The  $\mu$ DMFC achieves its maximum power density when the voltage is around  $0.2\text{-}0.4\text{V}$  and the output current density is tens  $\text{mA}/\text{cm}^2$ , much lower than the requirement of common electronic devices. In one word, it is a critical issue to improve the output to satisfy the voltage or current requirements of most portable electronic applications. The  $\mu$ DMFC stack is much suitable for portable electronics because of the safety and low-cost issue compared with other methods like operation at high temperature. The micro fuel cell array with planar structure was reported in literature [6], with the advantages of easy electrical interconnection and assembly. However, this structure takes up large area and may cause lateral ionic conduction due to the common PEM.

This paper reports the design, fabrication and characterization of an air-breathing  $\mu$ DMFC stack which consists of two air-breathing  $\mu$ DMFCs piled up together. Both the anode and cathode silicon plates are fabricated on a same wafer simultaneously by micro fabrication technology. The whole air-breathing  $\mu$ DMFC stack is assembled with PDMS and PMMA (PolymethylMethacrylate) holders. Experimental results show that the  $\mu$ DMFC stack achieves a much larger power density than a single cell.

### 2. STRUCTURE DESIGN

#### 2.1 Stack Structure

The air-breathing  $\mu$ DMFC stack contains two cells, as shown in Fig.1, consisting of one anode plate, two cathode plates, and two MEAs placed between alternately. Compared to the planar array structure, the stacked structure needs much smaller area which is especially significant for micro fuel cell because the packaging is generally much thicker than the miniature fuel cell itself. Since the packaging takes up much larger room than the MEAs and plates,  $\mu$ DMFC stack of which the packaging is almost as large as that of one  $\mu$ DMFC can efficiently shrink the entire volume. Besides, parasitic lateral ionic conduction is avoided because the MEAs are totally separated.

As shown in Fig.1, the fuel transport in the stack is arranged in parallel, i.e., the reactants flow through the two cells simultaneously. The parallel fuel supply mode has the advantages of low flow resistance and easy operation. Serpentine flow channels are employed to increase the flow rate and improve the product removal of parallel fuel supply. Parallel electrical connection is adopted in this design, although the stacked structure can also be applied for the series electrical connection. The two sides of the anode plate should be insulated with insulation layers like  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  in this case.

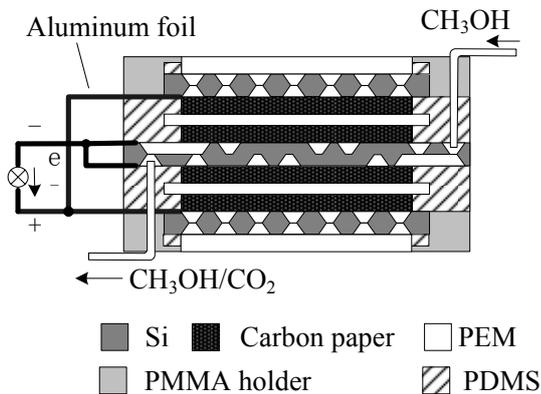


Fig.1 Schematic of the air-breathing  $\mu$ DMFC stack

### 2.2 Anode Plate

Fig.2 illustrates the structure of the shared anode plate. The serpentine flow channels on both sides of anode plate are designed to be parallel placed [7]. The flow patterns are connected at two ends via two thru-etched holes. The leading channels, which allow the methanol solution flow to the effective channel area contacting to the MEAs, are at one end of the flow channels of both sides. Actually the leading channels act as the extension of the feeding tubes because the flow channels of the anode are totally covered by the cathode plates. In the anode, the methanol solution flows into the  $\mu$ DMFC stack through the front-side leading channel from a feeding tube, and then flows across the two sides of anode simultaneously and continuously through the thru-etched holes. The fuel

finally leaves the fuel cells through the back-side leading channel from another feeding tube.

Modeling and simulations have been performed to optimize the anode flow patterns design. The results show that increasing the channel and rib width within the sub-millimeter scale can improve the  $\mu$ DMFC performance. Thus, the channel and rib width are designed to be 600 $\mu\text{m}$  wide.

