

Small PEMFC System with Multi-layered Microreactor

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Abstract

A small proton exchange membrane fuel cell (PEMFC) system with a multi-layered microreactor for methanol steam-reforming was prototyped as a power source for mobile electric applications. The multi-layered microreactor was designed using a computational simulation. It consists of four units: a methanol reformer with a catalytic combustor, a CO remover, and two vaporizers. The catalytic combustor for supplying reaction heat of reaction to other units was located on the top of microreactor. The microreactor was operated in a vacuum package to improve the system efficiency, and the suitable temperature distribution for the methanol steam-reforming was reached by supplying heat from the catalytic combustor. The small PEMFC has two humidifiers, which were composed of hollow fibers and a water holder. This system generated an output of approximately 2.5 W at 200 mA/cm².

Keywords: small PEMFC system, multi-layered microreactor, methanol steam-reforming, vacuum package, humidifier with hollow fibers

1 INTRODUCTION

Enhanced mobile electric applications lead to high electric power consumption and mass disposal of batteries. Therefore, we have needed high energy density and clean power source. Small PEMFC systems have attracted attention as a power source for mobile electric applications for potential to satisfy above requirements, and have been developed to replace conventional batteries. There are two types of small PEMFC systems at present: direct methanol fuel cells (DMFCs) and fuel reforming systems. Each type has its own problems. The DMFC systems have relatively low power density due to methanol cross-over and a low reaction rate of methanol oxidation over an anode electrocatalyst. On the other hand, although fuel reforming systems are in need of miniaturizing complicated reformers, these are able to obtain high power density compared to DMFCs. Therefore, we have been developing a fuel reforming PEMFC system with microreactors. These miniaturized microreactors are produced using a microfabrication technology. In previous studies, we carried out the H₂ production by methanol reforming using three microreactors, which consisted of a silicon and glass substrate, and the power generation using the 1 W class small PEMFC system [1, 2].

In this study, we have developed a multi-layered microreactor, which was integrated with several different functional reactors to improve the system efficiency, and tested the 2.5 W class power generation system to substantiate the possibility to drive digital gadgets, such as digital cameras.

2 DESIGN OF MICROREACTOR

The microreactor consists of four units: a methanol reformer with a catalytic combustor, a CO remover, and two vaporizers. The microreactor requires an appropriate temperature for each reaction. Therefore, the required dimensions for microreactors and microchannels were determined by the simulations of chemical reactions and thermal transfer including a radiation, using computational fluid dynamics (CFD). However, the design of vaporizer was optimized by experimental results. Each reaction heat was supplied from the catalytic combustor with the reformer. And the suitable temperature distribution for methanol reforming was established in a vacuum package, which was covered internally with Au thin film in order to prevent the radiant heat loss. The degree of vacuum was about 0.03 Pa, which prevent a heat transfer efficiently [3].

3 STRUCTURE OF MICROREACTOR

Figure 1 shows a photograph of the multi-layered microreactor developed in this study, and Figure 2 shows a structural diagram of this microreactor. Its external dimensions were 21 x 22 x 10.7 mm. The microreactor was constructed from thirteen glass substrates with serpentine microchannels and holes for gases passage, assembled using anodic bonding. The thermal insulating layer separated each unit thermally. Figure 3 shows the production processes of the microreactor. (a) Plate of glass containing Li ion was chosen as a substrate in order to connect each other easily by anodic bonding. (b, c) On one side of these glass plates, a Ta thin film as a bonding layer for anodic bonding, and an amorphous thin film of Ta-Si-O system which protects the Ta thin films from the damage by alkali-metal ions separating out to the surface, were sputtered. Further, a serpentine Au thin film heater, which was also used as a temperature gauge, was formed by sputtering and photolithography on the top substrate of each unit. Au is a suitable material for use as a temperature gauge because its electric resistivity changes linearly in the temperature range for microreactor operation. W and Ta films were formed between Au thin film and glass plate as a bonding layer for sputtering Au thin film. (d) All microchannels and holes for gases passage were formed by sandblasting. (e) The glass plate was then cut in several substrates with microchannels [4]. (f) The high-performance Cu/ZnO/Al₂O₃ catalyst, a commercial preferential oxidation of CO (PROX) catalyst, and a Pt (5 wt. %)/Al₂O₃ catalyst were deposited on the microchannel of the reformer, the CO remover, and the catalytic combustor, respectively. The high-performance Cu/ZnO/Al₂O₃ catalyst was developed by optimizing the conditions of temperature and pH during catalyst preparation, in our previous study [5, 6]. Before depositing each catalyst, an Al₂O₃ layer was formed on each microchannel by dip coating using Al₂O₃-sol in order to increase in the adhesive strength between the catalyst and the microchannel wall. (g) Each unit was assembled, and four units were then combined into a multi-layered microreactor by anodic bonding. The dimensions of microchannels are shown in Table 1, and these numeric values were decided based on the simulation results.

