# Design of a New Micro Direct Methanol Fuel Cell Utilizing MEMS Technology

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*Abstract:* In this paper, a special micro DMFC using MEMS technology is designed to work in circumrotating condition, which providing power using inertia over-load. The designed cell is a cylinder, anode channel is inside, cathode is outside and exposes to the air. When the overload exceeds the critical value, the liquid inside reserve tank will splash and comes into the two electrodes, and then the cell will be activated. The voltage, current density and work time of DMFC are calculated, fuel tank and active system are designed to satisfy the working condition, and the DMFC performance of serpentine and parallel flow fields is analyzed preliminary. A current collector open ration of 70% is chosen in the design of the DMFC, and effect of the open ratio on the performance of the DMFC is analysed simultaneously. Furthermore, cathode and anode plates are fabricated using a MEMS technology--3D KOH- etching. Although there are many experimental works to do to testify its performance, it is true that the flow field simulation is authentic and the primary design is feasible.

*Key-Words:* μDMFC, MEMS, design, KOH-etching, flow fields, circumrotating

## 1 Introduction

The research efforts and interests in fuel cell technology and development are increasing rapidly. Governments, companies and universities worldwide are gradually adapting to this new technology[1-4]. Due to high efficiency and low emissions, fuel cells display a great variety of potential applications. The absence of moving parts and an extremely simple mechanism make fuel cells very competitive for small-scale applications. Moreover, because of easily stored and instantly refueled of liquid fuels [5,6], direct methanol fuel cells (DMFCs) have significant potential to become a leading technology for energy conversion in a variety of applications .

Without external delivery devices such as pumps and compressor, DMFCs can be stored in their liquid or vapor state and delivered by passive means [7-10]. This type of passively operated fuel cell is appealing because it not only offers the advantage of a simpler and more compact system, but also eliminates the parasitic power losses for powering the ancillary devices required in the active DMFCs. The passive DMFCs utilize porous layers with wicking materials to deliver the dilute methanol solution to the fuel cell, mainly by diffusion, and control the methanol concentration in the anode inlet.

The proposed passive DMFC using MEMS technology design is to satisfy special condition, such as slightly circumrotating condition, providing power using inertia over-load [11]. The cell is a cylinder, anode channel is inside, cathode is outside and exposes to the air. When the overload exceeds the critical value, the liquid inside reserve tank will splash and come into the two electrodes. Then the cell will be activated.

## 2 Designs

A DMFC is an electrochemical cell that generates electricity based on the oxidation of methanol and reduction of oxygen. Consider the passive DMFC sketched in Fig.1, which consists a fuel tank, an anode flow channel / current collector (ACC), an anode gas diffusion layer (AGDL), an anode catalyst layer (ACL), a polymer electrolyte membrane (MEM), a cathode catalyst layer (CCL), a cathode gas diffusion layer (CGDL), and a cathode flow channel /current collector (CCC). On the anode, methanol is transported from the fuel tank to the ACL, where part of methanol is electrochemically oxidized to form $CO_2$, while the remainder permeates the membrane and reacts with oxygen on the cathode. The produced gas $CO_2$ transfers back to the fuel tank and is emitted to the

ambient. On the cathode, oxygen is passively taken from the ambient air to the CCL, where it is reduced to form water and heat. The generated water moves out through the CGDL by the capillary force. The heat generated in the fuel cell is lost from the CCC to the ambient.

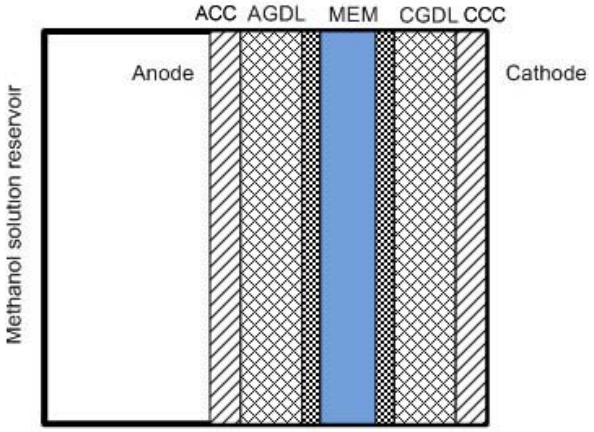



Fig.1 Schematic of the passive DMFC

## 2.1 Parameters Design

The proposed passive DMFC works in the same way as above mentioned and operates in a cylinder-shaped space. In order to utilize the space effectively, the DMFC is designed as a cylinder, its physical parameters and performance is shown in Table 1.

