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미세채널과 박막전극이 형성된 실리콘 기반 Micro PEMFC의 성능 특성

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The characterization of performance of silicon-based Micro PEMFC with microchannels and thin film electrodes

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1. Introduction

Miniaturized fuel cells are becoming attractive solutions to the ever-increasing need for portable electronic power sources, especially in response to the rapid growth of mobile computing devices and portable electronic telecommunications, including cellular phones, personal digital assistants (PDA), notebook computers, game devices and portable music systems. It is expected that these machines will become more numerous and more diverse in the coming years. Their use in these applications will require small volumes and small mass, but the performance should approach or exceed that of large systems. Fuel cells are well known of high energy density, a variety of fuel sources, and ease of scaling for application-specific power requirements. Fuel cells with polymer electrolyte membranes are particularly attractive because of low-temperature operation and relatively simple construction.

Recently, microfabrication has been emerging as an ideal technology for the miniaturization of chemical systems because of its well proven cost-effectiveness, reproducibility, and control [1]. Microchemical systems have many advantages over macrosystems, including increased rates of heat and mass transfer, increased safety as a result of smaller volume and enhanced temperature control, and reduced volume waste streams. Up to date, microchemical systems have been used to analyze DNA [2], release controlled amounts of drugs [3], and fabricate microelectrodes within a flow channel [4].

It shows that the adaptation of microfabrication to microchemical systems can be a successful technique. Therefore, we have used microfabrication technique in this study to make miniaturized fuel cells. It is possible that this study could be used to mass produce miniaturized fuel cells if integrated circuits are manufactured on silicon wafer chips.

One fundamental objective of this study is to adapt appropriate microfabrication methods for the production of miniaturized fuel cells within this range of application. Some of the strengths of microfabrication techniques include fine feature resolution, high repeatability, batch operations, integrated process sequences, and a variety of material transfer options.

2. Experimental

The starting material was a $500 \pm 24 \mu\text{m}$ thick p-type $\langle 100 \rangle$ oriented, double-side polished silicon wafer with resistivity ranging from 3 to $5 \Omega\text{cm}$. First, $1 \mu\text{m}$ thick silicon

dioxide layer, SiO₂, was deposited on both sides of the wafer surfaces for Si etch mask [5]. To make feed holes, the silicon dioxide layer on the backside of the wafer was patterned by photo-lithography. And then to get rid of the silicon dioxide layer onto the surface of the exposed windows, buffer oxide etchant (NH₄F : HF = 5 : 1) solution was used [6]. Anisotropic wet etching with tetramethylammonium hydroxide (TMAH) solution was applied to make feed holes on the exposed Si wafer. The silicon dioxide on the frontside wafer was etched using the same processes. Finally two sputtering steps were used to the frontside of the silicon wafer. 1000 Å thick chrome layer was deposited as adhesive, and then 5000 Å thick gold layer was deposited as current collector. Individual miniaturized fuel cell chips were separated by manual cleavage of the finished wafers. A single electrode chip is approximately 2.0 by 2.0 cm and 50 μm thick. The array of feed holes, which is designated as the active area, is 0.7 cm on a side. The feedholes are square (50 by 50 μm). The active area size, where a fuel cell catalyst was applied to, is considered to be an area of 0.49 cm² (0.7 by 0.7 cm).

The catalyst ink for electrodes was formulated in two ways.

First one is similar to PEMFC catalyst ink. 0.4 mg/cm² Pt/C was deposited by spraying with air brush for anode and cathode. The ink was applied directly to an area 1.0 by 1.0 cm centered over the feedhole array on the front of the electrode chip directly onto a silicon wafer substrate [7]. The Pt was dispersed in the liquid by sonication. This ink was applied by spray coating through a Teflon mask, drying with a convection oven, and repeating the spray-dry cycle to achieve the final mass loading. Nafion[®] ionomer was added as the bridge of H⁺ ion.

Second one was deposited by using DC magnetron sputtering machine. From 100 Å ~ 500 Å thick Pt layer was formed as anode and cathode.

Nafion[®]112 membrane was used as the proton exchange membrane. The membrane is prepared as follows. It is boiled in 3 wt% H₂O₂ solution for 1 hour and then rinsed in boiling deionized water for 2 hours to remove any organic compounds. It is then boiled in 0.5 M H₂SO₄ for 1 hour to remove metal compound and to replace Na⁺ with H⁺ in the membrane and finally rinsed in boiling deionized water for 2 hours.

Before using in a miniaturized fuel cell, the double-sided, catalyst coated membrane was hydrated in DI water overnight.

3. Result and discussions

Fig. 1 gives photograph of the active areas of the electrode design tested during the present investigation. Feed hole rib size were the primary variables in this electrode design. The sizes used here insured excellent liquid/gas handling in the individual electrodes. Changing each of the variables could be expected to have serious effects on pressure drop, catalyst utilization, and cathode flooding.

The chip design devised in the present study is simple and compact. But, it could be changed to get better performance in the ongoing study. Feedhole size could be reduced for the ease of fuel distribution, and the number of feedhole could be increased.

