Nanoporous Silicon Membrane Based Micro Fuel Cells for Portable Power Sources Applications

K. L. Chu*, M. A. Shannon**, R. I. Masel***

*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign
600 South Mathews Avenue, Urbana, Illinois, 61801, USA, kchu1@uiuc.edu
**Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign
1206 West Green Street, Urbana, Illinois, 61801, USA, mshannon@uiuc.edu
***Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign
r-masel@uiuc.edu

ABSTRACT

In this paper the preparation of nanoporous silicon membranes and their usage for the solid electrolyte in micro fuel cells compatible with silicon micro-fabrication technology is presented. The effects of different membrane structures and fuel concentrations were studied. And the micro fuel cell design for improved performances is discussed.

Keywords: nanoporous silicon, formic acid, fuel cell

1 INTRODUCTION

Silicon-based fuel cells are under active development for electrical power supply to micro systems by some research groups using perfluorinated polymer materials, for example Nafion membranes, as solid electrolyte [1-4]. But polymer materials are not suitable for silicon micro-fabrication technology due to its volumetric variation with changes in hydration level and its incompatibility with photolithography process. For solid electrolyte in micro-scale fuel cells, the proton conducting material reported in this work is based on a nanoporous silicon membrane, which was formed by electrochemically etching silicon in hydrofluoric acid solution and is compatible with current silicon micro-fabrication technology.

2 EXPERIMENTAL

Nanoporous silicon membrane fabrication procedure is shown in Figure 1. N-type antimony-doped silicon wafers with resistivity range from 0.005 to 0.02 Ω-cm were used. (Figure 1 A) Wafers were patterned by silicon nitride deposition and photolithography to obtain circular windows with diameter of 5.3 mm. (Figure 1 B and C) Silicon membranes with thickness of 50, 100, or 150 μm were obtained by wet-etching silicon-nitride-patterned wafer using KOH solution. (Figure 1 D) Nanoporous silicon was formed by electrochemically etching silicon membrane in an electrolyte solution consisted of wt. 49% hydrofluoric acid and ethanol (volume ration of 1:1), with anodic current density of 20, 40, or 80 mA/cm^2 applied to the silicon membrane. (Figure 1 E) The electrochemical etching was carried out in an AMMT etching system. Nanopores grew from one side of the silicon membrane to the other, and a thin silicon substrate layer beneath the nanoporous silicon layer was removed by reactive ion etching. (Figure 1 F)