Table 1 Parameters of DMFC

| | |
|---|---|
| Diameter (mm) | 41 |
| Height (mm) | 34 |
| Thickness (mm) | 1 |
| Voltage (V) | 1.3-2.0 |
| Current (mA) | ≥350 |
| Work time (s) | 200 |
| Active time (ms) | ≤100 |

1) Voltage

As we know, the ideal voltage of monomer DMFC is 1.184V, but it is only above 0.4V at normal temperature, so the amount the monomer cells is,

$$\text{Amount}=\frac{1.3\sim 2.0}{0.4}=3\sim 5 \text{ unit}$$

We design 4 monomer cells in series to obtain the design voltage. Because the monomer cell is very thin, it will not increase the volume largely to enhance the voltage.

2) Current

The discharge current density $i_0$ of DMFC is as high as 36mA/cm2, the current of whole area is,

$$I=i_0 \cdot A \qquad (1)$$

Where, A is the area of membrane electrode.

$$A=\pi \cdot R \cdot h \qquad (2)$$

Here, R is the diameter of cylinder membrane electrode, h is the height of membrane electrode. Because the diameter and height of DMFC is 41mm and 34mm respectively, we design the size of cylinder membrane electrode is 30mm diameter, 25mm height.

So, the area is calculated,

$A=\pi \cdot 30 \cdot 25 \approx 2356 \text{ mm}^2=23.56 \text{ cm}^2$

$I \approx 848 \text{ mA} > 350 \text{ mA}$

It should be found that the current of MDFC stack is much higher than required, even if the cell declines, it still satisfy the demand.

3) Work time

Work time is determined by the volume of reserve tank and methanol concentration mainly. So in order to calculate the work time, the volume of reserve tank should be determined first.

As we know, designed dimension of cylinder membrane electrode is 30mm diameter and 25mm height, the dimension of reserve tank should be smaller than it so as to install inside the cell. The diameter of reserve tank suggested is 20mm, height is 15mm.

So the volume of reserve tank is

$$V=\pi \cdot r2 \cdot h=4712.4\text{mm}^3=4.7124\text{ml} \qquad (3)$$

The methanol concentration suggested is 2mol/L, so the quality of active matter reaction fully is,

$$m_0=0.002\times 4.7124\times 32\approx 0.30159\text{g} \qquad (4)$$

So, the ideal capacity of cell is

$$C_0=26.8\cdot n\cdot \frac{m_0}{M}=\frac{1}{q}m_0=26.8\times 6\frac{m_0}{32}$$

$$=\frac{m_0}{0.199}\approx 1.5155\text{Ah} \qquad (5)$$

Where, $C_0$ -ideal capacity;

$m_0$ -quality of active matter reaction fully;

$M$ -mol of active matter;

n- electron amount of gain or loss

q-electrify quality of active matter.

thus，

Work time $t=C_0/I\approx 1.79\text{h} >> 200\text{s}$

As calculated above, work time is larger than required 200s greatly, the performance of design DMFC satisfies demand, and so it is feasible theoretically.

## 2.2 DMFC Stack Structure

In order to satisfy the needed voltage, we choose binding fuel cell as shown in Fig.2. Because it is plane membrane electrode, four monomer cells are

placed in series on the membrane. The main advantages [12-15] of the binding design are as follows:

(1) Reduce resistance.
(2) Suit to small power.
(3) Flexible sculpt.
(4) Border cells can share airproof area, decrease the area of airproof.
(5) Use common plastic to make the shell.
(6) Share air channel, simplify manufacture techniques.

The core part of this design is membrane electrode, 4 membrane electrodes can be preparation inside one cylinder proton exchange membrane (PEM), along with the bipolar plate, constitute the 4-cell unit. Polar plate is made from cover-metal plate, and 4 membrane electrodes are designed in series, all these make it come into true to require higher or other different voltage not need more enhancing voltage circuit, as shown in Fig.3.

