

Porous Silicon Fuel Cells For Micro Power Generation

Kuan-Lun Chu¹, Mark A. Shannon², Richard I. Masel¹

¹ University of Illinois, Department of Chemical and Biomolecular Engineering
600 S. Mathews, Urbana, IL 61801, U.S.A.

² University of Illinois, Department of Mechanical and Industrial Engineering
1206 W. Green, Urbana, IL 61801, U.S.A.

Abstract

The objective of this paper is to review recent progress in the production of porous silicon fuel cells for micro power generation. Previous work has demonstrated that an acid loaded porous silicon membrane could be a suitable proton conducting material that is compatible with silicon microfabrication technology. In this paper we present recent improvements to our previously published micro fuel cell designs that achieve 94 mW/cm² at 21 °C.

Keywords: Porous Silicon, Formic Acid, Micro fuel cell

1 - INTRODUCTION

In the past few years, there has been considerable interest in the development of miniature fuel cells for portable electronic devices due to their advantages over conventional batteries, including rapid recharging and much higher stored energy density. Among many options of fuel, previous work in our research group has demonstrated that direct formic acid fuel cells with novel electro-catalysis are interesting for micro power generation [1]. One key issue in device design is finding a solid electrolyte material that is compatible with standard silicon processing. One can fabricate a silicon-based miniature fuel cell by sandwiching a Nafion® membrane between two silicon chips [2], but Nafion® membranes shrink and swell in response to their environment so the sandwich often fails in practical operation. Previous work in our research group has shown that an acid loaded porous silicon membrane has a proton conductivity comparable to Nafion® and is compatible with standard silicon processing [3-4]. Similar concept for porous silicon based micro fuel cells was proved to work independently by another research group [5], but the reported performance also left significant room for improvement. In this paper we describe recent improvements in our devices that allow high power devices to be obtained.

2 - EXPERIMENTAL

The fabrication process for porous silicon membranes is illustrated in Fig. 1. Starting with silicon wafers, silicon nitride film was deposited by LPCVD and patterned as mask for both KOH etching (Fig. 1, A to D) and pore formation (Fig. 1, E). Three types of silicon wafers were used: first, n-type, highly antimony doped (donated as “n+Si”); second, n-type, moderately antimony doped (donated as “n-Si”); third, p-type, lightly boron doped (donated as “p-Si”). For “n+Si”, the window for porous silicon was a circle with diameter of 5.3 mm. For the other two types of silicon, the window for porous silicon was an array (12 by 12) of circles with diameter of 107 μm, and pitch of 320 μm. Pores were formed

by electrochemical etching of silicon substrate with various combinations of hydrofluoric acid solution and anodic current density. Reactive ion etching on silicon substrate backside

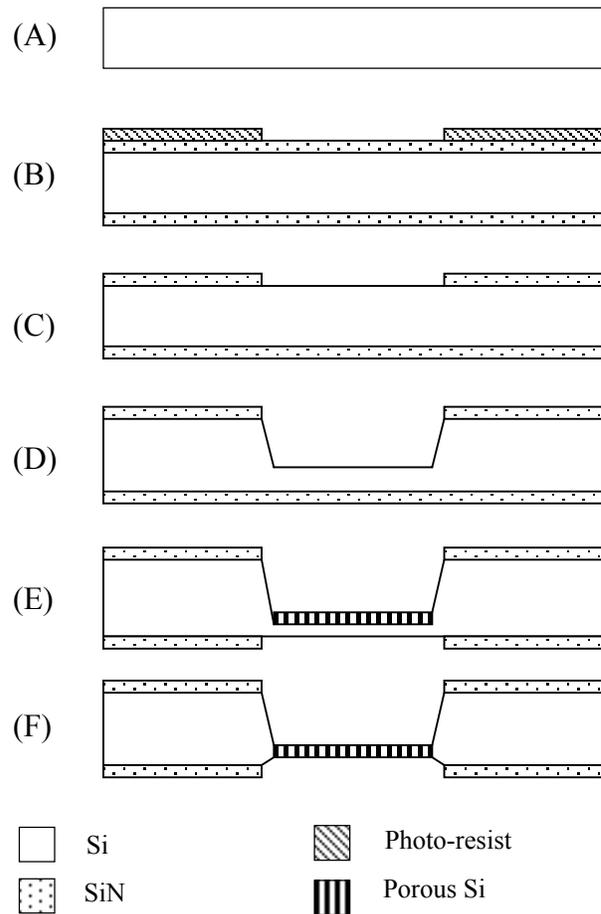


Figure 1 – Fabrication process of a porous silicon membrane

was applied to open up pores on the backside (Fig. 1, F). Micro fuel cells with structure illustrated in Fig. 2 were fabricated as follows. Cathode electrode was formed by painting one side of porous silicon surface with a catalyst ink consisting of w.t. 5% Nafion solution, millipore water, and platinum nanoparticles. Anode electrode was formed by painting the other side with a similar catalyst ink consisting of same solvent but with palladium nanoparticles. Current collector was formed by sputtering a gold-palladium alloy thin film on top of the catalyst film and painting gold ink at the edge of catalyst film. Performance tests were carried out at room temperature in ambient air without pumping neither fuel to anode or gas to cathode.