In Fig. 2. the shape of voltage versus current density curve is typical for a PEMFC. The initial drop of the polarization curve at very low current density was due to an electrochemical activating process, which was caused by the sluggish kinetics of oxygen reduction at the cathode surface. The subsequent linear decrease of the polarization

curve was due to ohmic over-potential, which was attributed to the ion flow through the electrolyte membrane, the electron flow through the electrode materials, and current collector.

When it is compared with other macro PEMFC unit cell, the peak power density is half of it. The reasons for the low peak power density may be described as follows:

(1) When the pretreated membrane and silicon wafer substrates are bonded, we do not use high pressure bonding.

(2) In the result of miniaturized fuel cells have higher contact resistance between Nafion[®]112 membrane and silicon wafer substrate than macro PEMFCs.

(3) Miniaturized fuel cells tested with macroscopic support hardware (e.g. copper wires, clip leads, etc.) may actually suffer to a greater extent from interface losses than large-scale cells. The best performance of miniature components can be demonstrated only after improved interfacing solutions are incorporated.



Fig. 1 Photograph of flow channels in electrode chip

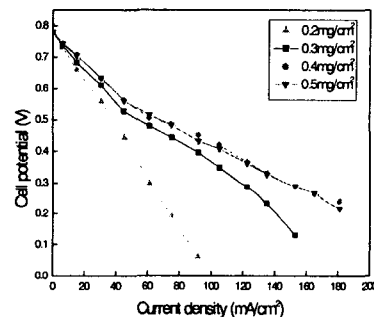


Fig. 2 Effects of catalyst loading on the performance of conventional MEAs

It is possible that direct comparison miniaturized fuel cells with sputter-coated MEA in Fig. 4 with miniaturized fuel cells using a conventional PEMFC MEA in Fig. 2.

Even though a measured performance of miniaturized fuel cells with sputter-coated MEA was half of that of conventional MEA, miniaturized fuel cells with sputter-coated MEA have some advantages:

(1) The amount of catalyst loading can be remarkably reduced by using sputter deposition catalyst coating method.

(2) The ease of approach to the thin-film fuel cells with multi-layers electrolyte deposited by sputter deposition.

The state of the art miniaturized fuel cells could be realized by incorporation with thin-film electrodes, electrolyte layers and silicon wafer structure manufactured by microfabrication process.

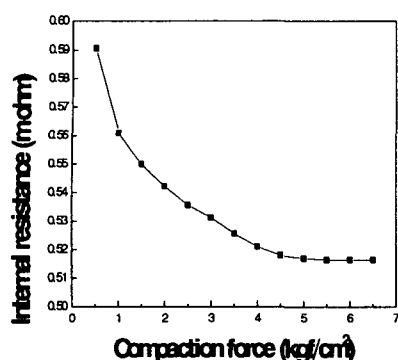


Fig. 3 Effect of compaction force on the internal resistance of a single cell with sputtering MEA

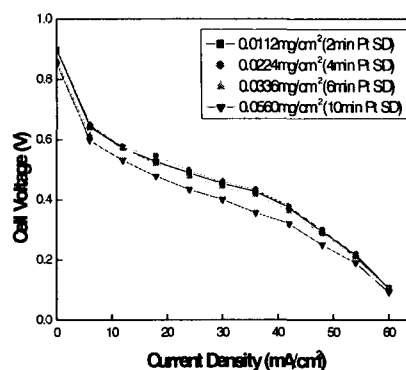


Fig. 4 Effects of catalyst loading on the performance of sputtering MEAs

4. Conclusions

Miniaturized fuel cells, which can be applied to portable electronic power sources, are being designed, fabricated, and tested in this study. Adaptations of microfabrication processes such as photolithography and silicon etching have enabled us to manufacture the miniaturized fuel cells. Some critical fabrication issues have been identified for realizing the design concepts. Especially integration concerns are important, because each component presents a set of mechanical, thermal, and electrochemical requirements that may conflict with other aspects of processing. The optimization of integrated sequences are ongoing works for improved performance. For the variety of application, stacking technologies are currently under development.

5. References

1. Ehrfeld, W., F. Golbig, V. Hessel, H. Lowe, and T. Richter, *Indust. Eng. Chem. Res.*, **38**, 1075 (1999).
2. Burns, M. A., B. N. Johnson, et al, *Science*, **282**, 484 (1998).
3. Santini, J. T., M. J. Cima, and R. Langer, *Nature*, **397**, 335 (1999).
4. Kenis, P. J. A., R. F. Ismagilov, and G. M. Whitesides, *Science*, **285**, 83 (1999).
5. Belyi, V. I., *Silicon Nitride in Electronics*, Materials Science Monographs, ed. 34, Elsevier, New York 1988.
6. Ristic, L., H. Hughes, and F. Shemansky, "Bulk Micromachining Technology," Sensor Technology and Devices, Chapter 3, L. Ristic, ed., Artech Hous, Boston, 49 1994.
7. Ren, X., M. S. Wilson, and S. Gottesfeld, *Proton Conducting Membrane Fuel Cells I*, S. Gottesfeld, G. Halpert, and A. Landgrebe, eds., PV 95-23, 252, the Electrochemical Society Proceedings Series, Pennington, NJ 1995.