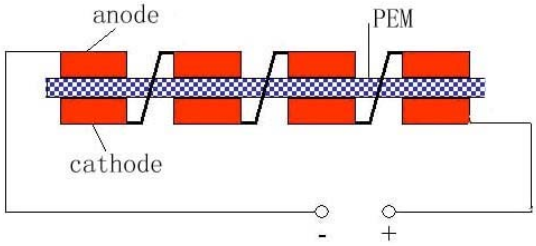


Fig.2 Binding fuel cell design

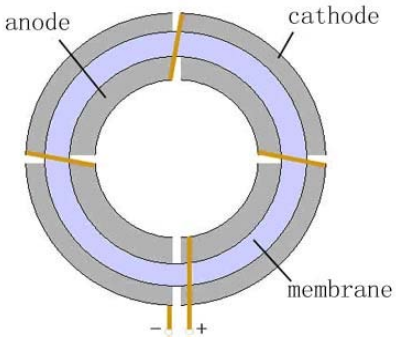


Fig.3 Electrode of DMFC

## 2.3 Fuel Tank (Methanol Solution Reservoir) Design

As former mentioned, in order to satisfy the working condition, the DMFC is designed as a cylinder. Similarly, in order to satisfy the working space, a columnar shell is chosen as the configuration of fuel tank. So the material has become the most important issue when the configuration has been determined. The demand of the fuel tank material concludes:

(1) The material should be consistent with methanol liquid solution.
(2) It would crack reliably and release the methanol solution when the cell is activated, and the fragment has no impact on cell discharge.
(3) It should have good sealed performance.
(4) It can outlive duty vibration, concussion and decline.
(5) It can be reserved for a long time without any quality and performance changed.

Based on above demands, the optional materials are: plastic, glass and metal. A plastic fuel tank has the advantages of high intensity and simple fabrication technique, but the quality and performance of the aging plastic can't be ensured after it is reserved for a long time. A metal fuel reservoir has the advantages of higher reliability; higher intensity which will enhance the ability of resisting vibration and concussion, but the structure will become more complex if a metal tank is selected because of its chemical unsteady. Moreover, both materials have a fatal disadvantage that is they don't suit to work in low overload situation.

Considering above demands synthetically, a cylindrical glass fuel reservoir becomes the only choice (as shown in Fig.4). As we know, glass is a frangible material, it has the lower ability of resisting vibration and concussion, and easy to crack especially when temperature changes rapidly. However, glass has a more steady chemical performance which is suit to reserve methanol solution, and it is easy to crack to release methanol quickly which is useful to active fuel cell apace. More importantly, it can work in low overload situation. If the structure design is appropriate, it should ensure to work normally to satisfy the working condition to over the disadvantages.

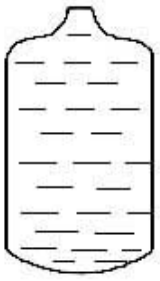
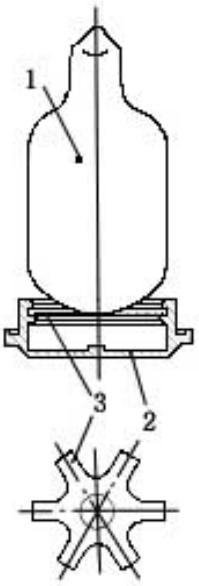


Fig.4 Glass methanol solution reservoir

## 2.4 Active System Design

The active system is a device that can make the fuel reservoir cracked exactly. Its design correlates with the fuel reservoir nearly. The different structure and material of the fuel tank result in different active system design.

In a general way, the most common active system includes a sustained ears pattern and a springing pattern. Compared to the former, the later has a more complex structure and a greater volume. So the simpler sustained ears pattern is adopted. The active system works in recoil condition when launched. That is, the glass reserve tank is supported by the sustain ears and cannot be moved in common conditions as shown in Fig.5. When the overload exceeds the critical value, the glass reserve tank will suffer from the recoil then press the sustained ears and drop from the safe position, cracking simultaneity.




