NANO CNTS AND MICRO ELLIPTICAL HOLES SUPPORTED Pt CATALYST FOR HIGH PERFORMANCE µDMFC

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Abstract: This paper proposes a novel reaction device for µDMFC with the combination of micro and nano structures for the enhancement of reaction area. The device combined micro porous Si thin film by DRIE with the growth of vertically-aligned CNTs (VACNTs) on the surfaces of micro holes to further increase the reaction area by 2~3 orders of magnitude. SEM clearly showed well controlled 50~80-µm-deep micro holes with CNTs growth on the sidewalls with the diameters of 80~100 nm and lengths of 5~12 µm. Pt particles deposited on CNTs by chemical reduction method can dramatically increase active sites of methanol oxidation in anodic half-cell system. It is demonstrated that the reaction performance is also improved dramatically when both the micro structures and CNTs are combined together.

Key words: reaction device, VACNTs, chemical reduction, anodic half-cell

1. INTRODUCTION

In DMFC, carbon-based electrodes were commonly employed as catalyst supports for reactions [1-3]. To increase reaction area as well as reduce catalyst loading and prevent corrosion, nano-catalysts were deposited on CNTs [4-6] grown on carbon paper/cloth, or graphite surface instead of the employment of Pt thin film. However, the fabrication of these conventional electrodes is not compatible with MEMS for µDMFC, since the loaded CNTs can only appear on the top surfaces of graphite, posing a longer pathway for methanol diffusion inside the structures of carbon-based electrodes thus greatly deteriorating the loading and reaction efficiency of catalysts. Therefore, we proposed a novel design to combine micro and nano structures for catalyst support and the fabricated device can be easily coupled in µDMFC.

2. EXPERIMENTAL
2.1 Design and fabrication of reaction device

We proposed a 3D design of micro reaction device for µDMFC and the devices were fabricated on a 4" Si wafer, as shown in Fig. 1 (a), which may utilize micro-holes coupled with CNTs (form of the diverging micro holes) to easily vent CO_2 gas produced during an oxidation of methanol in the anode [7], and the combination of micro and nano structures would enhance the transportation path and increase the reaction area of methanol to improve the efficiency [8].

The proposed micro reaction device is drawn in Fig. 1 (b). The increment of reaction area by micro holes with vertical sidewalls can be estimated by Eqs.

(1) to (4). The surface area of a single micro hole with vertical sidewall (A_s) can be expressed as

$$A_s = 2\ell d + 2\pi rd. \tag{1}$$

where ℓ, d, and 2r are the length, depth, and width of a micro hole, respectively. The total surface area of the reaction device was compared with a plane with the same projection area, and the surface area ratio (R_s) is calculated as

$$R_s = \frac{(2\ell d + 2\pi rd) \times n}{A}, \tag{2}$$

$$A = L \times W, \tag{3}$$

$$n = [L/(2r + \ell)] \times (W/2r). \tag{4}$$

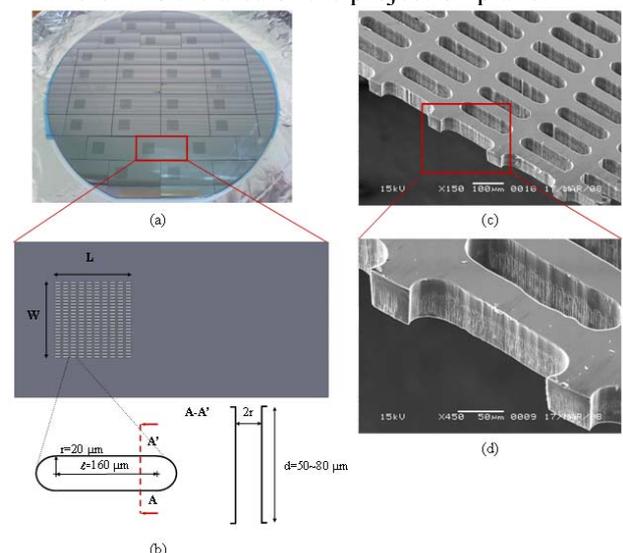where A is the area of the projection plane.

