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应用硅和非硅 MEMS 技术的微型直接甲醇燃料电池

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摘要：分别以硅和不锈钢材料为极板研制了两种结构简单、体积小、比能量密度高的微型直接甲醇燃料电池，并介绍了该电池的工作原理和结构。利用光刻、溅射和腐蚀等 MEMS 技术完成了硅基微型直接甲醇燃料电池的制作，实验测试表明，在室温条件下，使用 1.5 mol/L 甲醇溶液供液时其开路输出电压为 520 mV，最大输出功率密度达到 5.9 mW/cm^2；利用非硅微加工技术完成的不锈钢微型直接甲醇燃料电池，在室温下用 2 mol/L 甲醇溶液供液时开路输出电压为 650 mV，最大输出功率密度达到 15.8 mW/cm^2。

关　键　词：甲醇燃料电池；硅基技术；非硅微加工；微机电系统；最大功率密度
中图分类号：TM911.4　　**文献标识码**：A

Micro direct methanol fuel cells based on silicon and non-silicon MEMS technologies

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Abstract: Two kinds of micro Direct Methanol Fuel Cells(μ-DMFC) characterized by simple configurations, small sizes and high specific power densities are presented by using silicon and stainless steel as poles in this paper. The working principle and structure of the μ-DMFC are introduced. Then, the silicon μ-DMFC is accomplished using Micro Electro Mechanic System(MEMS) technologies such as lithography, depositing and etching. Experimental results show that the open circuit voltage is 520 mV and the peak power density can reach 5.9 mW/cm^2 for the silicon μ-DMFC at room temperature when the molar concentration of methanol solution is 1.5 mol/L. Moreover, the stainless steel μ-DMFC is fabricated using a non-silicon micromachining technology, and it can offer an open circuit voltage of 650 mV and a peak power density of 15.8 mW/cm^2 under the 2 mol/L methanol solution at room temperature. It is concluded that the performance of the stainless steel μ-DMFC is greatly better than that of the silicon μ-DMFC.

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Key words: methanol fuel cell; silicon-based technology; non-silicon micromachining technology; MEMS; peak power density

1 Introduction

With the development of portable electronic devices such as cellular telephones, notebook PCs, PDAs etc., the demands for cheap, efficient and light power sources have increased quickly. Moreover, the Direct Methanol Fuel Cell (DMFC) is a promising power source for portable applications due to its advantages of simple fabrication, clean environments and relatively high efficiency. The bipolar plates of conventional DMFC have been fabricated mostly with the graphite, nevertheless its brittleness brings the difficulty for the micro channel machining. Due to the development of MEMS technology, the integration of micro flow channels for μ-DMFC with small size and mass production is realized, it presents a wonderful prospect for the fabrication of portable power sources[1].

There have also been significant attempts to develop the μ-DMFC based on the MEMS technology. Kelly described a micromachining based fuel cell fabrication method, which used the perforated membrane oxide to present the methanol to an anode. They reported an open circuit voltage of 0.5 V and a short circuit current of 0.46 A/cm^2 at 323 K[2]. Sim reported the μ-DMFC consisting of one PEM and two silicon substrates with channels fabricated by micromachining techniques such as anisotropic etching and metal evaporation. The cell with the size of 16 mm × 16 mm × 1.2 mm was supplied with 1M methanol solution. The measured output voltage of the cell was 100 mV at 298 K, but its power was not measured[3]. Cha fabricated the all polymer μ-DMFC using UV-sensitive photoresists. The measured maximum power density was 8 mW/cm^2 and current density was 37 mA/cm^2[4]. Motokawa designed a MEMS-based μ-DMFC with an active area of 0.018 cm^2 and fabricated the anode and cathode micro channels arranged temperature using 2M methanol solution[5]. Lu developed the μ-DMFC with an active area of 1.625 cm^2 assembled by sandwiching the MEA between two micro fabricated silicon wafers. Extensive cell polarization test demonstrated a peak power density of 50 mW/cm^2 at 333 K and 16.5 mW/cm^2 at room temperature using 2M methanol solution under ambient pressure[6]. The design of μ-DMFC using silicon and non-silicon micromachining technologies is proposed in this paper. The experimental results show that the output characteristics of μ-DMFC based non-silicon machining technology are better than that of based on silicon machining technology.