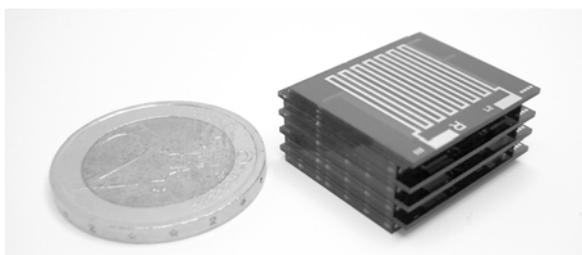


Figure 1. Photograph of microreactor

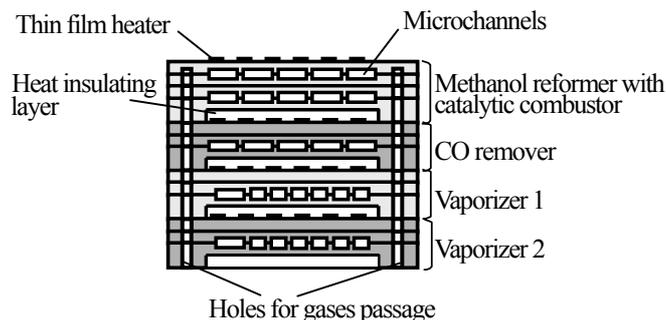


Figure 2. Structure of microreactor

Table 1. Dimensions of microchannels / mm

	Width	Depth	Length
Catalytic combustor	1.8	0.8	87.7
Reformer	1.8	0.8	95.6
CO remover	1.8	0.8	98.2
Vaporizer 1 and 2	A unique shape		

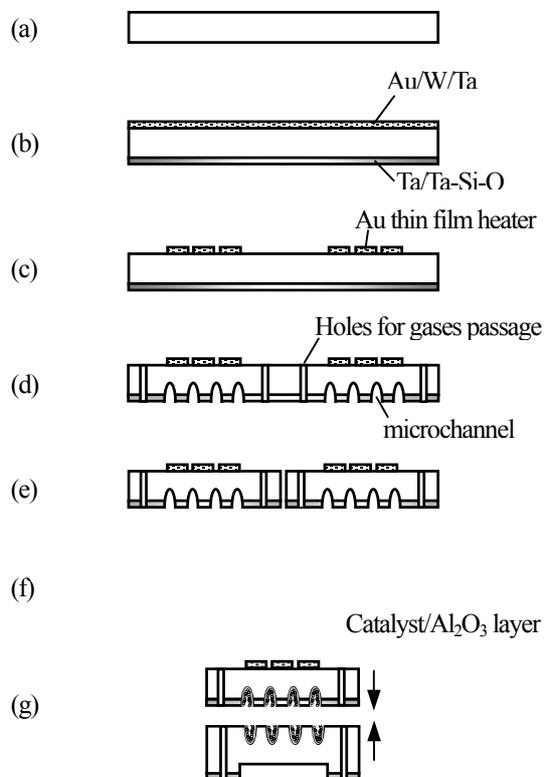


Figure 3. Production processes of microreactor

4 STRUCTURE OF PEMFC

The small PEMFC was stacked with four cells. Its size was 65 x 18 x 6.2 mm. The size was coordinated with the dimension of conventional Li ion secondary battery for a notebook PC (65 x Φ 18 mm). Figure 4 shows an outside view of the small PEMFC with humidifiers. Two humidifiers, which were composed of a hollow fiber module and a water holder, were joined to the current collectors on both the anode and cathode side. A reformat and air were fed to anode and cathode electrodes through inner side of the hollow fibers, respectively. The humidity of the gases reached over 90 % RH at 30 °C after passing through the humidifier. The performance of this PEMFC attained over 6.0 W.