3 - RESULTS AND DISCUSSIONS

In our previous work [3], it's demonstrated that porous silicon membranes made using different anodic current densities have different proton conductivity values and also different fuel crossover values. Anodic current density has been known one of the key factors controlling the pore size, and in [3] the differences in proton conductivity and fuel crossover were explained by difference in pore sizes. Here, three different anodic current densities (20, 40, and 80 mA/cm²) were used to produce various porous silicon membranes from "n+Si" substrate with same thickness of 100 μm. SEM (scanning electron microscopy) images of porous silicon prepared from "n+Si" using different anodic current densities are shown in Fig. 3. Figure 3 A and B are cross sectional views of porous silicon made using current density of 20 mA/cm² and 40 mA/cm², respectively, with a sponge-like structure observed. For porous silicon made using 80 mA/cm², pore structure included both sponge-like (Fig. 3 C) and treelike (Fig. 3 D). This structural change was possibly due to electrolyte concentration gradient along the pores during pore formation. It can be seen that pore size in treelike structure is larger than that in sponge-like structure. But the difference is not significant, because the pore sizes are all within nano-meter range. To produce various porous silicon membranes with wider pore size range, "n-Si" and "p-Si" were used. SEM images of porous silicon prepared from "n-Si" and "p-Si" are shown in Fig 4.

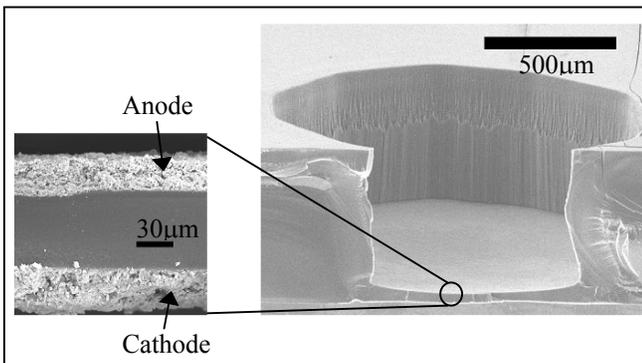


Figure 2 – SEM pictures of a porous silicon based micro fuel cell

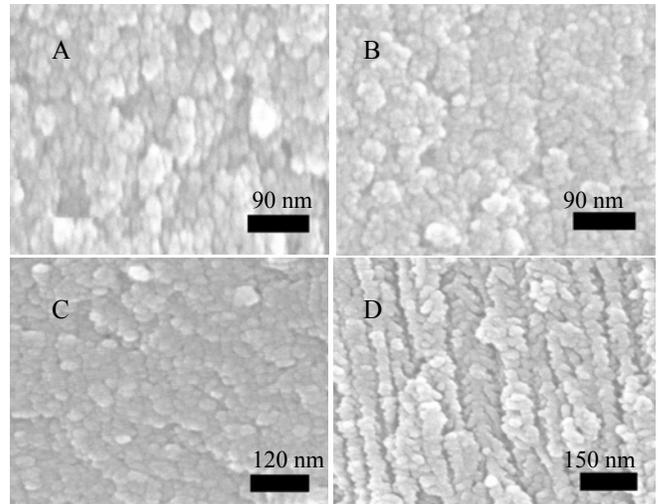


Figure 3 – SEM pictures of porous silicon membranes made from heavily doped n type silicon

Figure 4 A and B show the "microporous" structure and the "macroporous" structure, respectively. They were both made from "p-Si", but the pore sizes varied significantly due to different electrolyte solutions used for pore formation. Figure 4 C and D show the "mesoporous" structure from top and cross section of membranes made from "n-Si". It can be seen that mesoporous silicon has a lower pore density than all the other kinds of membranes.

Figures 5 to 10 are performance characterization for micro fuel cells constructed using "n+Si". Figures 11 to 12 are performance characterization for micro fuel cells made using "n-Si" and "p-Si". All data was obtained by using 5 M formic acid with 0.5 M sulfuric acid as the fuel, if not specified otherwise.

