

Micro and Nano Structured Reaction Chamber for High Efficiency Micro-DMFC

Chih-Hao Hsu, Yi-Shiuan Wu, *Fan-Gang Tseng, Chuen-Hung Tsai, and Ching-Chang Chieng
Engineering and System Science Department, National Tsing Hua University, Taiwan, ROC
*fangang@ess.nthu.edu.tw

Abstract

This paper proposes a novel chamber design for micro DMFC (Direct Methanol Fuel Cell) with the combination of micro and nano structures for the enhancement of reaction surface. The process combined micro porous Silicon thin film by angled DRIE with the growth of carbon nanotubes (CNTs) on the oblique surfaces to increase the reaction surface by 3-4 orders. By the loading of platinum nanoparticles on CNTs, this device would be applied to the anode or cathode in micro-DMFC. SEM images clearly showed well controlled 100- μm -deep micro wells with CNTs growth on the sidewall with a diameter of 31 nm and length of 5 μm . The testing of current density demonstrated a 1.8 times increment on the micro structured reaction surface for a surface ratio of 1.42 without CNTs. It is suggested that the reaction can be improved by orders of magnitude when both the micro structures and CNTs combine together.

Keywords: Micro DMFC, CNTs, Reaction chamber

1-Introduction

Carbon based (carbon paper, cloth, or graphite) electrodes are commonly employed in the reaction chamber of DMFC to support catalyst for reaction [1, 2]. To increase reaction surface and reduce catalyst loading, nano catalyst particles were deposited on CNTs [3, 4] grown on graphite surface instead of employing Pt thin film. However, the fabrication of graphite electrode is not compatible with MEMS structures for micro DMFC, and the loaded CNTs can only appear on the very top surfaces of the graphite electrodes, thus greatly deteriorate the loading efficiency of catalysts.

Besides, the formation of CO_2 bubbles at anode could block fuel liquid feeding and result in the decrease of cell performance [5, 6]. In this paper, we proposed a novel design to combine micro and nano structures for catalyst support. The reaction chamber would be thinner than conventional electrodes, which could not only shorten the distance for transportation of MeOH into reaction chamber but also provide more efficient diffusion path for proton exchange. The fabricated reaction chamber can also be easily coupled in micro fuel cell system.

2-Experimental

2.1-Design of the reaction chamber

The proposed reaction chamber is schematically shown in Fig.1. Methanol is transported into the angled micro holes with CNTs by capillary effect. Carbon dioxide, protons, and electrons will be generated on the inclined nano-structured surface through catalytic reaction. The combination of micro and nano structures would enhance the transportation path

and increase the reaction area of methanol to improve the efficiency of fuel usage.

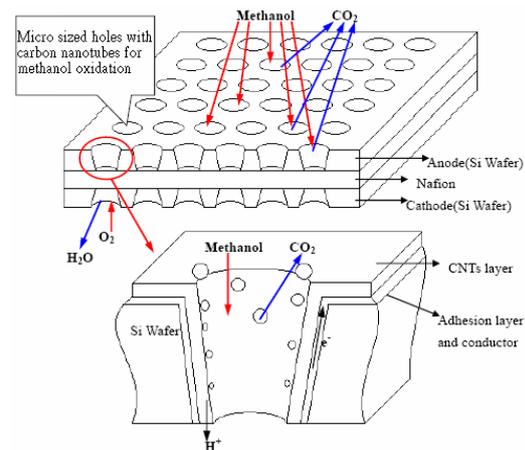


Fig.1 Schematic of the micro-/nano-structured reaction chamber for DMFC.

The increment of reaction area by micro holes with angled walls can be estimated by equation (1)-(3). The surface area of a single micro hole with angled walls can be expressed as:

$$2XD/\cos\theta + 2\pi(r + \Delta x)D/\cos\theta \quad (1)$$

Where X , D , $2r$, Δx , and θ are the length, depth, width, undercut, wall angle of the micro hole, respectively.

The total surface area of the 3D structure was compared with a plane with the same projection area, and the ratio is denoted as R .

$$R = \frac{[2XD/\cos\theta + 2\pi(r+\Delta x)D/\cos\theta]*N}{A(=5000*5000)} \quad (2)$$

$$N = [5000/(2r+2\Delta x)][5000/(X+2r+2\Delta x)] \quad (3)$$

Where A is the total area of the projection plane.

