EFFECTS OF NANOIMPRINT PATTERNS ON PERFORMANCE OF PASSIVE MEMS-BASED DIRECT METHANOL FUEL CELL

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Abstract: This paper presents our recent effort on application of nanoimprint technology into passive MEMS-based direct methanol fuel cell (DMFC) for chip-scale power-embedded system. We fabricated and characterized five kinds of micro DMFC with different nanoimprint pattern and catalyst layers. It was found that the measured fuel cell performance varied with the nanoimprinted patterns because they affected the continuity of the catalyst layer. The performance was the compromising between the nanoimprint pattern and the catalyst layer. This was mainly correlated to that the catalyst layer functioned as the current collector in the prepared micro DMFCs.

Key Words: Micro direct methanol fuel cell; nanoimprint; MEMS

1. INTRODUCTION

DMFC has inherent advantages over other battery technologies in particular for portable electronics application from the viewpoint of energy density and easy-to-recharge character [1]. Traditional DMFC and other proton exchange membrane fuel cell (PEMFC) generally consist of mechanically compressed sandwiches of graphite-based porous electrodes and proton exchange membrane. The sandwich structure, however, cannot be simply scaled down to fit into a form factor appreciated for portable electronic application because of fundamental difference introduced by changing the system size [2]. It is difficult to integrate graphite-based porous electrodes into micro DMFC by MEMS and microelectronic technology for distributed micro-sensors and other wireless application because of poor compatibility [2, 3]. Graphite-based porous electrodes, however, are necessary for forming triple-phase reaction interface between catalyst, electrolyte and fuels, which dominantly determines fuel cell performance. Consequently, MEMS-based DMFC shows much poorer performance than traditional DMFC [2, 4-5]. There is considerable interest in developing novel MEMS-based porous structures and materials to replace the graphite-based porous electrodes for facilitating the triple-phase reaction interface in the MEMS-based DMFC.

We recently succeeded in applying nanoimprint technology into passive MEMS-based micro DMFC [6]. The nanoimprinted micro DMFC has much higher open circuit voltage (OCV) and maximum power density (MPD) than literature results. The previous work [6] demonstrated that the nanoimprint technology is an excellent alternative to the traditional graphite-based porous electrode for developing high performance MEMS-based DMFC. In this work, we would extensively investigate the effects of different nanoimprint patterns on the performance of passive MEMS-based DMFCs. In addition, it is known that the catalyst efficiency is among the most important keys to high fuel cell performance. The catalyst efficiency has strong dependencies on the porous electrode. It could be inferred that the catalyst efficiency would also have strong dependency on the nanoimprint patterns formed on proton exchange membrane. As a result, we would investigate the dependencies through using Pt films with different thicknesses.

2. EXPERIMENTAL

Three kinds of nanoimprint pattern would be utilized in this work. Table 1 lists the pattern parameters. Nanoimprint moulds were made of silicon. Figure 1 (a) shows representative image of the prepared moulds. The bright area was the patterned area.

Nafion® 117 membrane was used as proton exchange membrane. The as-received Nafion® 117 membrane was treated as follows. Firstly, it was boiled in 10 wt% H_2O_2 for 2 hour at 80^{o}C and rinsed in de-ionized water at 80^{o}C for 1 hour. Then the membrane was immersed in 10 wt%

H_2SO_4 at 80°C for 1 hour and finally cleaned in de-ionized water at 80°C for 1 hour. The nanoimprint of Nafion® 117 membrane was performed in a desktop thermal nanoimprint system (NI273, Nano Craft Tech. Corp., Japan) under the load of 30 MPa at 130°C. The de-moulding temperature was 60°C. Figure 1 (b) is optical image of the nanoimprinted membrane.

Table 1 Pattern parameters and thickness of Pt catalyst layer for the prepared micro DMFCs.