1-glass reserve tank, 2-sustain eras shelf, 3-sustain ears

Fig.5 Sustain ears active system

## 2.5 Tubular MEA and DMFC Preparation

As we know, most DMFC stack was designed in planar structure [16-19], which needs the expensive bipolar plates to transfer the reactants to every fuel cell and the electrons produced by electrochemical reaction to the load. Bipolar plates are a key component of fuel cells with multiple functions. They also remove heat from the active area and facilitate water management within the cell besides above mentioned. However, the peripheral equipments such as the tank, gas cylinders and pumps must be used for storing and transferring the reactants to sustain the DMFC system working normal, since the flow channel of the bipolar plates is narrow. The use of bipolar plates not only increases the stack's cost, but also involves certain difficulties to the system assembly and maintenance, for example, if one single fuel cell of the stack destroyed, the whole stack had to disassemble and assemble again.

As above description, bipolar plates contribute a significant part of the overall cost and the total weight in a fuel cell stack. The cost of bipolar plates occupies 60-70 percent of the whole DMFC [16-20], they have become the bottleneck of fuel cell industrialization.

Compared to planar structure of DMFC, the tubular DMFC has many advantages [19,20] as follows:

(1) Electrode reaction area is bigger.
(2) Easily airproofed.
(3) The connection pattern of stacks is agility; it can be in series, parallel connection or mixed.
(4) Good maintain ability.

Although there are many advantages in tubular DMFC, the tubular configuration is still rarely used in polymer membrane fuel cells due to lacking in commercialized tubular membrane electrode assembly (MEA). Fabricating the tubular MEA were brought forward by some researchers [21-29].Here, an idea of designing tubular DMFC was proposed to overcome the disadvantages of planar DMFC[30,31].(The design DMFC is a cylinder, so it can be considered a tubular DMFC).

There are many descriptions for the MEA preparation [32-40]. Similarly, the tubular MEA preparation consist a polymer membrane, a cathode catalyst layer, an anode catalyst layer and gas diffusion layer. In this work, a pretreated Nafion 115 membrane was employed, The pretreatment procedures included boiling the membrane in 5 vol.% $H_2O_2$, washing in deionized water, boiling in 0.5M $H_2SO_4$ and washing in deionized water for 1 hour in turn. After that, the membranes were washed by deionized water to remove the excess metal species once more. The pretreated membranes were pressed between two porous materials to keep clean and dry prior to the fabrication of MEA. Single-side ELAT electrodes from ETEK were used in both anode and cathode, where carbon cloth (E-TEK, Type A) were used as the backing support layer with 30 wt.% PTFE wet-proofing treatment.

Electro-catalysts used in the anode and the cathode were 28.9% Pt–Ru black (Johnson Matthey) and 30%Pt black (Johnson Matthey), respectively. The fabrication of anode and cathode is as follows: first, quantitative anode and cathode catalysts were

weighed and put into two beakers, mixed with quantitative deionized water and isopropyl alcohol; then the mixture was ultrasonic dispersed for 30 minutes. Second, adding quantitative Nafion solution, and ultrasonic dispersed for 30 minutes again. Then, the mixture volatilized under the temperature of 50℃, and the catalyst ink was achieved. Last, used the air-brush to spray the catalyst ink and then a thin layer of Nafion solution on the membrane, the MEA was prepared[30,31].

The prepared MEA were put both sides of the pretreated MEM, enlaced onto a smooth metal column with anode inside and cathode outside, fixed with two semicircular mould, then hot-pressed at 120 ℃ and 15 MPa for 1-2 minutes, the tubular MEA was manufactured now[30,31], and the cutaway view is shown in Fig.6. Here, in order to form the cylinder, a clamp for manufacturing tubular MEA was needed.