Curves in Fig. 5 and 6 were obtained using micro fuel cells with three different porous silicon membrane thickness (50, 100, and 150 μm), all made using anodic current density of 80 mA/cm². The fuel cell polarization curves in Fig. 5 show that the thinner porous silicon membrane, the lower open cell

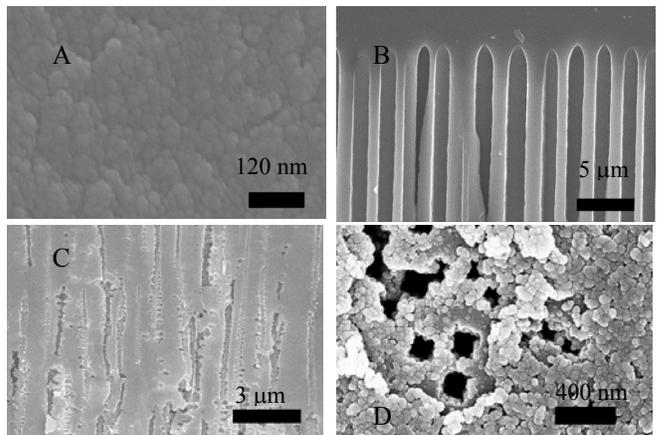


Figure 4 – SEM pictures of porous silicon membranes made from moderately doped n type and p type silicon

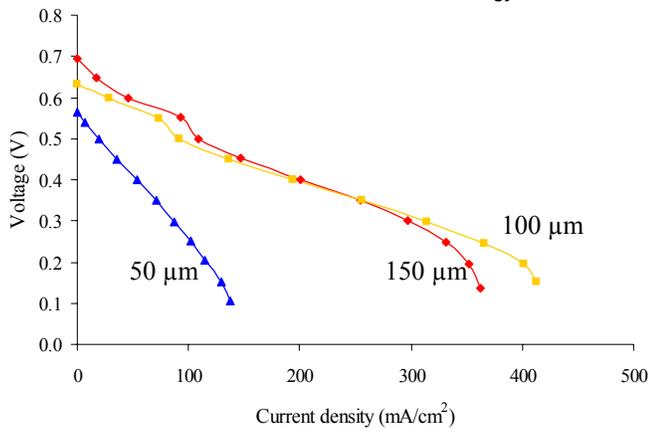


Figure 5 - Fuel cell polarization curves with three different porous silicon membrane thickness.

voltage obtained. It is possible that fuel crossover from anode to cathode increased as porous silicon thickness decreased, thus lowered the open cell voltage. Figure 6 shows the power density curves derived from the polarization curves in Fig 5. The micro fuel cell with 100 µm thick porous silicon produced the highest peak power density among the three.

For micro fuel cell with 100 µm thick porous silicon membrane made using 80 mA/cm² as anodic current density, three fuel solutions with different formic acid concentrations of 1 M, 5 M, and 9 M were used to test the fuel cell performance. From Fig. 7, it can be seen that open cell voltage decreased as formic acid concentration increased. This decrease in open cell voltage was possibly caused by increase in the fuel permeation across membrane. And fuel cell performance suffered fuel transport limit more significantly when using 1 M formic acid than when using the others, as can be observed from the more rapid drop of current density output in Fig. 7. This rapid drop of current density output contributed to lower power density output when using 1 M formic acid than the other two concentrations, as shown in Fig. 8.

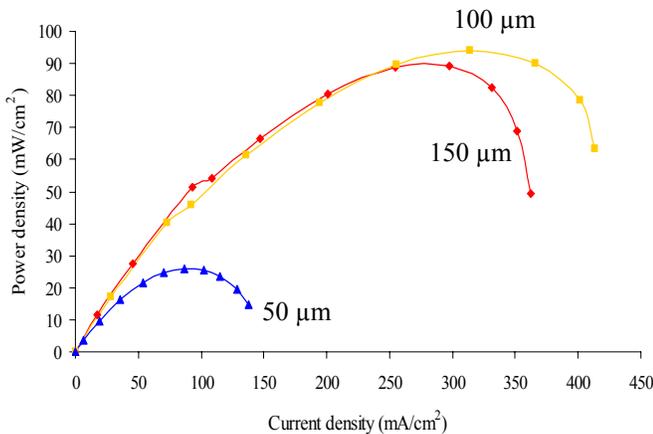


Figure 6 - Fuel cell power density curves with three different porous silicon membrane thickness.

