A long-term stable power supply μDMFC stack for wireless sensor node applications

Z. L. Wu[1], X. H. Wang[12]*, F. Teng[1], X. Z. Li[1], X. M. Wu[1] and L. T. Liu[1]

[1]Institute of Microelectronics, Tsinghua University, China
[2]Tsinghua National Laboratory for Information Science and Technology, China

Email: wxh-ime@mail.tsinghua.edu.cn

Abstract. A passive, air-breathing 4-cell micro direct methanol fuel cell (μDMFC) stack is presented featured by a fuel delivery structure for a long-term & stable power supply. The fuel is reserved in a T shape tank and diffuses through the porous diffusion layer to the catalyst at anode. The stack has a maximum power output of 110mW with 3M methanol at room temperature and output a stable power even thought 5% fuel is the remained in reservoir. Its performance decreases less than 3% for 100 hours continuous work. As such, it is believed to be more applicable for powering the wireless sensor nodes.

1. Introduction

Direct methanol fuel cell (DMFC) is one type of electrochemical energy conversion device which directly converts the chemical energy to electricity. The μDMFC has been the promising power source for wireless sensor nodes work in extreme environment, because of its high energy density, instantaneous recharging, the simple system design and environmentally friendly[1-2]. In the last decades, many researchers have been attracted to develop the active μDMFCs and their components, such as catalysts, membrane electrode assembly (MEA) membranes, anode and cathode plates, etc [2-4]. More recently, the passive air-breathing μDMFCs have been more attractive than active ones because they don't need extra pump or air blower acting as ancillary devices and consequently have much simpler structures, lower cost and higher fuel utilization [3, 4]. In fact, a single unit μDMFC can only output a limited potential and power. Therefore, the passive air-breathing μDMFC stacks are required to meet the practical application.

Several studies on the development of passive μDMFC stacks have been reported. Baglio et.al reported a monopolar three-cell stack connected in series with different catalyst loading and methanol concentration, it can provide a peak power density more than 20mW/cm^2 at ambient conditions [5]. Zhu et.al proposed a novel assembly method for μDMFC stack, which is beneficial to decreasing the internal resistance by using multi-layer bonding technique [6]. N. Hashim et.al developed a six-cell stack with laminated structures connected in series, and the mount of single cells in the stack can be easily extensible for realizing a higher output [7]. However, there remain some common challenges in passive μDMFC stacks, i.e. fuel and oxygen self-supply, enough power and long-term & stable output, which are the most important and most difficult also [8]. Many reported stacks employed small reservoirs and operated only several minutes or hours [6, 9-10].

Therefore, we design and fabricate two kinds of passive, air-breathing 4-cell μDMFC stack with

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

different fuel delivery structure for a long-term stable power supply. The stacks were operated completely at room conditions. The constant current discharge, the constant voltage output and long-term operation ability of the two prototypes were tested. In addition, one of the prototypes can output a stable power even thought the fuel in the reservoir is nearly used up. The results have potential contribution for the development of passive DMFCs stack.

2. Design

We design a passive μDMFC stack, consisting of 4 single cells with back-to-back distribution and a shared fuel reservoir sandwiched in the middle, as shown structure A in Fig. 1. The fuel diffuses through the diffusion layer to the catalyst at anode, and the oxygen is self air-breathed by the cathode, on which the hydrophilic capillary channels are arrayed along the ribs of the windows to remove excessive water out.

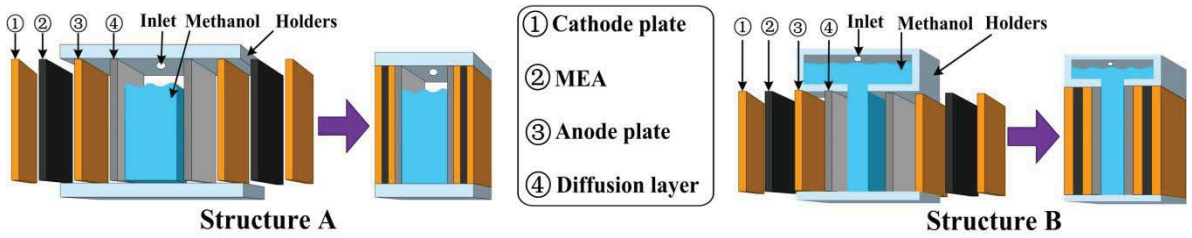


Fig.1. A passive μDMFC stack consists of 4 single cells with back-to-back distribution and a shared reservoir sandwiched in the middle. A T shape fuel reservoir above the stack is designed improvably to supply fuel to the stack continuously, as shown in structure B.