Fig. 1 schematic diagram of the micro devices and SEM micrographs of micro elliptical holes with vertical sidewalls

Given d, the relationship between surface area ratio and hole width can be calculated: 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 40 μm, the surface area ratio can approach 2.15 (d=80 μm). The fabrication process of the device is illustrated in Fig. 2, starting with the elliptical wells by two steps of deep Si RIE. The lithography is operated on a bare (100) Si wafer, and the fabrication process of the device is depicted as follows: the PR was patterned on the backside of a Si wafer for the first DRIE etching to release the micro porous film as the backbone structure of the reaction device (a) and (b). Then, front side DRIE etching was performed to form micro holes with vertical sidewalls (c). The thickness of the porous Si thin film was fabricated about 50~80 μm (d) and the fabricated micro holes are shown in Fig. 1 (c) and (d).
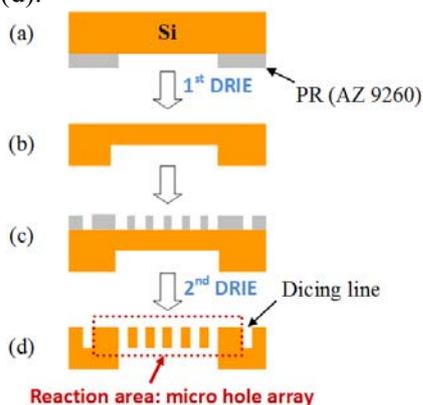

Fig. 2 fabrication process of the micro device

2.2 CNTs synthesis and characterization

The catalyst film was deposited by sputter on the plane surface and inside the holes of the micro device. In this case, Ni/Al/Ti thin films were respectively deposited as the catalyst/electron conduction/adhesion layers for CNTs growth on both bare Si plate and porous substrates. The CNTs were synthesized via thermal CVD by introducing a mixture of ammonia (NH_3) and ethylene (C_2H_4) at 800 °C at atmospheric pressure, and thus the CNTs/Ni/Al/Ti/bare Si (CNTs/Si-based) plate and porous electrodes can be obtained [9]. Then, the morphology and detailed micro structure with CNTs were investigated by SEM (JEOL JSM-6380).

2.3 Pretreatment and preparation of CNTs-supported Pt catalysts

After the CNTs growth, the hydrophilic treatment of CNTs was conducted in 6 M H_2SO_4 at 80 °C for 1 h. The synthesis of Pt colloid was carried out in ethylene glycol solution [10]. Then, Pt supported on CNTs, denoted as Pt/CNTs, was obtained and Pt loading on CNTs was confirmed by inductively coupled plasma-mass spectrometer (ICP-MS, Perkin Elmer，SCIEX ELAN 5000). Finally, the micro-nano structures were characterized by SEM (Hitachi-S4800 FE-SEM), and TEM (JEOL JEM-2010, LaB_6).

2.4 Electrochemical evaluation

All electrochemical measurements were performed in a three-electrode electrochemical cell at room temperature and the related setup is shown in Fig. 3 [11]. For the preparation of working electrodes, the reaction area of the Pt/CNTs/Si-based plate and porous catalysts were defined as 1 cm^2 and 0.25 cm^2, respectively. A Pt mesh and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. N_2 gas was purged for the removal of dissolved oxygen in the electrolytes before the experiment started. First, the characteristics of the two electrodes were measured by CV (cyclic voltammetry, potential scan range: -0.25 to 1.0 V, electrolyte: 0.5 M H_2SO_4 aqueous solution, and scan rate: 50 mV/s). In this paper, all voltammograms refer to the features in the fifth cycle, where steady-state response was obtained.
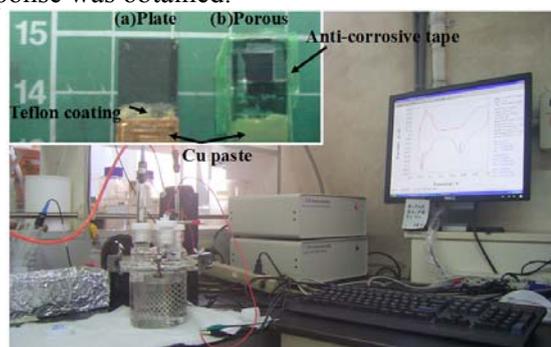

Fig. 3 image of the electrochemical measurement system. Inset: Pt/CNTs/Si-based electrodes [11]

For the performance analysis of anodic half-cell, the CV (potential scan range: -0.2 to 0.9 V, and scan rate: 20 mV/s) and potentiostatic method for 1 M CH_3OH + 0.5 M H_2SO_4 aqueous solutions was used to measure electrocatalytic properties of Pt catalysts and specific activity from the oxidation of methanol can be characterized. All experiments were carried out at room temperature at atmospheric pressure. The reaction area was defined and covered by anti-corrosive tape on the border for electrochemical test, as shown in Fig. 3 inset.