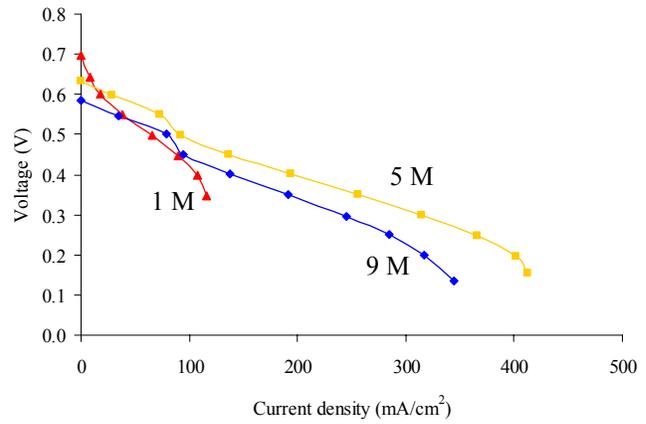


Figure 7 – Fuel cell polarization curves with three different formic acid concentrations (100 µm thick porous silicon).

The effect of pore size on fuel cell performance can be seen from Fig. 9 to 12. In the case of “n+Si”, micro fuel cell with porous silicon made using 40 mA/cm² produced higher open cell voltage than the other two, as can be seen in Fig. 9. But the difference in open cell voltage is less than 0.05V. Under the same operation voltage, micro fuel cell with porous silicon made using 80 mA/cm² produced higher current density and also higher peak power density than the other two (Fig. 9 and 10). For micro fuel cells made using “p-Si” and “n-Si”, Fig. 11 shows that open cell voltage of fuel cell with a “microporous” silicon membrane can be 0.2 V higher than that with a “macroporous” silicon membrane. The current density output and power density output of the fuel cell with a “macroporous” silicon membrane are much higher than that with a “microporous” silicon membrane (Fig. 11 and 12). These results reflect the effect of large difference in pore size on fuel cell performance. But fuel cell with a “mesoporous” silicon membrane (made from “n-Si”) shows significantly lower open cell voltage and current density than the other two. This could be contributed to the extra low pore density of the membrane produced from “n-Si” substrate (Fig. 4 C).

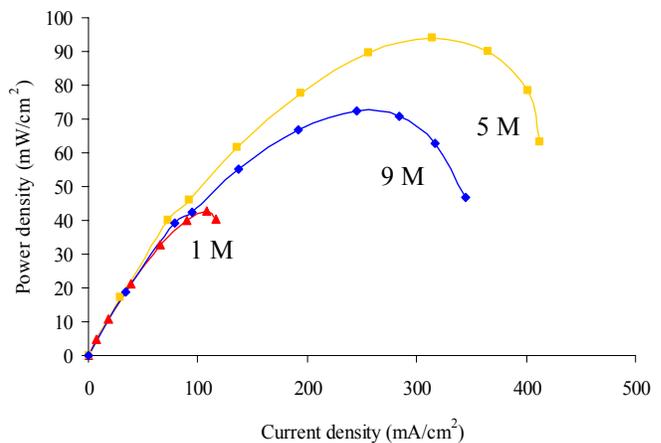


Figure 8 – Fuel cell power density curves with three different formic acid concentrations (100 µm thick porous silicon).

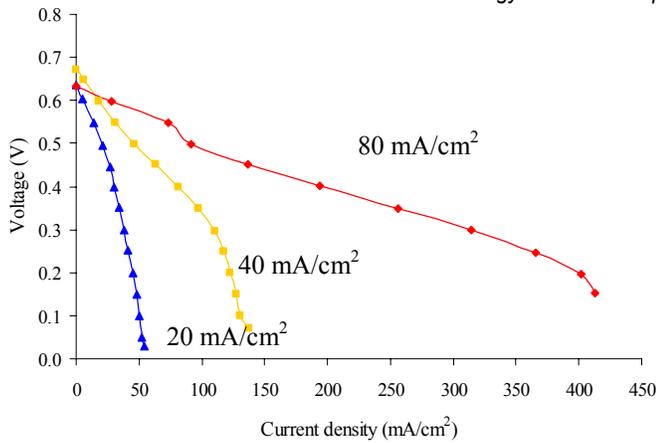


Figure 9 – Fuel cell polarization curves with porous silicon membranes of three different pore sizes.

4 - CONCLUSIONS

From the above results, it can be concluded that using 5 M formic acid with 0.5 M sulfuric acid as fuel, 100 μm thick porous silicon produced from highly doped n type silicon using high anodic current density (80 mA/cm^2) gave the best micro fuel cell performance in general. Various parameters and conditions were examined to characterize the porous silicon based micro fuel cells, and factors such as fuel crossover, proton conductivity, and fuel transport limit were proposed to explain the observations. The fuel cell peak power density reached 94 mW/cm^2 at current density level of 314 mA/cm^2 when fuel cell voltage being 0.3 V. This power output is three times of that reported in our previous work [4].