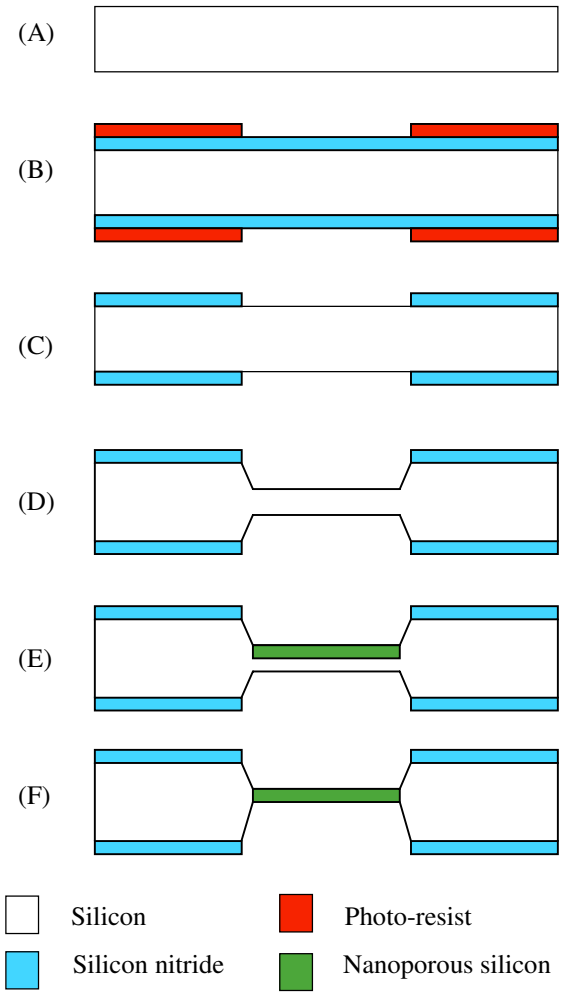

Figure 1. Nanoporous silicon membrane fabrication process

Membrane-electrode-assembly (MEA), the majoe part in micro fuel cell, was made by direct ink-painting technique. Ink of platinum nanoparticles, Millipore water, and Nafion solution was mixed and painted on one side of membrane as cathode, and ink of same solvent but with palladium nanoparticles was painted on the other side as anode. The catalyst ink was dried by heating samples on a hot-plate. After catalyst films were formed, a 5 nm thick gold-palladium alloy film was sputtered on top of catalyst layers on both sides. Then current collector was formed by painting gold ink on top of the sputtered thin film. The final structure of MEA is shown in Figure 2.

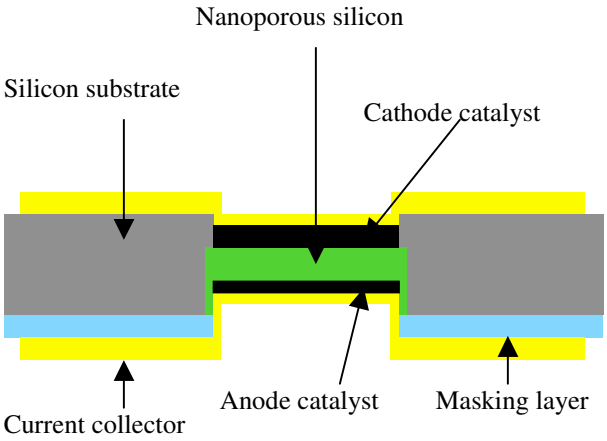

Figure 2. Membrane-electrode-assembly (MEA)

The microstructures of nanoporous silicon membranes were characterized by scanning electron microscopy (SEM). A Teflon cell was used to hold the MEA for fuel cell performance tests. Polarization curves were obtained using different formic acid concentrations of 1M, 5M, or 9M as fuel for the anode. The cathode was air-breathing. No pumping was done for either anode or cathode.

3 RESULTS AND DISCUSSION

The SEM image of nanoporous silicon membrane made by 40 mA/cm^2 and 80 mA/cm^2 are shown in Figure 3, 4, and 5, respectively. The nanopore diameter in membranes made by 20 mA/cm^2 (not shown here) and 40 mA/cm^2 are almost uniform throughout the membranes. But in the case of 80 mA/cm^2, it is observed that nanopore diameter increases with depth, as shown in Figure 4 and 5. It is proposed that nanopores started growing from the substrate surface with relatively small diameter. As nanopores grew deeper into the substrate, electrolyte concentration decreased due to mass transport limit, and thus lead to increased nanopore diameter. This phenomenon is more significant when nanopores were formed by higher current density.