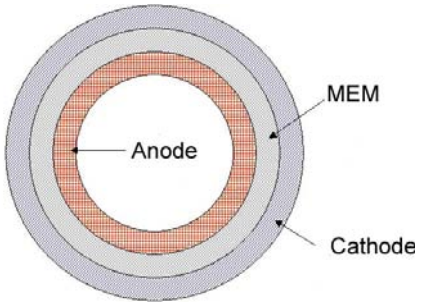


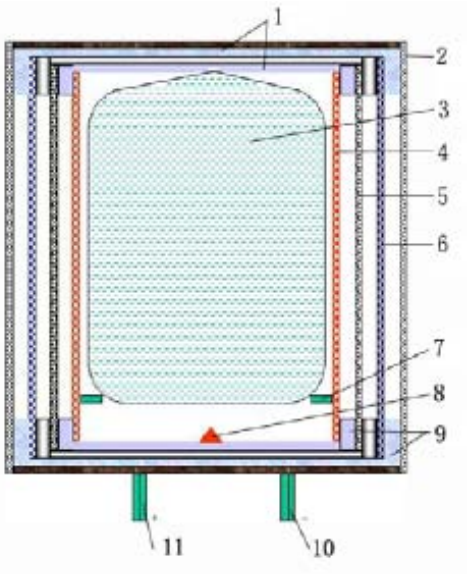

Fig.6 Cutaway view of tubular MEA

## 2.6 Configuration of DMFC

A design drawing of the DMFC fuel cell stack, including seated active system, fuel reserve tank and feed system, is shown in Fig.7, and the assembled configuration is shown in Fig.8. The wall of cylinder shell is made of lacunaria material, which will expose the cathode to the air effectively in order to supply enough oxygen when reaction needed. Two plastic cylinder poles made membrane electrode into cylinder, so as the cell has the maximal discharge area to ensure the cell work stably for a long time under the loose discharge current. At the same time, it ensures the cell has the maximal interior space to place the glass reserve tank and other complement, and ensures the cell performance.

The whole cell is a cylinder, the centre is a glass reserve tank, storing up concentration certain methanol liquid, holed by sustained ears and fixed by groove. Near the reserve tank is cylinder fuel polar plate, the outer is air pole. Between the air pole and polar plate is membrane electrode suit. The three discreteness are insulated fixed to the shell and airproof wholly. Each of fuel pole and air pole has cathode and anode.

The actuator is modeled into the shell of cell. When system provide power using inertia over-load, it will work automatically，whereas it doesn't move due to the sustained ears at equability. When the overload exceeds the critical value, the glass reserve tank will suffer from the recoil then press the sustained ears and drop from the safe position, cracking simultaneity. Liquid will splash and come into two electrodes through inner anode, and the cell is actuated. The cell begins to discharge, and it will work for 200s continuously or longer time.




1-insulated fixed piece, 2-lacunaris shell, 3-reverve tank, 4- polar plate; 5-MEA, 6-air pole, 7-sustained ears, 8-prominency of sustained ears, 9-insulated fixed piece, 10-cathode, 11-anode

Fig.7 Structure of the fuel cell

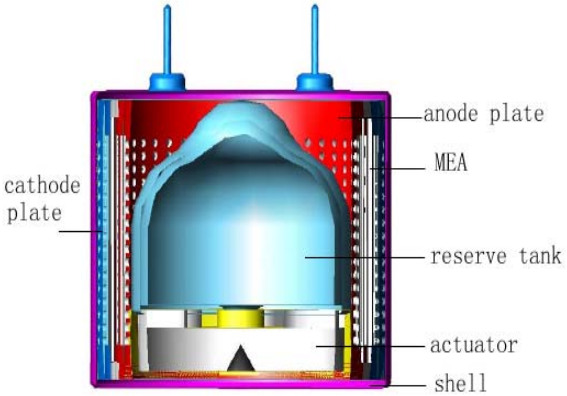



Fig.8 Assembled configuration of DMFC

# 3 Performance Analysis

### 3.1 Flow Field Analysis of the Anode

As we know, the main tasks of these flow-field plates are to act as current-collectors and to guarantee distribution of fuel or air over the reaction surface area as well as removal of products from the cell. Since DMFCs suffer from large over-potential mainly at the anode and the computation would be significantly more complex if the cathode is involved[41-51], so the anode flow field is analyzed independently first. To save the computational expense, a unit region of the anode, as illustrated in Fig.9, can be taken from the entire cell as the computational domain, which can be divided into three zones: flow field channel, AGDL, and ACL. The model is formulated based on the following general simplifications and assumptions [41-51]:

(1) The fuel cell is assumed to operate under steady state conditions.
(2) There is no pressure difference between the compartments.
(3) Anode current collector and AGDL are well insulated from the ambient. No heat is lost from these components to the ambient. Thus, the temperature at each of these components is the same as that at ACL.
(4) Since the variation in the fluid viscosity and density with temperature is relatively small in the calculated range, these properties are considered to be constant.
(5) Considering only $CO_2$ in the anode gas phase, the methanol vapour and water vapour transport is ignored.