	Bottom diameter of the convex	**Average height & spacing of the convex**	**Thickness of Pt film**
Cell 1	0.5 μm	0.06; 1 μm	20 nm
Cell 2	2 μm	0.8; 1 μm	20 nm
Cell 3	0.5 μm	0.06; 1 μm	20 nm
Cell 4	2 μm	0.8; 1 μm	50 nm
Cell 5	2 μm	0.8; 2 μm	50 nm

Figure 2 shows fabrication sequence of the MEMS-based micro DMFC. Trapezoid channel was prepared in silicon wafer by dry etching method (Fig. 2 (b)). The trapezoid channel was 260 μm wide at the top, 150 μm wide at the bottom and 80 μm deep. Figure 3 are views of the prepared separator and the trapezoid channel. 1 mm-in-diameter through hole was prepared from the back side for fuel inlets (Fig. 2 (c)). Thin Ti and Pt film (20 and 150 nm thick, respectively) were deposited at the front side for better electronic conductivity (Fig. 2. (d)). Then the nanoimprinted Nafion® 117 membrane was coated with thin Pt catalyst film and sandwiched with the prepared Pt-coated Si separator (Fig. 2 (e)). 20 and 50 nm-thick Pt films were used. Table 1 lists the parameters of the prepared micro DMFCs.

The prepared micro DMFCs were tested with a potentiostat (SI1287 Electrochemical Interface, Solartron) at room temperature. Aqueous 1 M methanol solution was fed into the cell through the through-hole with a syringe. When OCV reached a stable value, the cell performance was characterized from current-voltage (I-V) curves at a scan rate of 10 mV/s. We also examined the nanoimprint of Pt-coated Nafion® 117 membrane and corresponding micro DMFCs.

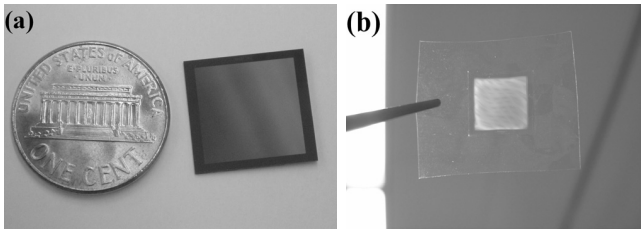


Fig. 1 View of (a) the prepared mould for the nanoimprint procedure and (b) the nanoimprinted Nafion® 117 membrane.

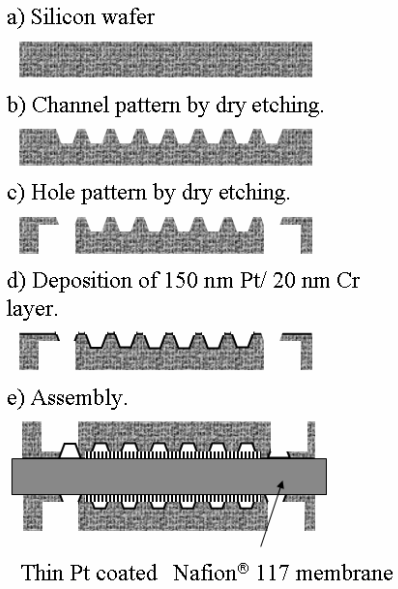


Fig. 2 Fabrication sequence of MEMS-based micro DMFC.

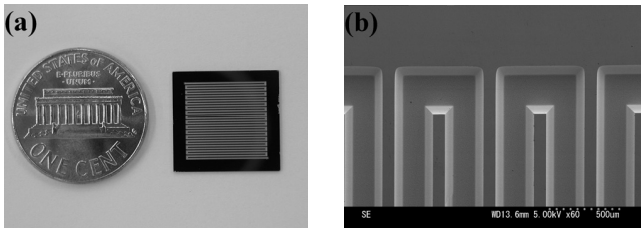


Fig. 3 (a) View of the prepared Pt-coated Si separator. (b) SEM image of the prepared trapezoid channel structure.