2 Working principle of DMFC

Fig. 1 illustrates the basic structure of the DMFC: a positively charged flow anode, a negatively charged flow cathode and a MEA between the anode and the cathode. The anode and cathode are in contact with the MEA. An aqueous methanol solution and oxygen from air are fed into the anode and cathode respectively. Through electrochemical reactions with water, the methanol is oxidized and it produces electrons, protons, and carbon dioxide. The electrons produced at the

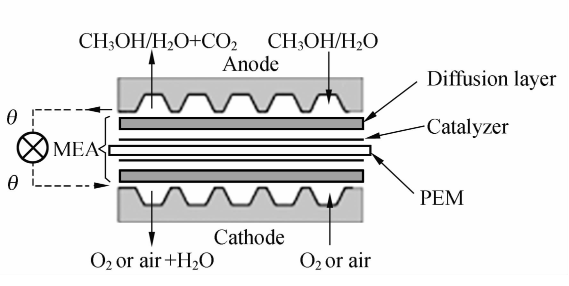

Fig. 1 Working principle of DMFC

anode carry the free energy charges of the chemical reaction, and perform electrical work through the external load. Otherwise, the protons transport through a proton exchange membrane to the cathode, where the electrons come back from the external circuit to form water with the protons. In the oxidation and deoxidization process of electrochemistry reactions, the electricity power is exported continuously.

3 Fabrication of silicon-based μ-DMFC

A schematic of the steps to fabricate the μ-DMFC is given in Fig. 2. The starting material of the μ-DMFC is (500±20) μm-thick 7.5 cm(3 in) n-type ⟨100⟩ oriented silicon wafer polished on the front side. Firstly, the thermal silicon dioxide with a thickness of 1 μm for an etch mask is grown. The silicon dioxide on the front side of the wafer is patterned by photolithography. The channels are etched using the anisotropic etching process performed with KOH solutions with concentration of 40% at 313 K. The silicon wafer is etched 120 μm deep. Another alkaline etching using electrochemistry reaction is followed to fabricate a through-hole structure with a diameter of 1 mm, allowing the methanol fuel to flow in and the carbon dioxide to exhaust out. Subsequently, the silicon dioxide with a thickness of 1 μm is grown thermally on the surface of the silicon wafer. To collect current and minimize the contact resistance between the MEA and the silicon wafer, a gold layer of 1 μm is sputtered on the channels of the wafer, preceded by 50 nm titanium layer just beneath the gold layer to promote adhesion.

DuPontTM Nafion 117 has been used as the proton exchange membrane of the μ-DMFC. The catalyst for the anode is coated with the Pt-Ru/C noble metal, and the loading of Pt in the anode catalyst layer is 4.0 mg/cm^2. The catalyst for the cathode is carbon-supported Pt, and the loading of Pt in the cathode catalyst layer is 4.0 mg/cm^2. The carbon paper is utilized as the diffusion layer of the μ-DMFC. So these parts are assembled to form the membrane electrode assembly. Finally, the MEA is sandwiched between the catalyzed anode and the cathode to create an integrated μ-DMFC with a active area of 0.64 cm^2. Fig. 3 shows the plane view structure of prototype μ-DMFC fabricated using a micro machining technology. The size of the assembled μ-DMFC is 18 mm×10 mm×1.8 mm, and the active area of anode and cathode is 8 mm×8 mm. The performance of the μ-DMFC is assessed at ambient temperature using the oxygen of the air as the oxidant. The tests are carried out at different concentrations of methanol solution. The result shows that the high performance appears at 1－2 mol/L methanol solution. The μ-DMFC based on MEMS under 1.5 mol/L methanol solution at room temperature is measured, and its peak power density achieves 5.9 mW/cm^2 as shown in Fig. 4.