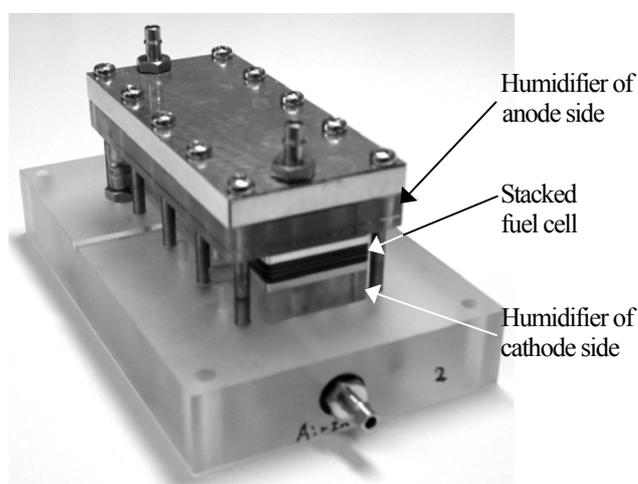


Figure 4. Small PEMFC with humidifiers

5 POWER GENERATION TEST

A schematic of a power generation system is shown in Figure 5. Before starting the experiment, the microreactor was set up inside a vacuum package (51 x 45 x 35 mm, SUS304) with Au coat to reflect the radiant heat (IR reflectivity of Au: 98 %). The inner pressure of the vacuum package was held at approximately 1.2×10^{-2} Pa using a rotary pump and an oil diffusion pump. In starting the catalytic combustion, the microreactor was first heated by applying a voltage to the Au thin film heater so that the temperature of the vaporizer 2 for the catalytic combustor reaches to approximately 100 °C. Methanol, passed through the vaporizer 2, and air were then fed to the catalytic combustor for heating the microreactor. The Au thin film was not used as a heater after starting catalytic combustion, but as a temperature gauge. Before the methanol reforming, the reforming catalyst and the PROX catalyst were pretreated in H₂ stream at 250 °C for 1h. After the temperature distribution of the microreactor was stabilized for H₂ production, a methanol aqueous solution (S/C = 1.2, mol ratio) was fed to the reformer through the vaporizer 1 at 2.3 ml/h of the liquid-bases feed rate. Reforming was carried out at 280 °C using heat supplied from the catalytic combustor. A small amount of methanol as an unreformed reactant, which may bring about the unsteady behavior of PROX, was eliminated from the reformed gases by passing through a cold trap, and the produced gases were then introduced to the CO remover with air as an oxidant. The temperature of each unit was estimated from the resistance of the Au thin film heater. The produced gases were analyzed using a micro gas chromatograph, and supplied to the small PEMFC. The performance of PEMFC was measured by the automatic electric loads system.