3. RESULTS AND DISCUSSION

3.1 Preparation of nano- and micro-nano structures

Two different electrodes were prepared: one with Pt/CNTs on flat Si substrate (Pt/CNTs/Si-based plate),

and the other with Pt/CNTs inside porous Si substrate (Pt/CNTs/Si-based porous). In Fig. 4 (a), the width and length of the fabricated reaction holes with vertical sidewalls by DRIE were 40 μm and 160 μm and followed by sputtering deposition of Ni/Al/Ti layers respectively on the micro porous substrate. After thermal CVD, dense CNTs can be observed on the plane surface (c) and the sidewalls of the micro holes (d). The length and diameter of the CNTs inside the holes can be measured with a diameter of 80~100 nm, length of 5~12 μm, and density of 10^{10}~10^{11}/cm^2, respectively. In addition, the CNTs inside the micro hole from top to bottom had a gradient distribution of length to form a diverging micro reaction hole, as shown in Fig. 4 (b).
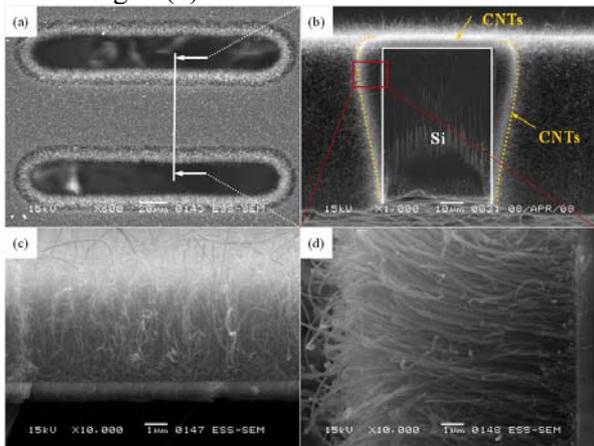

Fig. 4 SEM details of the micro device with CNTs growth inside the holes: (a)top view, (b)cross sectional view of the micro holes, (c)the CNTs growth on the plane surface and (d)on the sidewall of the micro hole.

3.2 Electrosorption of hydrogen on Platinum

Pt particles were successfully deposited on the CNTs/Si-based electrodes by chemical reduction. The voltammograms shown in Fig. 5 inset are similar to that of a polycrystalline Pt electrode reported by Vielstich [12]. Peaks for the hydrogen redox reaction in the negative potential region and the redox reactions of oxygen-like species on Pt surface in the positive potential region can be clearly seen.
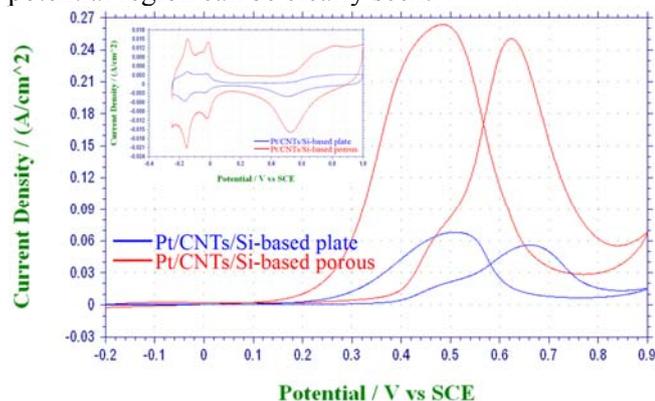

Fig. 5 The comparisons of peak potential and peak current density for the two different electrodes. Inset: Hydrogen

electrosorpion voltammetric profiles for the (a)Pt/CNTs/Si-based plate (blue line), and (b)Pt/CNTs/Si-based porous catalysts (red line).