To design the anode, flow fields of two different channels, parallel and serpentine, were studied in the model. Besides mentioned assumptions above, the Navior-Stokes equations were used as the basic transport equations. Butler-Volmer equation was used to describe the electrochemical reaction, incorporated with the User Defined functions. Some physicochemical properties of the DMFC are given in Table 2. Numerical simulations were performed with CFD software. The result shown in Fig.10 indicates that the output power of the serpentine flow field is similar in most cases to that of parallel channels, but higher under high current density. In order to simplify the design, we choose the parallel flow field, as shown in Fig.11.

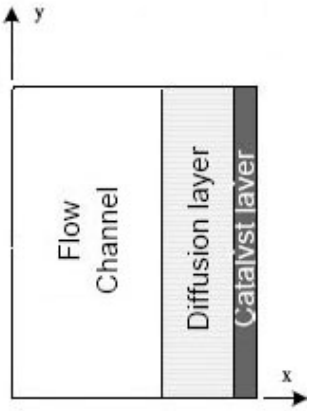



Fig.9 The computation domain of anode.

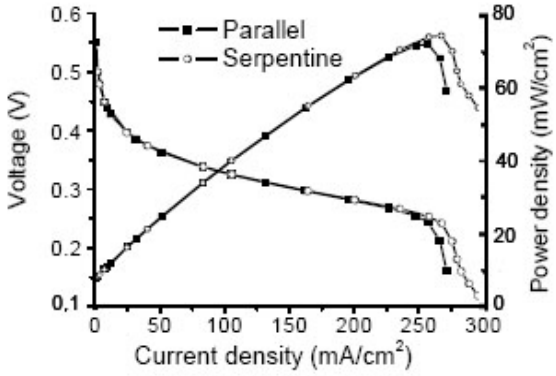



Fig.10 Polarization curve using of serpentine and parallel flow fields at 40℃ (using 2M methanol solution).

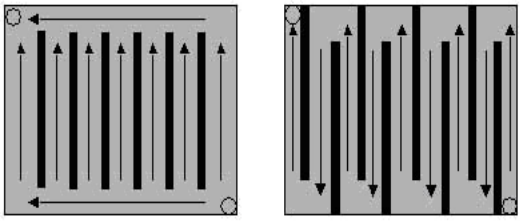



Fig.11 Investigated flow-fields for DMFC. (a)Parallel and (b) serpentine.

Table 2 Physicochemical properties of the DMFC

| | |
|---|---|
| Width of channel / rib (μm) | 400 |
| Depth of channel (μm) | 200 |
| Thickness of AGDL and CGDL (μm) | 300 |
| Thickness of ACL and CCL (μm) | 10 |
| Thickness of ACC and CCC (μm) | 500 |

### 3.2 Effect of Current-collector Open Ratio

It has been known that the cell performance increases with the open ratio by fixing the sum of channel and rib width, particularly at high current densities [51]. The improved cell performance as the result of increasing the open ratio can be primarily

attributed to the enhanced mass transfer rates of both methanol and oxygen. The reasons resulting in increased mass transfer rates are as follows:

(1) The specific area of mass transfer increases with the open ratio, yielding higher mass transfer rates of both methanol and oxygen.
(2) The rib width decreases with the open ratio, providing a shorter distance of mass transfer from the channel region to the rib region in the GDL and thereby resulting in the higher methanol and oxygen concentration under the ribs.
(3) The gas $CO_2$ on the anode and liquid water on the cathode are more easily to be removed from the rib region to the outside as the open ratio increases.

Based on above conclusions, a current collector open ration of 70% is chosen in the design of the DMFC, and the sketch of anode plate is shown in Fig.12. The cell performance in which situation is analyzed simultaneously as shown in Fig.13.

