A MEMS BASED MINIATURE HYDROGEN FUEL CELL FOR PORTABLE POWER GENERATION

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ABSTRACT

MEMS based fuel cells have been proposed as replacements for batteries in distributed sensor networks, on chip power, and implantable devices. In this paper we will present the design and fabrication of new MEMS based fuel cells that show a factor of 4 higher power output than any MEMS based hydrogen/air fuel cell reported previously. Our approach is to base the fabrication on a single wafer compared to conventional two bonded wafers. Our hybrid microfabricated hydrogen fuel cell has an open cell voltage of 1.02V, a peak power density of 284 mW/cm² and fuel utilization rate close to 90%.

INTRODUCTION

Portable devices have become much more feature packed and require much more power than before. However, they have been facing a persistent problem as rechargeable battery technology hasn't kept pace with the rapid advancements in chip designs. Bridging that gap may now be possible through fuel cells, a clean-energy technology that produces electricity from the electrochemical reactions between hydrogen and oxygen. Potential military applications are: a lightweight alternative to the heavy batteries soldiers have to carry into battle to power various high-tech gears.

Fuel cells convert chemical energy directly to electric power. There are different types of fuel cells characterized by the electrolyte material. Among them, proton exchange membrane (PEM) fuel cells are regarded as most suitable for portable applications. Figure 1 shows a schematic of a typical PEM fuel cell and how it works. Using hydrogen as the fuel, reactions at the anode and cathode of the PEM fuel cell are:

The protons produced at the anode are transported through the proton exchange membrane to the cathode, and the electrons travel through the external circuit thereby producing electricity. Protons and electrons are reacted with oxygen at the cathode with water being the only product. Catalyst layers on the electrodes are necessary for both anode and cathode reactions to occur efficiently.

Figure 1: Schematic of a typical PEM fuel cell.

Recent interests have been on MEMS microfabrication rather than traditional manufacturing processes due to ease of miniaturization and reduction of cost. The high cost to build fuel cells is one of the biggest impediments to their commercialization. Traditionally, fuel cells are built similarly to a car, with pieces manufactured separately and then assembled. There is high variability, and the process is costly and time consuming. With microfabrication, instead of assembling the separate parts, the fuels cells are made by addition and subtraction on a base structure; the same way current microelectronic devices are made.

Previous works on MEMS based fuel cells can be categorized into four different areas [1]: Silicon base structures, porous silicon as the membrane, metal based materials, and polymer based materials such as PDMS and PMMA. Silicon based fuel cells will be the focus on this paper since silicon is the most common material used in MEMS, and many fabrication techniques have already been developed. Several groups have worked in this area using a conventional "sandwich" method: fabrication was done on two separate silicon wafers along with MEA and sandwich it with a proton conducting layer. Table 1 shows the fuel cell peak power performance reported for H₂/O₂ system and open cell voltage (OCV) vary among different system designs.

In this paper we will present the design and fabrication of new MEMS based fuel cells that show a factor of 4 higher power output than any MEMS based hydrogen/air fuel cell reported previously [4-9]. Our approach is to work on single wafer MEMS fabrication. The advantage of fabricating using only a single wafer compared to two wafers is ease of miniaturization by eliminating the need for bonding two separate wafers onto a Nafion® sheet. Our design uses a hybrid proton conducting membrane: silicon base structure filled with Nafion® ionomer solution.

EXPERIMENTAL

Microfabrication of Silicon Dies

The Si based micro fuel cells were fabricated from 100 mm P type boron-doped double sided polished prime <1-0-0> SOI wafers (Ultrasil Corp., Hayward, CA) with 300 μm thick handle wafer (0.1-1.0 ohm-cm resistivity), 40 μm thick device layer (1-10 ohm-cm resistivity), and 0.5 μm thick buried oxide using conventional MEMS fabrication processes. Square windows of 2.4 mm x 2.4 mm were patterned on the handle wafer (anode side) while a 6 x 6 array of circular windows of 100 μm diameter and 100 μm apart were patterned on the device layer (cathode side) as shown on Fig. 2.