The structure A has many characteristics which is benefit for a passive stack for practical application; for example, the back-to-back cells distribution is help for maximizing the air-breathing area of cathode as well as feeding the fuel by a simple and shared reservoir, furthermore, the stack works in vertical direction can make sure each cell is supplied with uniform methanol, which can make the stack output a relative big overall power.

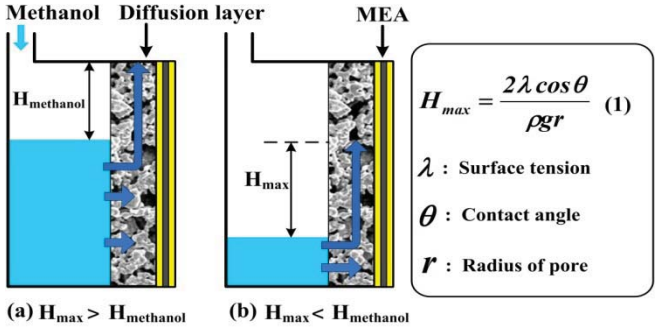


Fig.2. Schematic of a vertical passive μDMFC with a porous diffusion layer in the case of the solution does not cover the whole surface of the diffusion layer after long-term work, the μDMFC may be supplied with insufficient fuel.

However, an actual question has exposed after a very long time operation for this passive stack: the liquid level of the methanol solution in the reservoir will change with operation time, and the μDMFC may be supplied with insufficient fuel in the case of the methanol solution is not completely full in the reservoir. As described in Fig. 2(a), when the liquid level of methanol are not very low, methanol solution can be sucked to the top by the capillary force, making sure that the whole catalyst layer can be supplied with fuel. However, the maximum sucking height of the solution, H_{max}, is usually not big

enough to suck the fuel to the top while the level of the methanol solution is low, as shown in the Fig. 2(b). This is because the radius of diffusion layer pores is often a little big, avoiding the shortage of methanol diffused to the catalyst layer, as the equation (1) in Fig. 2(b) expressed. Therefore, a new structure, a T shape fuel reservoir with very narrow lower part and fat upper part (volume ratio,1: 9), is designed improvably to feed the passive stack continuously, as shown structure B in Fig 1. In this way, the liquid level will not decrease until more than 90% fuel in the reservoir has been used. Furthermore, it is also easy for adding an extra reservoir in this structure for realizing a longer work time if necessary, so the stack with structure B is believed to have a long-term and stable output.

3. Experimental

3.1. Fabrication

The structure and fabrication of the silicon based plates of the μDMFC is very similar to our previous work [8]. Both the anode and cathode plates are fabricated by using MEMS techniques, detailed in Fig 3, while the fabrication process of the silicon plates consist of four steps.

(a) 20μm thick thermal oxide and 100μm thick Si_3N_4 layers are deposited on both sides of a 500 μm thick 4 inches double-polished (100) silicon wafer, acting as the mask layers for KOH etching.
(b) Double side lithography technology is introduced to form the flow structure of the anode and cathode plates. In the cathode plate, the patterns of windows and capillary channels in both sides are formed.
(c) KOH-timed etching is employed to anisotropically etch the silicon wafer until the windows are through and capillary channels are formed.
(d) Then 20nm thick Cr and 200nm thick Au are deposited on back side of wafer acting as the current collecting layer.

The fabricated anode and cathode plates are shown in Fig 4(a) and 4(b) respectively. Fig 4(c) shows the SEM photograph of the capillaries channel along the rib of the cathode window.

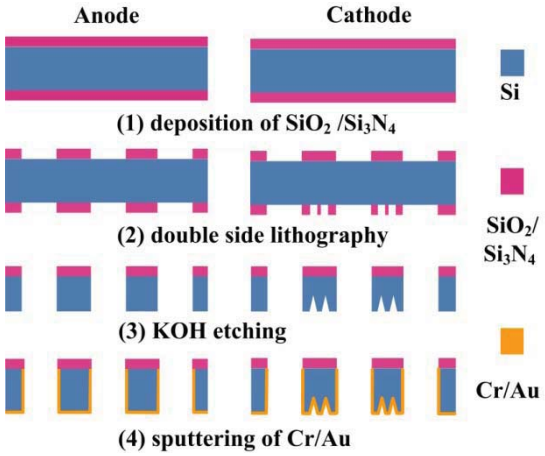


Fig.3. The fabrication processes of the silicon anode and cathode plates.