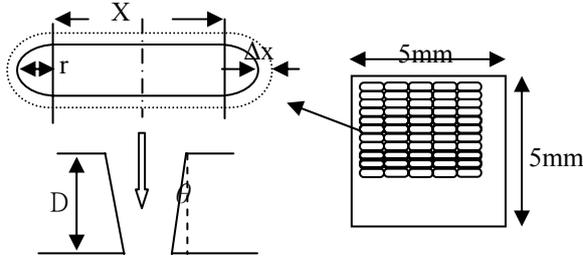


Fig.2 Schematic of the micro hole with angled wall.

Given $D=100\mu\text{m}$, $\Delta x=20\mu\text{m}$, and $\theta=15^\circ$, the relationship between surface ratio R and hole width $2r$ can be expressed in Fig. 3. The smaller width of the holes the larger surface area could be obtained. However, the resolution of micro fabrication and the volume required for the accommodation of CNTs as well proton exchange membrane would keep the hole size in micro scale. When the width of holes is reduced to $3\mu\text{m}$, the surface ratio R approaches 7.

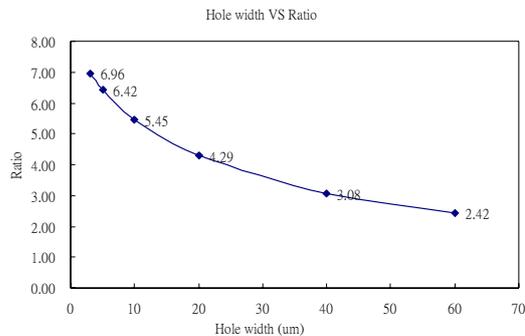


Fig.3 The relationship between the surface ratio R and the width $2r$ of the wall.

2.2-Fabrication process of the reaction chamber

The fabrication process of the device is shown in Fig. 4. Photoresist was patterned on a bare (100) Si wafers (4a) for the first DRIE etching process to form micro holes with oblique walls at 75° (4b). Then, back side DRIE etching was performed to release the micro porous film as the backbone structure of the reaction chamber (4c and 4d). The thickness of the porous Si thin film was fabricated 100 micron in the

current research.

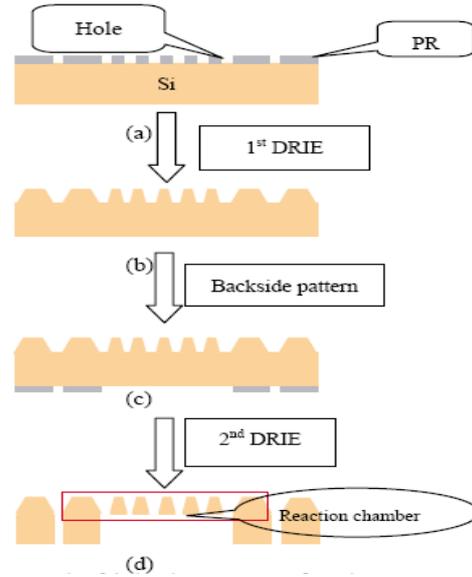


Fig.4 Fabrication process of the reaction chamber

Afterward, 1.5 nm thick Fe thin film was sputtered on the device surface and inside the holes. Finally, CNTs were grown by Thermal-CVD process on the device. The complete micro-nano structures were characterized by scanning electron microscope (SEM). The electrochemical properties of the reaction device without CNTs was tested by cyclic voltammetry (CV) with 0.5M H_2SO_4 and 1M MeOH solution as electrolyte at 28°C and 1atm.

3-Results and discussions

3.1-CNTs grown in micro holes

Figure 5 shows the fabricated reaction chamber with a hole width of $130\mu\text{m}$ and length of $270\mu\text{m}$ and coated with 1.5nm Fe layer. After Thermal-CVD process, dense CNTs can be observed. The length and diameter of the CNTs on the oblique sidewalls can be estimated with a diameter of 31 nm, length of $5\mu\text{m}$, and density of 10^{10} - $10^{11}/\text{cm}^2$, respectively.

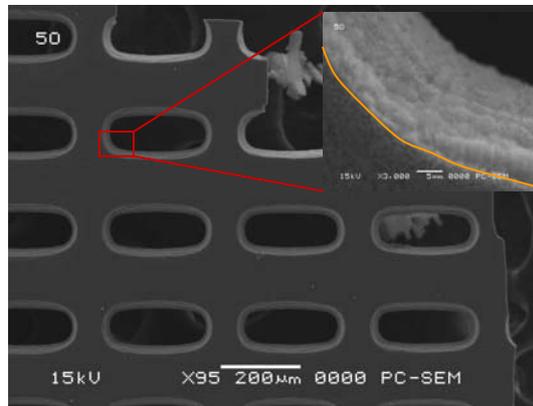


Fig. 5 SEM image of the holes on the porous silicon film with $X=270\mu\text{m}$ and $2r=130\mu\text{m}$. The inset depicts the close-up of the side wall.