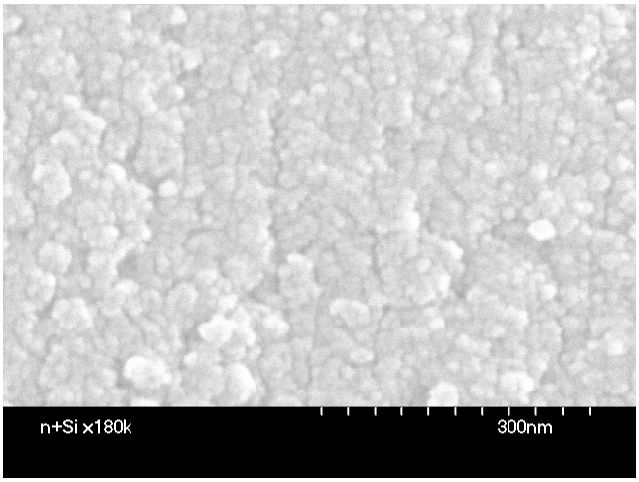

Figure 3. SEM image of nanopores formed by 40 mA/cm^2

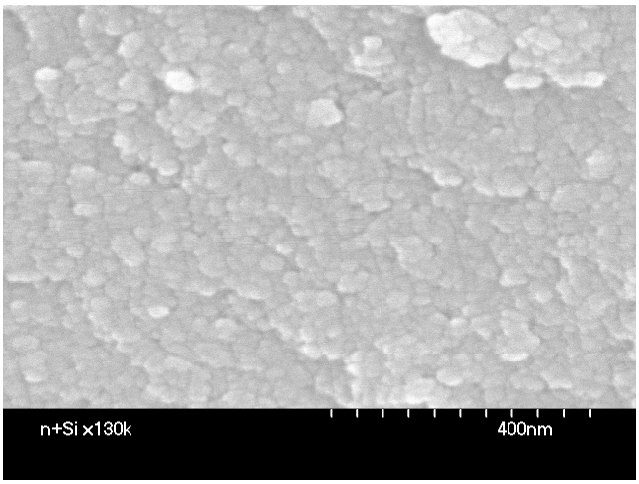

Figure 4. SEM image of nanopores formed by 80 mA/cm^2, close to the substrate surface

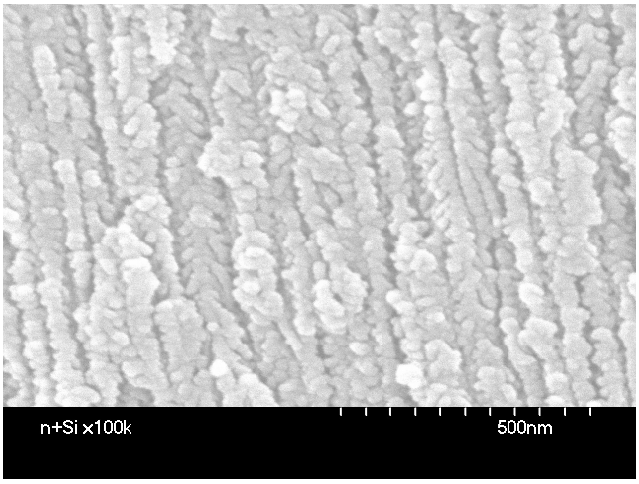

Figure 5. SEM image of nanopores formed by 80 mA/cm^2, deep into the substrate

Cleantech 2007, ISBN 1-4200-6382-0

Using 5 M formic acid as fuel plus 0.5 M sulfuric acid to increase fuel solution conductivity, polarization curves in Figure 6 show that micro fuel cell with 150 µm thick nanoporous silicon membrane gives higher open cell voltage of 0.695 V than the other two thickness (50 µm and 100 µm). It can be seen that the thinner membrane in a miniature fuel cell, the lower open cell voltage it produces. Figure 7 shows the power density curves of miceo fuel cells with these three membrane thickness.

Comparing polarization curves and power density curves in Fig. 6 and Fig. 7, it can be seen that micro fuel cell with 100 µm thick membrane achieves higher current density than 150 µm thick membrane in the high current region, and thus its maximum power density, which is 93.99 mW/cm^2, is higher than that of 150 µm thick membrane, which is 89.44 mW/cm^2.

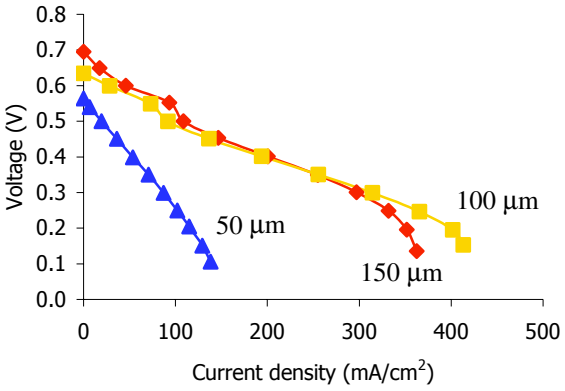

Figure 6. Polarization curves of micro fuel cells with three different thickness of nanoporous silicon membrane