3. RESULTS AND DISCUSSION

Figure 4 are SEM images of the nanoimprinted patterns on Nafion® 117 membrane. Micro convex structures were formed and uniformly distributed on Nafion® 117 membrane. It is noteworthy that micro crack morphology was dominant in either

the nanoimprint or the unmodified area. It has been known that the micro crack morphology was resulted from the fracture of thin Pt film owing to large volume expansion and shrinkage of Nafion® membrane [7]. The micro crack morphology was important for high catalyst efficiency herebecause it assisted in providing surface sites for the triple-phase reaction interface between fuels, catalyst and electrolytes without the deterioration of electrical conductivity. The structure of the prepared micro DMFC here in particular required that it was necessary for the thin Pt film to keep continuity because it had the function of collecting electrical current.

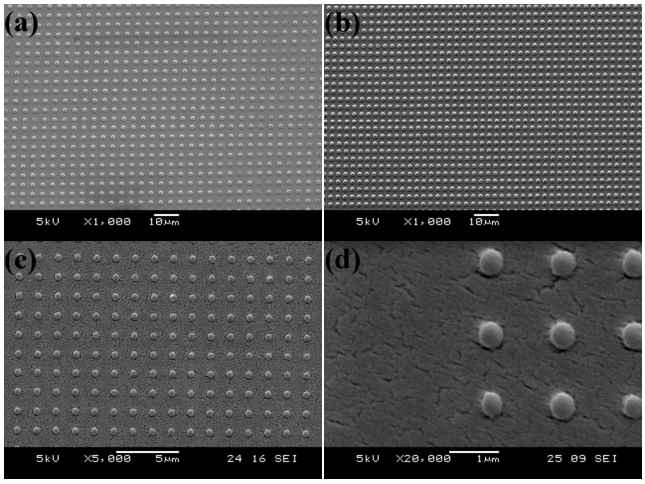
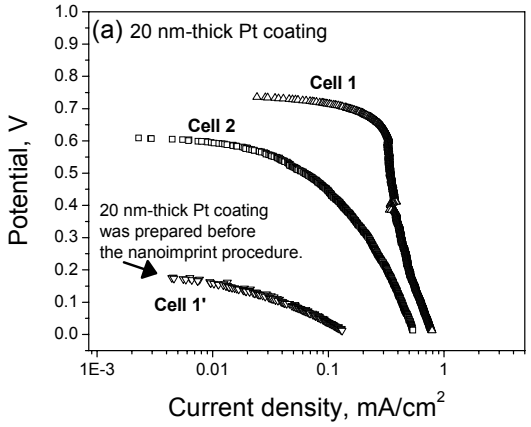
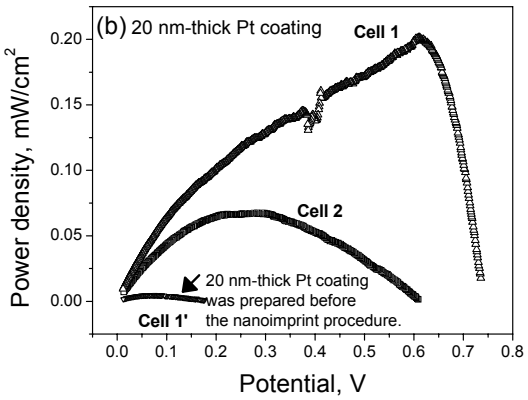
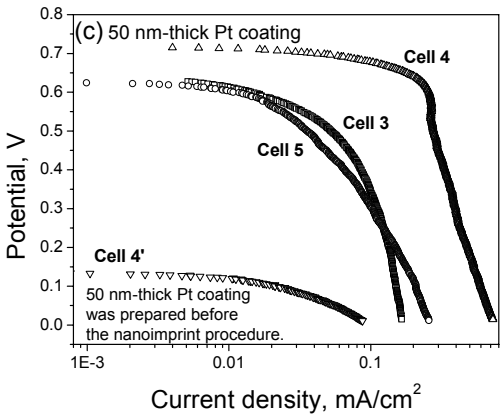


Fig. 4 SEM images of the nanoimprinted patterns consisting of micro convex with (a) 2 μm-in-diameter and 2 μm-in-spacing, (b) 2 μm-in-diameter and 1 μm-in-spacing, (c) and (d) 0.5 μm-in-diameter and 1 μm-in-spacing.