Table 1: A comparison of the performance of our device operated on H_2 at 25 °C to those reported previously. We only included references where hydrogen was the fuel and the peak power was more than 10 mW/cm².

	Open Cell Voltage (V)	Cell Area (mm ²)	Design	Peak Power Density (mW/cm ²)
Yu <i>et al.</i> [8]	0.95	506	Silicon wafers bolted to conventional MEA	195 (with pure O ₂ running on the cathode side)
Modroukas <i>et al.</i> [5]	0.85	100	Silicon wafers bonded to conventional MEA	70 (with flowing air on the cathode side)
Meyers <i>et al.</i> [4]	0.9	n/a	Silicon wafers bonded to conventional MEA	63 (with pure O ₂ running on the cathode side)
Yeom <i>et al.</i> [7]	0.95	44	Silicon wafers bonded to Nafion®	35 (with stagnant air on the cathode side)
Zhiyong <i>et al.</i> [9]	0.96	143	Silicon wafers bonded to Nafion®	13.7 (with pure O ₂ running on the cathode side)
Pichonat <i>et al.</i> [6]	0.8	7	Nafion® filled silicon MEA	18 (with pure O ₂ running on the cathode side)
Our Device	1.02	5.76	Nafion® filled silicon MEA	284 (with stagnant air on the cathode side)

Figure 2: (Top) Picture showing finished wafer from cathode side and anode side views. (Bottom) Picture taken from microscope focusing on one device; showing the circular channels from cathode side and square window from anode side.

Figure 3 shows the microfabrication steps for the making of the Si dies: (A) the native oxide layer was removed by immersion in the buffered oxide etch (BOE) solution and the wafer was cleaned by 3:1 by volume of sulfuric acid and 30 wt% hydrogen peroxide; (B) roughly 100 nm thick silicon nitride layer was grown on both sides of the wafer by low pressure chemical vapor deposition (LPCVD); (C) photolithography using AZ 4620 photoresist was applied to pattern on the silicon nitride of the handle wafer (anode side) to make the square windows (2.4 mm sides); (D) dry etching using an inductively coupled plasma deep reactive ion etcher (ICP-DRIE, Plasma-Therm SLR770) was done to create square windows in the nitride layer on the anode side; (E) photoresist was removed by photoresist stripper AZ-400T, then 300 μm exposed silicon substrate was wet etched to the oxide

layer using a 35% potassium hydroxide solution at 85°C with silicon nitride as the mask; (F) again, using standard photolithography, a 6x6 array of circular windows (100 μm diameter) was patterned on the silicon nitride of the device layer (cathode side); (G) dry etching using ICP-DRIE was done to create the circular windows in the silicon nitride on the cathode side; (H) dry etching using the BOSCH process was done to etch 40 μm exposed silicon substrate down to the oxide layer; (I) dry etching using a Freon reactive ion etcher system (Freon RIE, PlasmaLab) was done to etch through the oxide layer; (J) using a DC-Magnetron sputtering system, roughly 150 nm of gold (50 nm of chrome as an adhesion layer) was sputtered (everywhere on both sides of the wafer except the openings on both sides) to serve as the current collector.

Figure 3: Microfabrication steps for silicon fuel cell dies.

Preparation of Membrane Electrode Assembly

The membrane electrode assembly (MEA) was directly applied on the fabricated silicon structure as shown on Fig. 4. To prepare the MEA, ~28 μL of 5 wt% Nafion® ionomer 1100 EW (Solution Technology Inc., Mendenhall, PA) was applied to the membrane area to fill the channels for proton conduction as well as to serve as an adhesion layer for the anode and cathode catalyst layers. The Nafion® layer was then allowed to dry. A leak test was performed using an in-house device. Catalyst inks were then prepared by dispersing platinum black (HiSPEC 1000, Alfa Aesar, Wardhill, MA) with Nafion® solution, Millipore water, and isopropanol via sonication. Using the direct paint method, the catalyst inks were painted onto the Nafion® layer of the anode and cathode to form the membrane electrode assembly. The resulting catalyst loading was approximately $20 \text{ mg}/\text{cm}^2$. In addition to the membrane area, a small amount of catalyst ink was painted onto the gold current collectors to provide electrical connection.