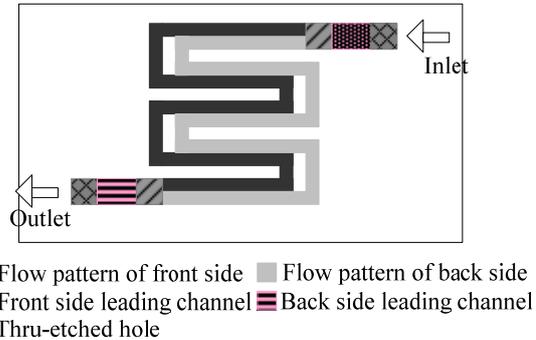


Fig.2 Schematic of the shared anode plate

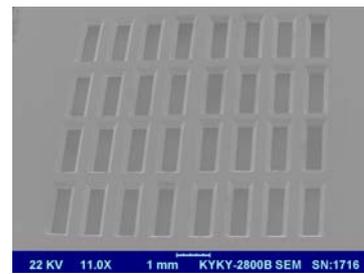


Fig.3 SEM photo of the cathode plate

### 2.3 Cathode Plates

In order to design the proper air-breathing cathode structure, the opening area, the contact area with the MEA, and the stiffness of silicon structure have to be considered together. Normally the first two factors are conflicted with each other because of sharing the same effect area. The larger the opening area on the cathode plate has, the more easily the air transports to the MEA through the cathode, nevertheless, the less contact area with the MEA to collect the current and higher risk of fracture. A similar dilemma will happen if too small opening windows are used. The pyramid structure of the open windows formed by KOH etching is also needed to be considered because of the variation of the cross-section area which influences the air transportation along the holes. The larger the size of a single open window is, the smaller this kind of structure influence the air transportation through the plates. But the size and distribution of the windows on the effect area also affect the current collection of the cathode. According to our previous work [4], a grid structure is adopted, as shown in Fig.3, featuring the half of the effective area opening to the air on one side to draw in the oxygen and the half contacting with the

MEA on the other side to collect the electricity. The open windows are designed to be an array of lathy rectangles of which the short side with length of 700 $\mu$ m, long enough to ignore the influence of the area variation, is shorter than half of the long side.

### 3. FABRICATION

#### 3.1 The Plates

Thanks to micromachining techniques and double-side lithography, the two-side structures of the anode and cathode are fabricated on a same wafer at one time as their processes are exactly the same. The fabrication processes of the anode and cathode plates are presented in Fig.4. The detailed steps are as followed:

- 1) SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> films are deposited as the mask layers on both sides of 400 $\mu$ m thick double-polished <100> silicon wafer by thermal oxidation and LPCVD respectively.
- 2) The two-side structures patterns are formed by double-side lithography. For the anode plate, the flow patterns include flow channels, leading channels, and the connect hole on both sides. For the cathode plates, the patterns are open areas on both sides. RIE is used to remove the Si<sub>3</sub>N<sub>4</sub> mask under the developed photoresist.
- 3) The two-side structures are etched using KOH timed etching. The resist layers, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, are removed by HF solution after etching.
- 4) Ti/Pt layers are sputtered for current collection with the thickness of 2000 $\text{Å}$  on both sides of the silicon wafer.

Fabricated silicon plates are shown in Fig.5.

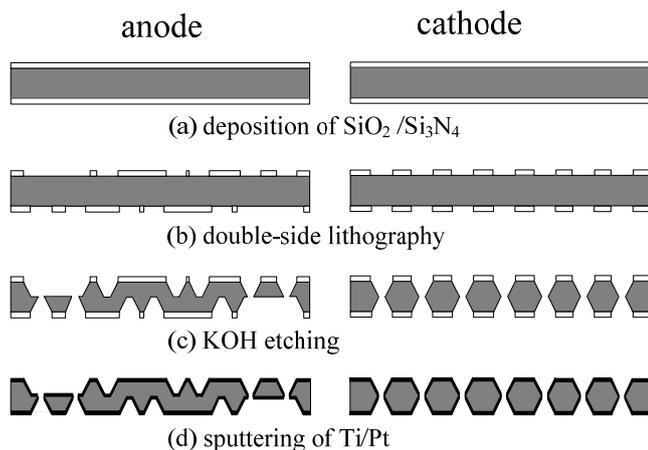


Fig.4 Fabrication process of the silicon plates

#### 3.2 The MEA

The MEAs using in this stack are made by hot pressing two catalyst-coated (anode: 4.0mg/cm<sup>2</sup> Pt-Ru, cathode: 1.5mg/cm<sup>2</sup> Pt) carbon papers, which the cathode one is wet-proof and the anode one is

hydrophilic, together with the PEM, Nafion 117 in between.

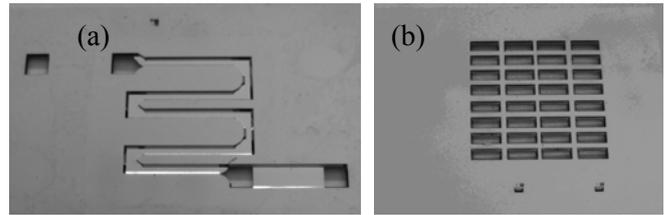


Fig.5 Photos of the fabricated silicon plates  
(a) The fabricated anode plate with both-side patterns  
(b) The fabricated cathode plate

#### 3.3 Assembly

PMMA (PolymethylMethacrylate) holders and PDMS are used to assemble the stack. The PDMS mainly plays three roles in the packaging, such as, (a) the sealing gaskets around both sides of the MEA; (b) buffering layers between either of the anode/cathode holders and its corresponding plate; and (c) the fixture of feeding tubes, respectively. The PMMA holders are used for protecting fragile silicon plates and providing a sufficient and uniform pressure, which keep the fuel cell hermetic and improve the contact of the MEA and the plate to reduce the contact resistance. The assembled air-breathing  $\mu$ DMFC stack is shown in Fig.6, and Table1 illustrates its dimensions. No leakage has happened during the daylong testing, indicating that this assembly method is effective and reliable.