3.3 Half-cell performance analysis

Fig. 5 shows the CV measurements for the two different electrocatalysts, Pt/CNTs/Si-based plate and porous catalysts, respectively. The peak potential/peak current density for methanol oxidation on the plate and porous catalysts are respectively 0.660 V/56.2 mA/cm^2 and 0.624 V/250.4 mA/cm^2, demonstrating 4.5 times higher current density (specific activity) achieved on the combination of CNTs with Si micro wells for Pt support. Based on the volume of catalyst deposited onto the surface of CNTs with the same projection area of 0.25 cm^2, the Pt loading on the Pt/CNTs/Si-based plate and porous catalysts were respectively measured to be 0.025 mg/cm^2 and 0.117 mg/cm^2 by ICP-MS, exhibiting 4.7 times higher Pt catalyst loading resulted from much more active Pt surface area on the micro Si porous device with CNTs. On the other hand, the mass activity of Pt for the Pt/CNTs/Si-based plate and porous catalysts are similar through the calculations of current density represented by mass: 0.561 A/mg and 0.534 A/mg, respectively, suggesting the mass catalytic activity on different electrodes for the electrooxidation of CH$_3$OH is almost the same.

3.4 Particle size and distribution of Pt on CNTs

The Pt nanoscale details on the surface of the catalyst-supported CNTs for the Pt/CNTs/Si-based plate and Pt/CNTs/Si-based porous catalysts were respectively investigated in Fig. 6(a) and Fig. 7(a) using TEM and EDS. From the low magnification TEM images, it is visible that the deposited Pt nanoparticles, which can provide reaction sites for the electrooxidation of methanol, were distributed on the entire surface from top to base ends of the CNTs. The size distributions of Pt particles on CNTs for the plate and porous electrodes were also obtained by direct measuring over 100 particles from high magnification TEM micrographs, and the corresponding histograms of which were shown in Fig. 6(b) and Fig. 7(b), respectively. These results showed that the particle size distribution of the most spherical Pt particles deposited on CNTs for the plate and porous electrodes were similar. The mean size of Pt nanoparticles was estimated to be 4~5 nm for the two Pt/CNTs/Si-based catalysts.
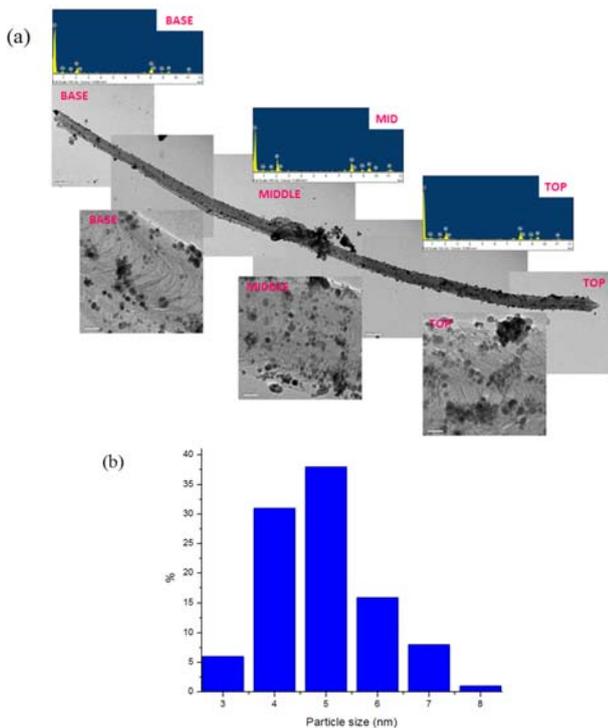
Fig. 6(a)TEM and EDS analysis of Pt particles deposited on CNTs/Si-based plate electrode, and (b) the corresponding histogram of the size distribution of Pt particle.
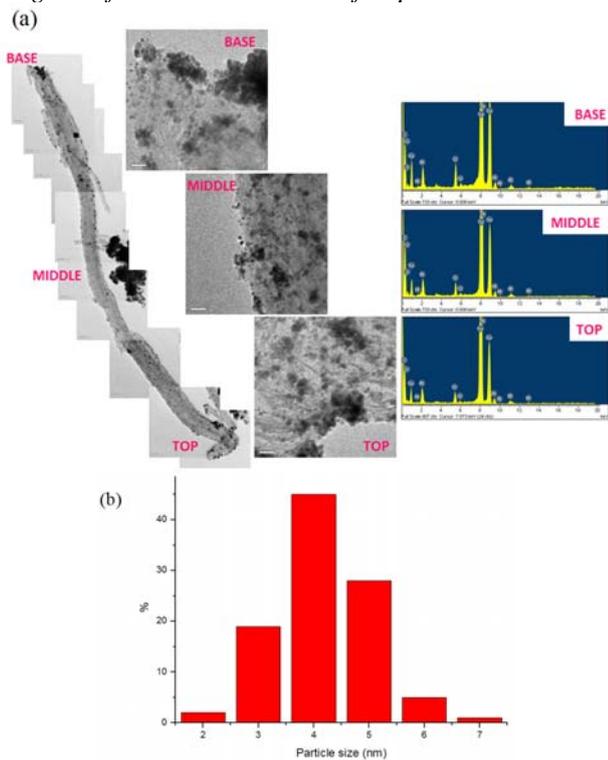