ACKNOWLEDGMENTS

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.

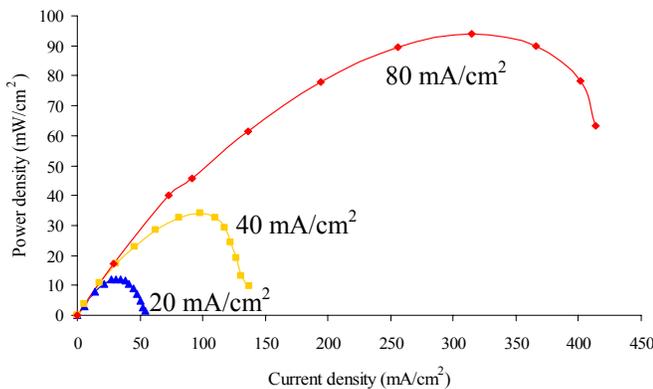


Figure 10 – Fuel cell power density curves with porous silicon membranes of three different pore sizes.

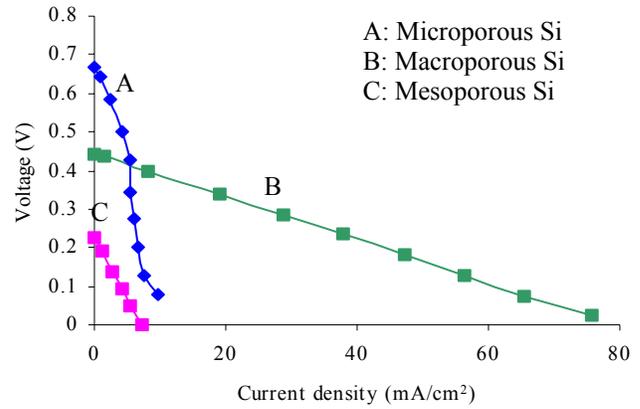


Figure 11 – Fuel cell polarization curves with three different pore sizes ($80 \mu\text{m}$ thick porous silicon).

Micro and Nanotechnology Laboratory in University of Illinois at Urbana-Champaign also provided uses of microfabrication facility.

REFERENCES

- [1] Rice, C., *et al.*, "Direct Formic Acid Fuel Cells", *Journal of Power Sources*, Vol. 111, No 1, pp. 83-89, 2002.
- [2] Lu, G. Q., *et al.*, "Development and Characterization of a Silicon-based Micro Direct Methanol Fuel Cell," *Electrochimica Acta*, Vol. 49, No 5, pp. 821-828, 2004.
- [3] Gold, S., *et al.*, "Acid Loaded Porous Silicon as a Proton Exchange Membrane for Micro Fuel Cells," *Journal of Power Sources*, Vol. 135, No 1-2, pp. 198-203, 2004.
- [4] Chu, K.-L., *et al.*, "A Nanoporous Silicon Membrane Electrode Assembly for On-Chip Micro Fuel Cell Applications", *IEEE Journal of Micro-Electro-Mechanical Systems*, Vol. 15, No 3, pp. 671-677, 2006.
- [5] Pichonat, T., *et al.*, "Development of Porous Silicon-based Miniature Fuel Cells", *Journal of Micromechanics and Microengineering*, Vol. 15, No 9, pp. S179-S184, 2005.

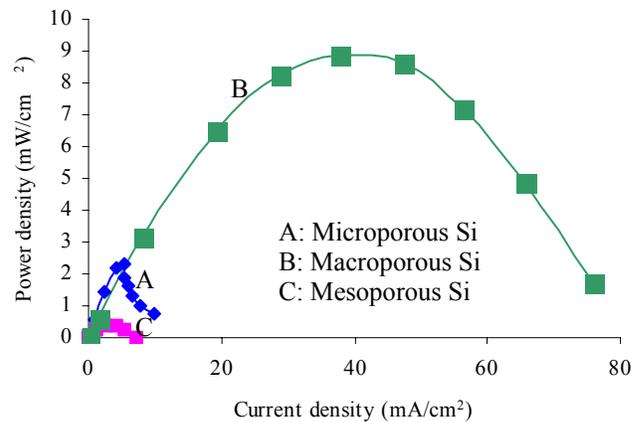


Figure 12 – Fuel cell power density curves with three different pore sizes ($80 \mu\text{m}$ thick porous silicon).