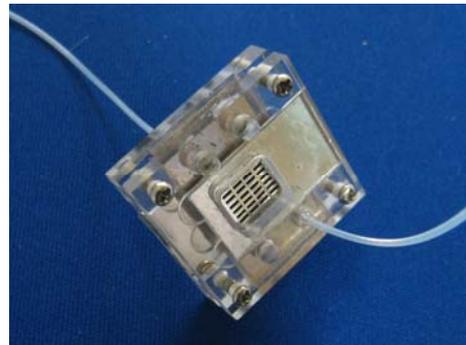


Fig.6 Assembled air-breathing  $\mu$ DMFC stack, using by PDMS and PMMA holders.

Table 1: Dimensions of the  $\mu$ DMFC stack (unit: mm)

Total size <sup>1</sup>	29.0×29.0×5.6
Effective thickness <sup>2</sup>	2.8
Plate area	27.2×13.8
Channel area	7.8×7.8
Channel width	0.6
Channel depth	0.2
Rib width	0.6/ 1.8

<sup>1</sup> Including holders

<sup>2</sup> Plates and MEAs only

#### 4. RESULTS AND DISCUSSION

The assembled air-breathing  $\mu$ DMFC stack has been tested on an electrochemical interface, Solartron SI1287, under room temperature and ambient pressure. The performance curves including the output voltage and the power density versus the current density are plotted in Fig.7. The experimental results show that the prototype has an open circuit voltage of 0.45V and the maximum power density of 3.85mW/cm<sup>2</sup>, when fed with 1M aqueous methanol at 0.10ml/min. The performance of the  $\mu$ DMFC stack is much better than that of a single cell, 2.31mW/cm<sup>2</sup> [4], while the volume is far less twice than that of the single one. It should be pointed out that the stack consists of two single cells piled up, but the power density of the stack is lower than double of that of a single cell. The reasons are probably as follows: (a) the resistance of the stack is larger than half of the single cell resistance due to the same contact resistance of both the stack and single cells between the external circuit and the electrode; and (b) the low flow rate of CH<sub>3</sub>OH solution would affect the performance of stack although the stack has a better utilization efficiency of fuel because of the double reaction area.

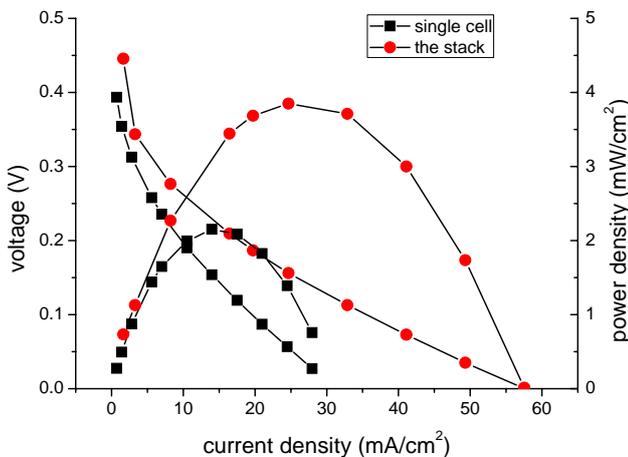


Fig.7 Performances of the air-breathing  $\mu$ DMFC stack and a single cell tested with 1M methanol at 0.1 ml/min under room temperature (25 °C) and ambient pressure.

#### 5. CONCLUSION

A silicon-based air-breathing  $\mu$ DMFC stack which consists of two air-breathing  $\mu$ DMFCs featured by an anode plate shared is reported. The serpentine flow channels on both sides of shared anode plate are designed to be parallel placed and parallel electrical connection is adopted. Thanks to micromachining techniques and double-side lithography, the two-side structures of the anode and cathode plates are

fabricated on the same wafer simultaneously. Experimental results show that the prototype generates a maximum power density of 3.85mW/cm<sup>2</sup> which is almost double of power density of the single cell, and an open-circuit potential of 0.45V, while the volume of the air-breathing  $\mu$ DMFC stack is far less twice than that of the single cell. The output power of the stack is lower than double of that a single cell generates due to probable reasons such as high resistance of the stack and low flow rate of parallel structure.

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