Fig. 7(a)TEM and EDS analysis of Pt particles deposited on CNTs/Si-based porous electrode, and (b)the corresponding histogram of the size distribution of Pt particle.

4. CONCLUSIONS

In this paper, the novel porous Si thin film device with micro and nano structures was designed and fabricated for the enhancement of reaction area in µDMFC. The specific surface area of the micro porous device without CNTs was about 2 times higher than that of a plate substrate. The vertically-aligned CNTs were directly grown on the plane surfaces and sidewalls of the fabricated micro holes by thermal CVD. For the preparation of electrocatalysts, Pt particles were deposited on the entire surface of the CNTs for the CNTs/Si-based electrodes by chemical reduction. The CV results showed that the porous catalyst had higher electrocatalytic activity, which can achieve 4.5 times higher than that of the plate catalyst [13]. Furthermore, the Pt/CNTs/Si-based porous catalyst using a low catalyst loading of 0.117 mg/cm^2 performed as a superior anode from excellent electrochemical activity of methanol oxidation [14]. The higher catalytic performance of the porous catalyst is attributable to much more active surface area of Pt resulted from higher catalyst loading compared to the plate catalyst. From the experimental results, the Pt/CNTs/Si-based porous catalyst is suitable not only in methanol electrooxidation but also as an anode electrode in µDMFCs.

REFERENCES

[1] Shimizu T et al. 2004 Design and fabrication of pumpless small direct methanol fuel cells for portable applications *J. Power Sources* **137** 277–283

[2] Lu G Q et al. 2004 Electrochemical and flow characterization of a direct methanol fuel cell *J. Power Sources* **134** 33-40

[3] Mathias M F et al. 2003 *Handbook of fuel cells—fundamental, technology and application* (Wiley Publishing)

[4] Tang H et al. 2004 High dispersion and electrocatalytic properties of platinum on well-aligned CNT arrays *Carbon* **42** 191-197

[5] Han K I et al. 2004 Studies on the anode catalysts of carbon nanotube for DMFC *Electrochim. Acta* **50** 791-794

[6] Li L et al. 2008 Electrochemical durability of carbon nanotubes at 80°C *J. Power Sources* **178** 75–79

[7] Hwang J J et al. 2005 Ethanol-CO$_2$ Two-phase Flow in Diverging and Converging Microchannels *Int. J. Multiphas. Flow* **31** 548-570

[8] Hsu C H et al. 2006 Micro and nano structured reaction chamber for high efficiency micro-DMFC *Technical Digest of PowerMEMS 2006 (UC Berkeley, USA, 29 November-1 December 2006)* 211-214

[9] Juang Z Y et al. 2004 On the kinetics of carbon nanotube growth by thermal CVD method *Diamond & Related Materials* **13** 2140-2146

[10] Bock C et al. 2004 Size-selected synthesis of PtRu nano-catalysts: reaction and size control mechanism *J. Am. Chem. Soc.* **126** 8028-8037

[11] Wang S K et al. 2007 Electrocatalytic properties improvement using carbon-nanotubes implantation with platinum coating on buffer substrate *J. Power Sources* **167** 413–419

[12] Vielstich W et al. 2003 *Handbook of fuel cells-fundamentals, technology and applications* (New York, John Wiley & Sons Publishing)

[13] Liu H et al. 2006 A review of anode catalysis in the DMFC *J. Power Sources* **155** 95–110

[14] Liu Z et al. 2007 Pt and PtRu nanoparticles deposited on single-wall CNTs for methanol electro-oxidation *J. Power Sources* **167** 272–280