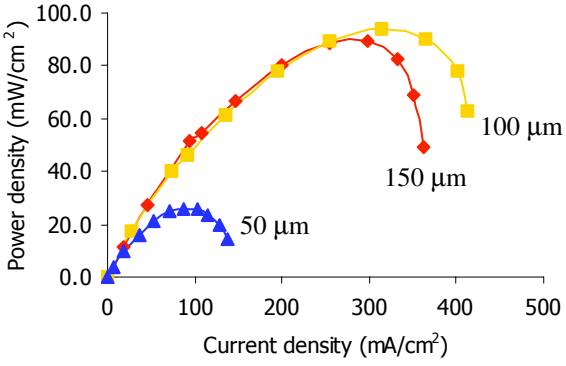

Figure 7. Power density curves of micro fuel cells with three different thickness of nanoporous silicon membrane

Polarization curves and power density curves of micro fuel cells with nanoporous silicon membrane with same thickness of 100 µm but made by three different current densities of 20, 40, and 80 mA/cm^2, are shown in Fig. 8 and 9, respectively. It has been reported that for nanoporous silicon produced from n-type silicon substrate, nanopore diameter increases with current density used for nanopore formation [5]. Micro fuel cell with membrane produced using 80 mA/cm^2 gives higher open cell voltage than the other two. Under the same operation voltage, micro fuel cell with membrane produced using 80 mA/cm^2 also gives higher current density and maximum power density.

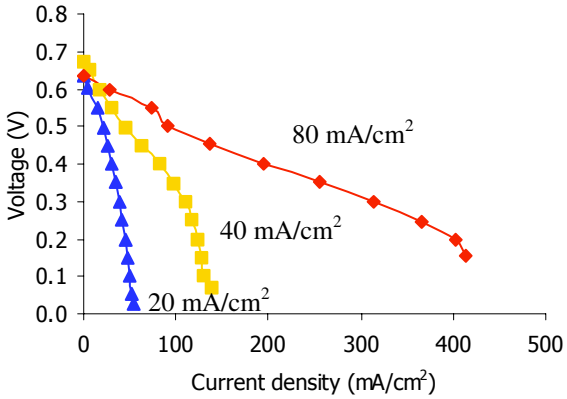

Figure 8. Polarization curves of micro fuel cells with three different nanopore formation current densities

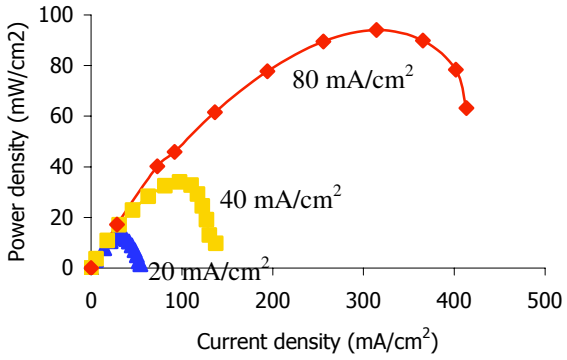

Figure 9. Power density curves of micro fuel cells with three different nanopore formation current densities

For micro fuel cell with 100 µm thick membrane, three fuel solutions with different formic acid concentrations of 1 M, 5 M, and 9 M were used to test the fuel cell performance. The results are shown in Figure 10 and 11. Open cell voltage decreases with formic acid concentration. Micro fuel cell performance suffers transport limit more significantly when using 1 M formic acid than when using 5 M and 9 M, as can be seen from the more rapid drop of current density along forward scan of polarization curves. And this rapid drop of current density contributes to lower power density output when using 1 M formic acid than using the other two fuel concentrations. Micro fuel cell

performance was better when using 5 M formic acid than 9 M in terms of open cell voltage, current density, and power density output.