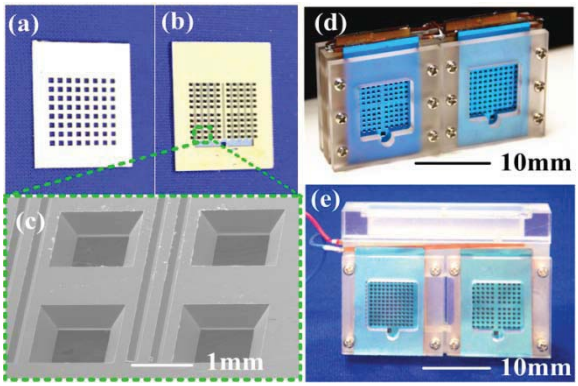


Fig.4. The photographs of fabricated anode plate (a), cathode plate (b) and the SEM image of the capillary channels on the cathode plate; two prototypes, stack A (d)with structure A and stack B(e) with structure B are assembled.

3.2. MEA preparation

The Nafion 117 membrane (DuPont) is used as the proton exchange membrane (PEM), with catalyst loading of 5.0 mg cm^2 Pt/Ru black at the anode and 4.0 mg cm^2 Pt black at the cathode. The PEM with catalyst is sandwiched between two carbon papers (TGP-H-090, Toray), which served as gas diffusion layers (GDLs), and then hot-pressed at 140◦C and 30 atm for 2 min to form the MEA. The carbon papers on cathode side are waterproof while those on anode sides are modified to form a hydrophilic surface. The whole area of the MEA is 18mm × 24mm, with an active area of 14mm × 15mm.

3.3. Assembly

The fabricated methanol and water plates are bonded together using PDMS bonding technique to form anode structure. Then the anode structure is assembled with the cathode plate using PMMA holders and PDMS material, sandwiched with a MEA in between. Two prototypes are assembled, i.e. stack A with structure A (Fig 4(d)) and stack B (Fig 4(e)) with structure B.

4. Test and discussion

The performances of two prototypes with different fuel delivery structure are tested in completely passive mode, i.e. the anode reservoir is filled with pure methanol and the cathode is air-breathing, at room temperature and 40% relative humidity.

Firstly, in order to test the output performance of prototype A, the reservoir is full of 3M methanol solution, the constant current is applied and the output voltage is monitored for a period of 1 minute until the final steady-state value is recorded. The I-V curve and power curve are shown in Fig 5. The prototype A achieves an open circuit voltage of 1.1V, maximum current of more than 800mA and maximum power of more than 110mW. Then we test the output stability of prototype A as fewer and fewer methanol solution is remained in reservoir. The corresponding I-V curves and power curves are recorded when remained methanols are about 50% and 5%, as shown in Fig 5. The maximum output power has a 20% drop when 50% methanol is remained in the reservoir, while that is only about 20mW as 5% methanol is remained in the reservoir. This obvious decrease of power output is attribute to the amount of methanol diffused to the anode catalyst is not enough, with the existence of gravity.

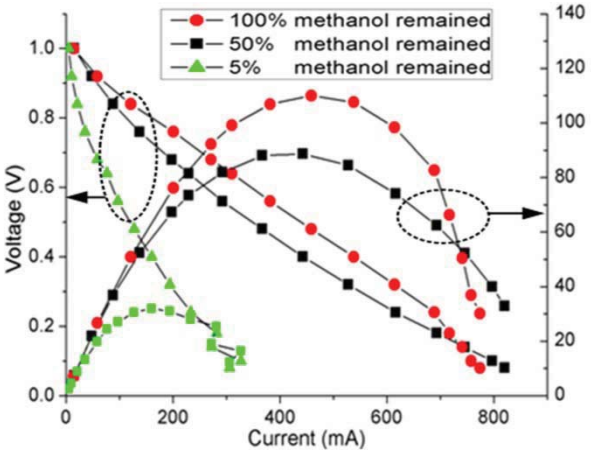


Fig.5. The prototype with structure A has a maximum power output of 110mW, and it decreases seriously as the amount of fuel decreases.

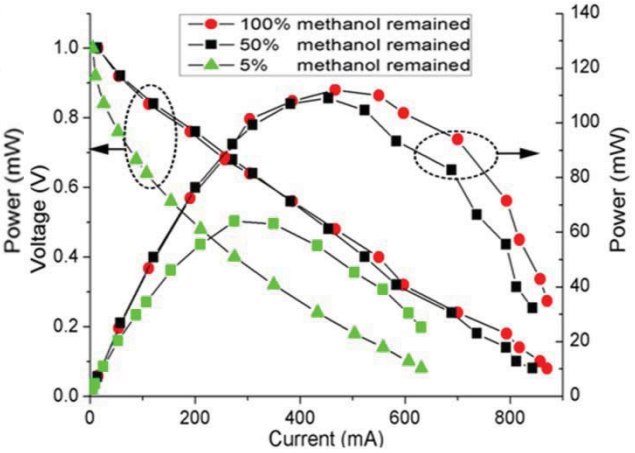


Fig.6. The stack with structure B can employ a stable power output even thought the remained fuel is about 5%.