Fig.12 Sketch of anode plate of the fuel cell

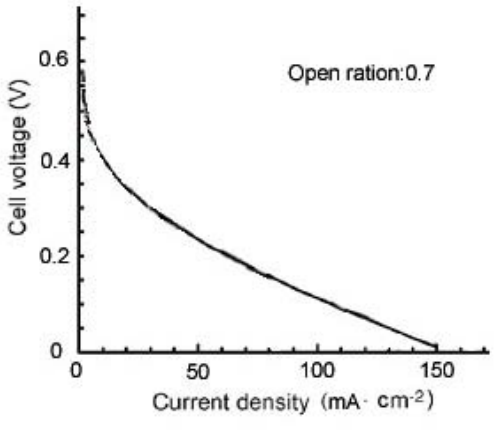



Fig.13 Effect of the open ratio on the performance of the DMFC.

## 4 Fabrication using MEMS technology

Besides silicon substrate, miniaturized fuel cells are also made of other materials, e.g. stainless steel [52,53]. However, since those materials can seldom make a fuel cell with a channel of less than 1mm wide, those fuel cells can hardly be regarded as micro fuel cells. With the rapid development of the past decade, MEMS technology has been developed into a mature technology that can provide several solutions to implement a design. MEMS technology has the advantages including high precision, good repeatability and easy batch-production. Silicon microfabrication can now easily make a pattern with the feature resolution of several micrometers.

Here, a new method is proposed to address these issues. This method has been implemented by first using double-sided lithography to transfer different but interrelated patterns (designed according to certain considerations) onto each side of the cathode plate, and then using KOH timed etching to etch through the wafer. Thus a unique 3D KOH-etched cathode structure is formed.

The MEMS fabrication process of the silicon plates, shown in Fig.14, was modified and optimized on the basis of the previous process [54]. The detailed steps are as follows: (a) Thermal oxide and PCVD SisNa were deposited as the mask layers on both sides of a double-polished silicon wafer; (b) Double- sided lithography was used to form the patterns of micro-channel and feeding holes(for the anode) or patterns contacting the MFA(for the cathode) on the front side of the silicon wafer(top side of the wafer in Fig.14, at the same time form aligned feeding holes(for the anode) or the patterns exposed to the air(for the cathode); (c) KOH timed etching was used to anisotropically etch the wafer until the feeding holes were etched through; (d) Finally 0. 8μm Ti/Cu and 0. 2μm Au were sputtered onto the front side of the silicon wafer to form the current collecting layers.

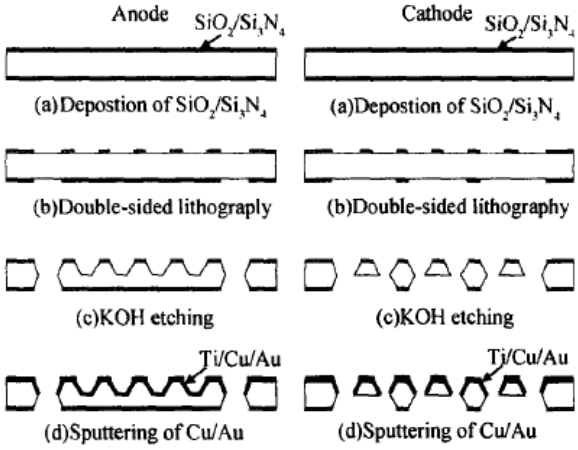



Fig.14 Fabrication process of the anode and cathode plates

The experiment of the power density of MEMS prototype is under way.

## 5 Conclusion

In this paper, a new micro DMFC is designed to work in special condition such as slightly circumrotating condition, providing power using inertia over-load. In order to satisfy the working condition, the DMFC is designed as a novel cylinder. The voltage, current density and work time of DMFC are calculated, fuel tank and active system are designed to satisfy the special working condition, and the DMFC performance of serpentine and parallel flow fields is analyzed preliminary. The result shows that the output power of the serpentine flow field is similar in most cases to that of parallel channels, but higher under high current density. In order to simplify the design, we choose the parallel flow field. More over, a current collector open ration of 70% is chosen in the design of the DMFC, and effect of the open ratio on the performance of the DMFC is analysed simultaneously. Furthermore, cathode and anode plates are fabricated using a MEMS technology--3D KOH-etching. Although there are many experimental works to do to testify its performance, it is true that the field simulation of cathode side is authentic and the primary design is feasible.

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