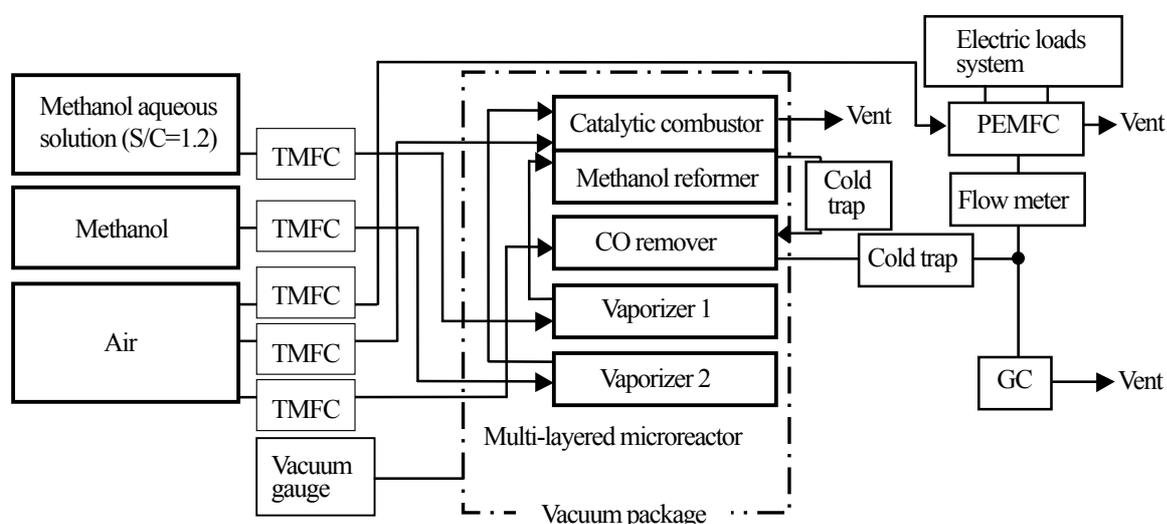


Figure 5. Schematic of testing system of microreactor

The measured temperature of each unit during the methanol reforming is shown Table 2, as compared to the simulated data. With the electrical power of 2.5W of H₂ produced, the temperature of the CO remover, in which the exothermic reaction occurs, was slightly higher than the simulated value, because the simulation excluded the effect of reaction heat in order to save the calculation time. It is also possible that another heat pass, such as the holder used to fix the microreactor to the vacuum package, was present in the experiment and not in the simulation. However, the temperature distribution of the microreactor during H₂ production approached the result of simulation [7].

Figure 6 shows the IP and IV characteristics of the small PEMFC. The maximum power density attained approximately 130 mW/cm² at 200 mA/cm² @0.65 V per cell. In other words, the total output was 2.5 W. A supplied reformat compositions were approximately 70 % of H₂, 30 % of CO₂ and under 50 ppm of CO. Although the capacity of the developed PEMFC is more than 2.5 W, the multi-layered microreactor was designed in the range of 2.5 W to produce H₂. Therefore, the power density was relatively lower than the inherent performance. When the performances of the reactor and the PEMFC are balanced, the system efficiency would be further improved.

Table 2 Experimental result of temperature distribution compared to simulated value / °C

	Simulated value	Experimental result
Reformer	280	280
CO remover	173	182
Vaporizer 1	133	135
Vaporizer 2	109	102

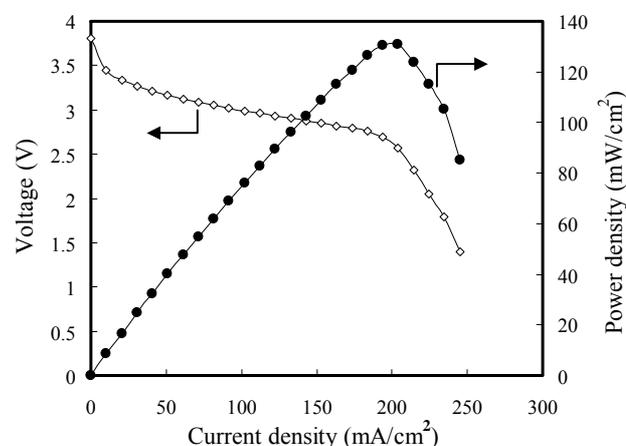


Figure 6. IP characteristics of fuel cell

6 CONCLUSIONS

We developed the anodic bonding method for combining between plural glass substrates, and produced the multi-layered microreactor, which integrated with several different reactors. The microreactor, which was designed using the computational simulation, was assembled with thirteen glass substrates. It reached the necessary temperature distribution for methanol steam-reforming in the vacuum package designed for thermal isolation, and operated with high efficiency. Moreover the small PEMFC system with the microreactor was developed. As expected, this system generated an output of approximately 2.5 W at 200 mA/cm². Since it was proven in this study that the integrated microreactor in the vacuum package has basically high thermal efficiency, further optimization is under way to improve the performance for mobile applications with relatively high power consumption, such as notebook computers.

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