MINIATURIZED SILICON-BASED DIRECT METHANOL FUEL CELL

Yi Zhang*, 1, Haoshen Zhou2, Toshihiro Itoh1, Ryutaro Maeda1

1Advanced Manufacturing Research Institute, National Institute of Advance Industrial Science and Technology (AIST), Tsukuba, Japan
2Energy Technology Research Institute, National Institute of Advance Industrial Science and Technology (AIST), Tsukuba, Japan

Abstract: This work presents design and characterization of a miniaturized silicon-based direct methanol fuel cell (DMFC). Three-phase reaction interface between catalyst, fuel and electrolyte is successfully formed by utilizing nanoimprint technology instead of conventional graphite-based porous electrodes. The prepared micro DMFC has an open circuit voltage (OCV) of about 0.51 V while the Pt catalyst load is only about 0.04mg/cm². The performance deterioration resulted from the silicon-based rigid package is also discussed. New package technology is necessary for enabling more compact and thinner micro DMFC in on-chip power application.

Key words: Micro fuel cell, nanoimprint, MEMS

1. INTRODUCTION

Direct methanol fuel cell (DMFC) is attractive for micro energy technology because of its inherent advantages including simple structure, easy-to-recharge character and abundant fuel resource [1]. Like other polymer electrolyte membrane fuel cell, DMFC consists of sandwiched structure of polymer electrode membrane with mechanically compressed porous electrodes. The porous electrodes have functions of catalyst support, fuel distribution and product purging [2]. The conventional porous electrodes are mainly made of graphite whisker-based porous material, which is also called carbon paper. As a matter of facts, the sandwiched structure can not be simply miniaturized by microfabrication technology for micro systems applications because there have not MEMS-based porous structure alternatives well enough to the carbon paper-based porous electrode [2-4]. Therefore, there are considerable interests in developing MEMS-based porous structures for micro DMFC and fuel cell applications [2-4].

Recently, we have successfully utilized nanoimprint technology in micro DMFC for high catalyst efficiency and high cell performance [5-6]. By using the nanoimprint technology, the prepared micro DMFC even has the cell performance comparable to some commercial membrane electrode assembly-based micro DMFCs without using the conventional porous electrodes [3]. However, a socket assembly technology is utilized in previous work. It is unknown what will be for the micro DMFC in an independent package. In this work, we would examine the micro DMFC in a traditional rigid Si-based package.

2. EXPERIMENTAL

Figure 1 is fabrication sequence of micro DMFC in this work. Si was used for the preparation of separators. The anode side had trapezoid channel structures for fuel distribution. The trapezoid channel was prepared by dry etching method and coated with 150 nm-thick Pt/20 nm-thick Cr film. The fabrication details were provided in our previous work [5-6].

Fig. 1 Fabrication sequence of micro DMFC.

The cathode side was made by the same process. The cathode side had the channel structure through the wafer with width of 280 µm for air breathing. It was also coated with the Pt/Cr film for better electric conductivity. Nafion 117 membrane was used as polymer electrolyte membrane. Micro pillar pattern (500 nm in diameter, 60 nm in height and 1 µm in spacing) was formed on the Nafion 117 membrane and coated with 20 nm-thick Pt film as catalyst. The nanoimprint process was mentioned in details in the
previous report [5-6]. Then the nanoimprinted polymer electrolyte membrane was directly sandwiched with the prepared Si-based electrodes by mechanical pressing at 6 MPa and fixed with epoxy material along the edge. Figure 2 is the schematic of the prepared micro DMFC. Figure 3 is the optical photo of the prepared micro DMFC.

The prepared DMFCs were characterized by using a potentiostat (SI1287 Electrochemical Interface, Solartron). Figure 4 is the experimental setup of the fuel cell test. 1 M methanol solution was introduced by using a syringe. Once the solution filled the whole anode side, no more operation would be done for the fuel circulation. When open circuit voltage (OCV) reached a stable value, the fuel cell performance was characterized from current-voltage (I-V) curves at a scan rate of 10 mV/s. A micro DMFC using the Nafion 117 membrane without the nanoimprint modification was also characterized for comparisons.

![Fig. 2 Schematic structure of the prepared micro DMFC.](image)

![Fig. 3 Photo of the prepared micro DMFCs.](image)

![Fig. 4 The experimental set up for fuel cell test.](image)

![Fig. 5 Measured performance of the prepared micro DMFCs.](image)

3. RESULTS AND DISCUSSION

Figure 5 is the measured cell performance for the prepared micro DMFCs. The unmodified micro DMFC has much lower performance. It has the OCV of about 0.12 V and negligible power output. In other words,
the fuel cell reaction was not well established in the unmodified micro DMFC. This is frequently encountered in those micro DMFCs without the presence of porous electrodes [2-4, 7-9]. For example, Onoe et al. [7] reported a MEMS-based micro DMFC with an OCV of about 0.15 V by using pure Pt catalyst and 1 M methanol solution. Sim et al. [8] reported a microfabricated micro DMFC with an OCV of 0.1 V. Seo and Cho [9] demonstrated a micro DMFC with an OCV of about 0.33 V and 0.056 mW/cm². This supported the conclusion that it is necessary to develop a MEMS-based porous structure for developing a ‘healthy’ micro DMFC.

The nanoimprinted micro DMFC showed much higher OCV than the unmodified one. The OCV was about 0.51 V. The maximum power density was 0.026 mW/cm². Although it is still within the literature range for micro DMFCs with planar electrodes, the micro DMFC prepared in this work has much poorer performance than our previous report [5-6]. The only difference is that a socket assembly is used in the previous report. It is also noteworthy that the measured cell potential dropped rapidly with increasing current density, suggesting that there was high internal resistance.

Figure 6 is the SEM images of the nanoimprinted Nafion 117 membrane before inserted into micro DMFC. Micro pillar structure was uniformly distributed on the membrane surface. Micro cracks were visible in the nanoimprinted surface (see Fig. 6 (b)). The crack morphology resulted from that thin Pt catalyst layer, which was used as catalyst and for free from charging in the SEM observation, had fractured because of the volume variation of Nafion membrane upon water absorption and desorption. Although there are many tiny cracks, the Pt film is still complete.

Figure 7 is the SEM image of the nanoimprinted membrane after the fuel cell test. The membrane became ripple after the fuel cell test. The ripple morphology showed that the Nafion 117 membrane had expanded into fluid channel upon water absorption during the fuel cell test. The volume change was limited by the rigid Si structure so that it was localized in the channels. It is found that there is still the ripple morphology even after long-time dry and vacuum treatment. SEM observation further showed that Pt film had fractured on the ripple structure while not on the flat part. In particularly, the fracture is more severe near the bottom of the ripple structure. It is obviously different from the membrane morphology formed in the socket assembly. Therefore, it could be inferred that the Pt film can not correctly play the function of current collector owing to the fracture. Although the high OCV (0.51 V) implied that the fuel cell reaction had been established, the generated charges could not
be effectively collected and transported to the external circuit. The fuel cell performance thus was poor. This could explain the rapid drop of the cell potential in Fig. 5.

4. CONCLUSION

In this work, nanoimprint technology is provided to be excellent candidate technology for replacing the conventional carbon paper-based porous electrode for more compact and thinner micro DMFC. High OCV had been achieved but the power output was still not satisfied owing to the fracture of the catalyst layer. It demonstrated that new package technology is necessary for accommodating the volume variation of polymer electrolyte membrane. Another solution is to develop MEMS-compatible polymer electrolyte materials for micro DMFC application, as pointed out by Nguyen and Chan [3].

REFERENCES