Figure 4: Membrane Electrode Assembly for the Si fuel cell.

Hydrogen Fuel Utilization Rate Measurement

High fuel utilization rate of the fuel cell is essential for high energy density of the power generator device. The fuel utilization rate of the hydrogen fuel cell was obtained using a glass tube filled with hydrogen gas as shown on Fig. 5. The cell was run for 30 min from the hydrogen gas supplied from the glass tube. The water level at the glass tube was measured before and after the life test to estimate the amount of hydrogen supplied to the fuel cell.

Figure 5: Schematic of the apparatus for measuring hydrogen utilization rate.

Fuel Cell Testing

In order to test the fuel cell, a Teflon holder had to be fabricated in house as shown in Fig. 6. It consisted of two pieces. The bottom piece allowed hydrogen to flow over the anode, while the top piece allowed stagnant air to diffuse to the cathode. The test was to determine the performance of the fuel cell by determining the voltage-current (VI) relationship. The fuel cell was placed in the Teflon housing and connected to the potentiostat (Solartron SI-1287, Hampshire, UK). Dry hydrogen was passed over to the anode, and stagnant air was allowed to diffuse on the cathode. Once the fuel cell reached a steady OCV, the potential was then stepped from OCV to 0.1V.

Figure 6: In house made Teflon housing for silicon fuel cell.

RESULTS AND DISCUSSION

Hydrogen Fuel Utilization Rate

Figure 7 shows the life test curves obtained at various operating voltages. Table 2 summarizes the calculation results under various conditions. The utilization rate turned out to be quite high (83~90%) and the rate was higher at lower voltage (higher current) indicating that there is some fuel leakage during operation. Therefore, the fuel utilization rate may be enhanced if the fuel leakage is reduced.

Figure 7: Constant voltage life test for fuel utilization calculation with the setup shown in Figure 5.

Table 2: Some of the characteristics of our devices operating on pure hydrogen and stagnant air at 25 °C.

Voltage	Current (mA/cm ²)	Power (mW/cm ²)	Hydrogen utilization
0.4 V	710	284	
0.5 V	480	240	90.2%
0.6 V	310	186	88.9%
0.7 V	260	182	83.6%

Fuel Cell Performance

Table 1 and Figure 8 highlight the performance of our device. The fuel cell has an open cell voltage of 1.02V, a peak power density of $284 \text{ mW}/\text{cm}^2$ and fuel utilization rate close to 90%. Table 1 compares these results to several devices from previous literature. Prior to our work the best MEMS based hydrogen/air fuel cell only produced $70 \text{ mW}/\text{cm}^2$ compared to $284 \text{ mW}/\text{cm}^2$ in our device. Yu *et al.* [8] showed $195 \text{ mW}/\text{cm}^2$ by running pure oxygen on the cathode, but note that power is 4-5 times higher with oxygen than with air. Our device shows the highest power output of those shown previously, and it is a true MEMS device. There are no bolts or clamps holding on the MEA, and the device can be fully integrated with a miniature hydrogen generator as shown in Fig. 9.

Figure 8: A polarization curve at 25 °C with flowing hydrogen on the anode and stagnant air (air-breathing) on the cathode.

Figure 9: A picture of a hydrogen generator integrated with a silicon fuel cell both sitting on a penny.

Although the cell performance was greatly improved by the new MEA design, the performance still deviates from the ideal behavior as illustrated in Fig. 10. Low open cell potential is a sign of hydrogen crossover from the anode to the cathode side. The large slope of VI curve indicates that the current performance is mainly limited by parasitic resistance of the cell. Rapid drop of the cell voltage at high current density region designates mass transfer resistance mainly caused by the large amount of water produced at the cathode.

Figure 10: Comparison with ideal cathode limited behavior curve.

CONCLUSIONS

In this paper, single wafer fabrication process was successfully demonstrated. Our hybrid microfabricated hydrogen fuel cell has shown an open cell voltage of 1.02V, a peak power density of 284 mW/cm² and fuel utilization rate close to 90%. The new MEMS based fuel cells show a factor of 4 higher power output than any MEMS based hydrogen/air fuel cell reported previously.

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