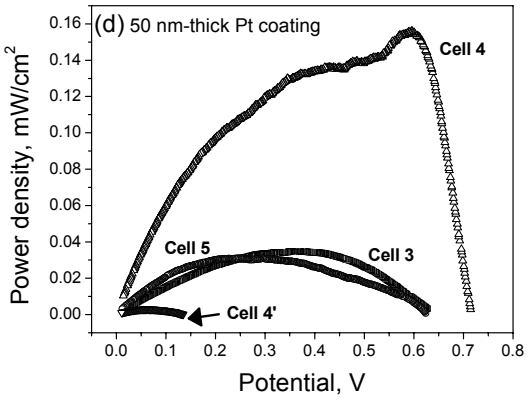


Fig. 5 *Measured performances of the prepared MEMS-based DMFCs. Cell 1′ and Cell 4′ were of the same nanoimprinted pattern as Cell 1 and 4 except that the nanoimprint procedure was after the deposition of Pt film.*

Figure 5 shows measured performance of the prepared MEMS-based micro DMFCs. When the Pt catalyst film was 20 nm thick, Cell 1 had the OCV of 0.74 V and the MPD of 0.2 mW/cm^2. Cell 2 had the OCV of 0.61 V and the MPD of

0.07 mW/cm^2. Cell 1′ only had the OCV of 0.18 V and negligible power output although the values were still within the literature reports on those MEMS-based DMFC without the graphite-based porous electrode [4-5]. The only difference between Cell 1 and 1′ was that the nanoimprint modification was performed after the deposition of Pt layer during the fabrication of the latter. When the Pt catalyst film was 50 nm thick, Cell 4 had the OCV of 0.72 V and the MPD of 0.16 mW/cm^2. Cell 3 and 5 had the OCV of 0.63 V and the MPD of 0.03 mW/cm^2 except that the MPD of the former was related to higher current density. Similar to Cell 1′, Cell 4′ had the OCV of 0.13 V and negligible power output. We had observed that the de-mold procedure became easier during the nanoimprint of the Pt-coated Nafion® 117 membrane. The thin Pt film would fracture during the nanoimprint procedure because the polymer deformation was localized in the micro convex pattern. Consequently, the thin Pt film became discontinuous and therefore could not properly play the role of current collector. In addition, the discontinued Pt film could not effectively assist in forming a continuous triple-phase reaction interface so that the reaction kinetics was low. As a result, Cell 1′ and 4′ had much poorer performance than their counterparts.

Cell 1 had the best performance although its surface enlargement was the least by the nanoimprint modification among the prepared micro DMFCs. Cell 3, however, that had the same nanoimprinted pattern and structure as Cell 1 except for the thicker Pt coating, had much poorer performance. Figure 5 demonstrated that the thicker Pt film was preferred for the nanoimprint pattern with large height aspect ratio (see Cell 1 and 3; Cell 2 and 4). It is known that the coverage of thin Pt film becomes poorer on the side wall of micro structure with larger height aspect ratio. With thicker Pt film, the side-wall coverage could be improved. However, if the Pt film was too thick, the fuel cell performance would decrease (see Cell 1 and 2). In other words, the measured performance was the compromising between the nanoimprinted pattern and the catalyst layer.

4. CONCLUSIONS

We extensively investigated the effects of the nanoimprinted pattern and the catalyst layer on the performance of the passive MEMS-based DMFC. The measured fuel cell performance had strong dependency not only on the nanoimprinted pattern but also on the thin catalyst layer. The thin Pt catalyst layer played the role of current collector in the prepared micro DMFCs so that its continuity was important for high fuel cell performance. This work showed that much better performance could be expected for the prepared MEMS-based micro DMFC if the nanoimprint patterns and the catalyst layers are optimized.

5. REFERENCES

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