Accordingly, the I-V curve, power curve and the output stability of prototype B are tested with the same work condition as prototype A. When the methanol is 100% full in reservoir, it has the same maximum power about 110mW, and there is almost no decrease for power when remained methanol is about 80% (Fig 6). Furthermore, it still has an output about 60mW when remained methanol is only 5%.It indicate that the prototype B has a much better output stability than prototype A.

Finally, the long time performances of prototypes are tested. The prototypes worke under a constant current condition in completely passive mode, at room temperature and 40% relative humidity, and the voltage was monitored and recorded till it fell down to 0V.The tested μDMFCs worked under a constant current of 250mA, with a certain amount of 3M methanol 4mL. As shown in Fig 7, the prototype A can only work about 180 minutes, while the prototype B can work as long as 300 minutes. These measurements are done for several times and the average value is chosen. In addition, the performance decreases of prototype B less than 3% for 100 hours continuous work.

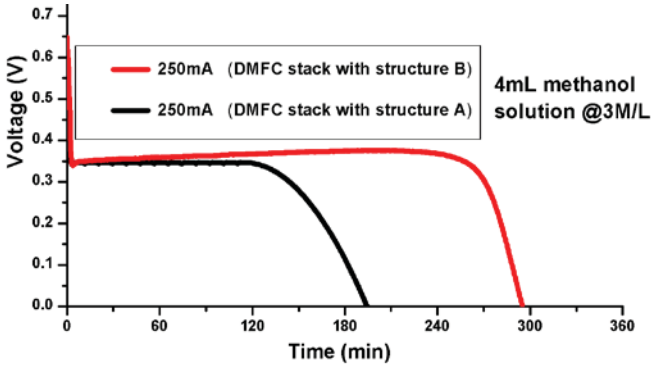


Fig.7. Both stacks are worked in a constant current, filled with 4mL methanol solution, stack B can work about 300 minutes stably, while stack A worked only 180 minutes.

5. Conclusions

We successfully demonstrate a passive, air-breathing 4-cell micro direct methanol fuel cell (μDMFC) stack featured by a fuel delivery structure for a long-term stable power supply. The fuel is reserved in a T shape tank and diffuses through the porous diffusion layer to the catalyst at anode. The stack has a maximum power output of 110mW with 3M methanol at room temperature and output a stable power even thought 5% fuel is the remained in reservoir. Its performance decreases less than 3% for 100 hours continuous work. As such, it is believed to be more applicable for powering the wireless sensor nodes.

Acknowledgment

This project is supported by the 973 program (No.2009CB320304), the National Natural Science Foundation of China (No. 60936003), and the 863 program (No.2009AA04Z319).

References

[1] Qian Zhang Design, optimization and microfabrication of a micro-direct methanol fuel cell with microblocks in anode structure, *Sensors and Actuators A* 154 (2009) 247–254
[2] D.D. Meng, A degassing plate with hydrophobic bubble capture and distributed venting for micro fluidic devices, *J. Micromech. Microeng.* 16(2006) 419–424.
[3] Y. Jiang et.al, Design, fabrication and testing of a siliconbased air-breathing micro direct methanol fuel cell, *J. Micromech. Microeng.*16 (2006) 233–239.
[4] Yan'an Zhou et.al, A water collecting and recycling structure for silicon-based micro direct methanol fuel cells, *International journal of hydrogen energy* 37(2012) 967-976
[5] Baglio Optimization of properties and operating parameters of a passive DMFC mini-stack at ambient temperature , *Journal of Power Sources* 180 (2008) 797–802
[6] Zhu et.al, A novel assembly method using multi-layer bonding technique for micro direct methanol fuel cells and their stack, *Sensors and Actuators A* 188 (2012) 246– 254
[7] N. Hashim et.al, Design, fabrication and testing of a PMMA-based passive single-cell and a multi-cell stack micro-DMFC, *International journal of hydrogen energy* 34 (2009) 8263 – 8269
[8] Xiaohong Wang et.al, An air-breathing micro direct methanol fuel cell stack employing a single shared anode using silicon microfabrication technologies, *Journal of Micromechanics and Microengineering*, 19 (2009), 094012
[9] Zhu et.al, Development of a passive direct methanol fuel cell (DMFC) twin-stack for long-term operation, *Journal of Power Sources* 193 (2009) 649–655
[10] T.S.zhao et.al, A small mono-polar direct methanol fuel cell stack with passive operation, *Journal of Power Sources* 178 (2008) 118–124