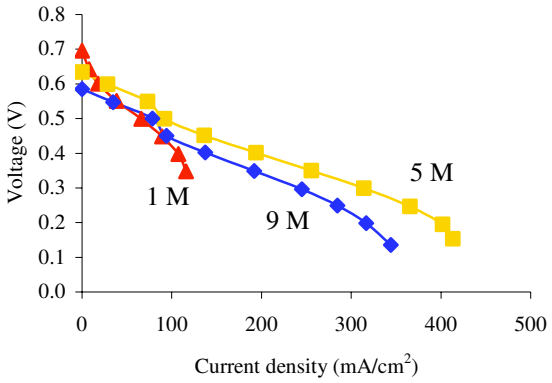

Figure 10. Polarization curves of micro fuel cells with three different formic acid concentrations

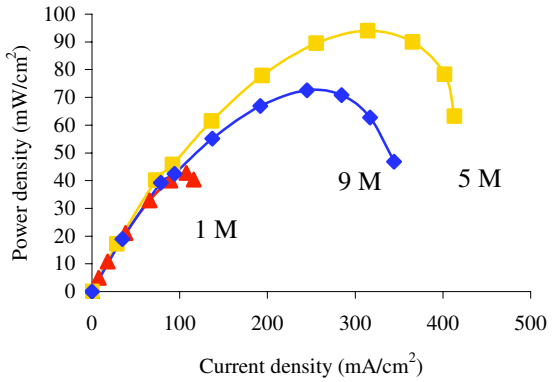

Figure 11. Power density curves of micro fuel cells with three different formic acid concentrations

Summarizing the above results, it can be seen that fuel cell performance improves as nanopore size in the membrane increases. And this is proposed mainly due to proton conductivity improvement. It can also be seen that fuel cell performance degrades as membrane thickness decreases. The reason is proposed to be increase in fuel crossover through the membrane as thickness decreases. And when different fuel concentrations were used for performance test, effects of fuel transport limit and fuel crossover can be seen in the cases of using 1 M and 9 M formic acid, respectively. And thus using 5 M formic acid for miniature fuel cells with 100μm thick membrane gave the best performance.

4 CONCLUSIONS

In this study nanoporous silicon membrane based micro formic acid fuel cells were demonstrated to be potentially promising for power generation for portable electronic devices. The fuel cell peak power density reached 93.99 mW/cm^2 at current density level of 314.37 mA/cm^2 when fuel cell voltage being 0.3 V. The effects of nanoporous silicon membrane thickness, nanopore size, and formic acid concentration on micro fuel cell performance were studied as well. Fuel crossover, proton conductivity, and fuel transport limit were proposed to explain the observation. Using 5 M formic acid with 0.5 M sulfuric acid as fuel, 100 μm thick nanoporous silicon membrane made using the highest current density in this study (80 mA/cm^2) gave the best micro fuel cell performance.

5 ACKNOWLEDGEMENT

This research is funded by the Defense Advanced Research Projects Agency (DARPA) under U.S. Air Force grant F33615-01-C-2172. Any opinions, findings, and conclusions or recommendations expressed in this manuscript are those of the authors and do not necessarily reflect the views of the Defense Advanced Projects Research Agency, the U.S. Air Force, or the Department of Energy. Micro and Nanotechnology Laboratory and Material Research Laboratory in University of Illinois at Urbana-Champaign also provided uses of microfabrication facility.

REFERENCES

[1] G. Q. Lu, C. Y. Wang, T. J. Yen, and X. Zhang, Electrochimica Acta, 49, 821, 2004.
[2] K. Shah, W. C. Shin, and R. S. Besser, Sensors and Actuators B, 97, 157, 2004.
[3] T. J. Yen, N. Fang, and X. Zhang, Applied Physics Letters, 83, 4056, 2003.
[4] J. S. Wainright, R. F. Savinell, C. C. Liu, and M. Litt, Electrochimica Acta, 48, 2869, 2003.
[5] V. Lehmann, R. Stengl, A. Luigart, Material Science and Engineering B, 69, 11, 2000.