The estimated surface area is about $1400 \text{ cm}^2/\text{cm}^2$, which is about 3 orders of magnitude larger than that of a plane surface.

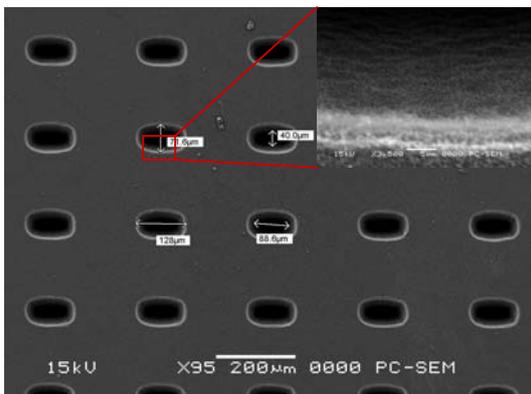


Fig. 6 SEM image of the holes on the porous silicon film with $X=130\mu\text{m}$ and $r=70 \mu\text{m}$. The inset depicts the close-up of the side wall.

Figure 6 shows the fabricated reaction chamber with a hole width of $70 \mu\text{m}$ and length of $130 \mu\text{m}$ and coated with 4.5nm Fe layer and 10nm Al layer with dense CNTs. Fe layer has poor adhesion with Si substrate. As a result, Al thin layer will be employed to promote the adhesion and serve as the electron conductive layer.

3.2-Cyclic Voltammetry

The completed reaction device with a total dimension of $1\text{cm} \times 1\text{cm}$ and the effective reaction area $0.45\text{cm} \times 0.45\text{cm}$ at the center of the device is shown in Fig. 7. Pt $10\text{nm}/\text{Ti}$ 10nm was deposited on the reaction chamber and the device was covered by anti-corrosive tape on the border for electrochemical test.

Table 1 shows the CV test results of difference devices. Sample A contains only a plane surface with an area 0.2025 cm^2 and the surface area ratio is denoted as 1. A-1 to A-3 represent structured devices with calculated surface area ratio from 1.42 to 1.52, respectively.

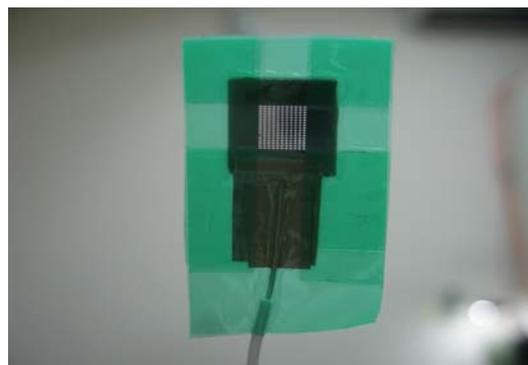


Fig. 7 The OM picture of the completed device for CV test

The peak current density ratios depicts similar trend to the surface area ratios, but the values are higher. The possible reason may come from the porous micro structures similar to a mesh, which can create local turbulence to promote gas transportation [6]. This nature incorporated with the hydrophilic surface property can also enhance methanol transportation throughout the reaction chamber.

In addition, from the current density result, the activity of the platinum catalyst for sample A can also be characterized as $0.1\text{A}/\text{mg}$, based on a 10nm thick Pt layer with a loading of $0.02\text{mg}/\text{cm}^2$. This result demonstrates a decent activity of Pt catalyst in this device when compared to electrodeposition method.

4-Conclusion

In this paper, porous silicon thin film with micro and nano structures was designed and fabricated for μDMFC for the enhancement of reaction area and fuel transportation property. CNTs were successfully grown on the sidewall of the holes with an aspect ratio ~ 2 . The surface area of the micro-structured device without/with CNTs was about 1.5 times or 3 order magnitude higher than that of a plane surface. The CV test results showed that the structured device had higher catalytic efficiency. The future work will optimize the design of the hole size and the surface area ratio to approach 7. And the CV test of micro structure with CNTs will be conducted

Table 1 CV test results of difference devices

sample name	peak current (A)	peak current density (mA/cm^2)	Peak potential (V)	Peak current density ratio	Hole Width (μm)	Hole Length (μm)	Surface area ratio
A	4.57×10^{-4}	1.92	0.59	1	n/a	n/a	1
A-1	6.998×10^{-4}	3.46	0.61	1.80	130	370	1.42
A-2	6.764×10^{-4}	3.34	0.62	1.74	120	300	1.43
A-3	6.647×10^{-4}	3.28	0.61	1.71	110	260	1.52

afterward.

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Acknowledgements

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