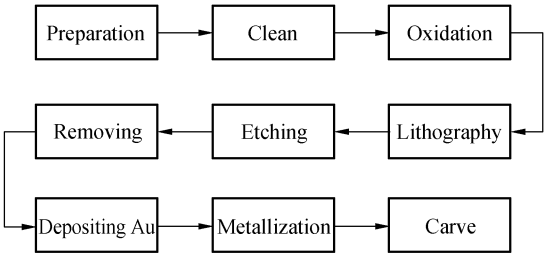

Fig. 2 Fabrication process of silicon μ-DMFC

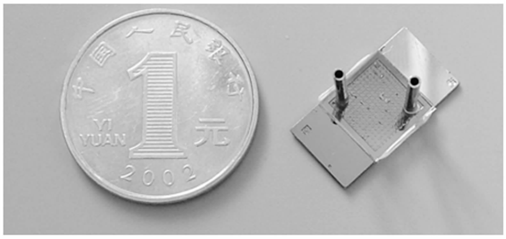

Fig. 3 Prototype photo of silicon μ-DMFC

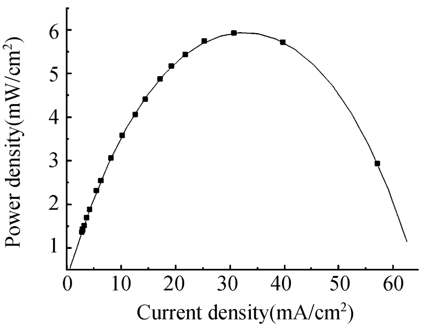

Fig. 4 Characteristic of silicon μ-DMFC

4 Fabrication of μ-DMFC based on non-silicon technology

It is found that the silicon anode plate may be splitted when the μ-DMFC works for very long time. The reason is that the silicon wafer is rather brittle to be disintegrated. If the μ-DMFC works for longer time, the MEA will absorb more water. The MEA swells large enough to break the silicon anode plate, so the metal mould is fabricated to stamp the anode and cathode plates of μ-DMFC with stainless steel. According to packaging a silicon-based μ-DMFC, the anode, MEA and the cathode are sandwiched to manufacture the μ-DMFC based on stainless steel as shown in Fig. 5. The μ-DMFC under 1.5 mol/L methanol solution at room temperature is measured, and the maximum power density achieves 15.8 mW/cm^2 as shown in Fig. 6.

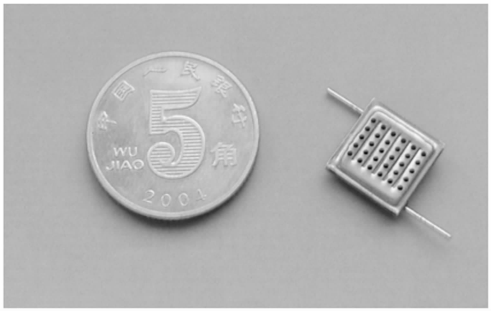

Fig. 5 Photo of μ-DMFC based on non-silicon technology

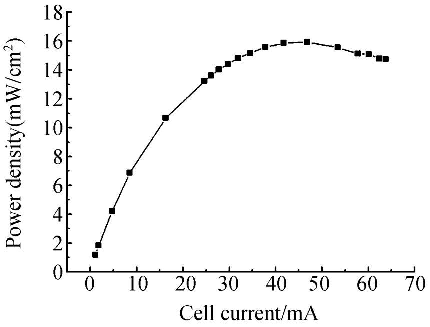

Fig. 6 Characteristic of stainless steel μ-DMFC

A comparison of performance of μ-DMFC cells based on silicon and based on stainless steel is shown in Fig. 7. Obviously, the performance of the cell made of the stainless steel plates is better than that made of the silicon plates, and the peak power density of stainless steel μ-DMFC is three times that of silicon-based μ-DMFC approximately. Using stainless steel as the plates of μ-DMFC, we can reduce the internal resistance and can improve the performance of μ-DMFC.

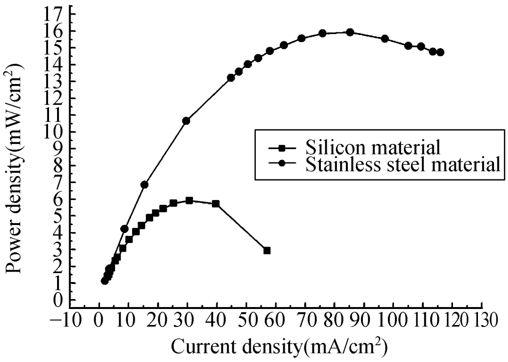

Fig. 7 Comparison of micro DMFC with different substrate materials

5 Conclusions

The μ-DMFC is fabricated on the silicon and stainless steel substrates respectively using the MEMS technology in this paper. The silicon-based μ-DMFC can not be packaged to cause higher internal resistances because of the brittleness of silicon. So the μ-DMFC based on the

stainless steel is completed using the micromachining technology. The μ-DMFC under 1.5 mol/L methanol solution at room temperature is measured, and the peak power density achieves 15.8 mW/cm^2. The μ-DMFC realized with the stainless steel can not only reduce the internal resistances greatly to improve the working performance, but also can be more suitable for the batch process than that of silicon-based technology.

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