FABRICATION OF A MICROMACHINED DIRECT METHANOL FUEL CELL

Kevin G. Stanley Q. M. Jonathan Wu Tom Vanderhoek Suwas Nikumb
National Research Council of Canada
kevin.stanley@nrc.ca, jonathan.wu@nrc.ca, , tom.vanderhoek@nrc.ca, suwas.nikumb@nrc.ca

Z. M. Walker
University of New Brunswick
t12zx@unb.ca

M. Parameswaran
Simon Fraser University
param@cs.sfu.ca

Abstract

Small electronic devices require small, compact and lightweight power supplies. Direct methanol fuel cells (DMFCs) offer the potential for double the lifetime of lithium ion batteries. We have designed a process for micromachining direct methanol fuel cells using traditional micromachining techniques and macro-assembly. Direct methanol fuel cells oxidize methanol through a catalytic reaction producing carbon dioxide and hydrogen. Hydrogen is further oxidized into hydrogen ions through a second catalytic reaction, producing electrons. We have micromachined flow fields and current collectors for the anode (methanol) side in both <100> and <110> silicon. Using laser ablation, we have opened fluidic channels through the back of the wafer for attaching fluid feed tubes. Aluminum is deposited as a current collector. The fuel cell is assembled using a commercial membrane electrode assembly (MEA), which contains the solid polymer proton exchange membrane (PEM) and catalysts. Sealing is provided using an epoxy. Simulated and actual results are presented.

Keywords: micromachinig, direct methanol fuel fell, laser ablation, assembly

1. Introduction

Microelectronics systems, from sensors to laptops, continue to demand more power. It is becoming increasingly clear that traditional chemical cells such as lithium-ion batteries will not be able to meet this power demand. Several researchers have attempted to use micromachining techniques to generate power from hydrocarbon sources. Attempts at internal combustion engines, turbines and other mechanical power sources have been investigated. However, we feel that fuel cells provide the best chemical to electrical conversion for micro power systems. In particular, micro direct methanol fuel cells (DMFCs) are a potential solution to the micro power problem.

A direct methanol fuel cell generates power through the reduction of methanol to carbon dioxide and hydrogen ions, and the oxidation of hydrogen ions with oxygen. The reaction occurs across a proton exchange membrane (PEM) which separates the two half reactions, allowing electrical energy to be extracted. The two half reactions can be written as:

$$CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6e^-$$
$$3\,O_2 + 12\,H^+ + 12\,e^- \rightarrow 6\,H_2O$$
$$2\,CH_3OH + 3\,O_2 \rightarrow 2\,CO_2 + 4\,H_2O$$

While the DMFC is not completely pollution free, it does generate a significantly larger amount of electricity for every mol of carbon dioxide than most compact energy sources. Even running at 50% efficiency, DMFCs produce ample electrical power.

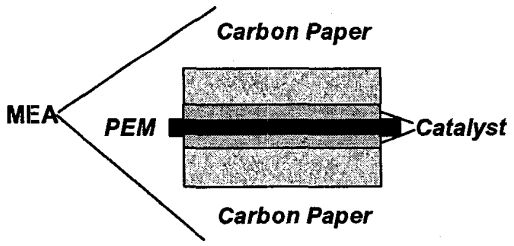

Figure 1: Example MEA

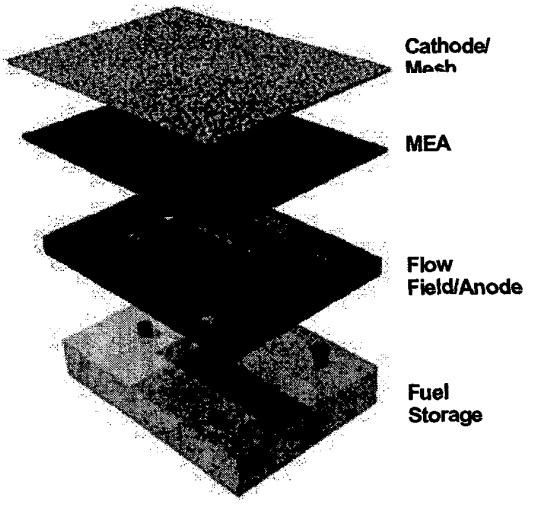

Figure 2: Example Fuel Cell

Fig. 2 shows an exploded view of a typical single cell DMFC. The internal layer structure of the MEA is shown in Fig. 1. The carbon paper serves as both a diffusion medium, and as a current collector for both the anode and cathode. The current from either electrode is collected through the carbon paper to the protective covering and the flow field. The anode catalyst is usually platinum-ruthenium. The cathode catalyst is usually platinum. The catalysts are usually painted or sprayed as a random field. While the random field yields high surface area it also requires a porous current collector to provide a bulk electrical contact to gather or distribute the electrons.

Several people have attempted to micromachine fuel cells. McLean, *et al.* described a number of possible benefits for micro scale fuel cells, including manufacturability and micro flow [1]. Kelly, Deulga and Smyrl described a micromachining based fuel cell fabrication method, which uses a perforated membrane oxide to present the methanol to the anode. They reported an open circuit voltage of approximately 0.5 V and a short circuit current of 0.46 A/cm^2 at 50 C [2]. Sim, Kim and Yang report a micro DMFC based on two identical flow plates, bound to the Nafion using a heat press for use in powering embedded medical sensors [3]. Using a sputtered gold catalysts/electrode instead of a commercial Pt-Ru catalyst and carbon electrode, they achieved an open circuit voltage of 0.1 V. No current measurements were made. Significant work has been accomplished at Los Alamos National Labs in direct methanol fuel cells, and small fuel cells. An overview of their work can be found in [4]. Hockaday, *et al.* have an advanced prototype of a micro fuel cell based on a plastic substrate and circuit board lithographic techniques [5]. Tompsett et al have designed a micro solid oxide fuel cell, using a bundle of thin yttrium stabilized zirconia tubes with painted cathode and anode catalyst and current collectors. For an overview of fuel cells and DMFCs please refer to [7]. For an overview of bulk micromachining techniques and microfluidics, refer to [8]. It is also worth noting that several companies, including Sony, Mitsubishi and Medis Inc. are designing micro DMFCs. However, they generally do not publish results until after patents have been issued, so it is difficult to ascertain their progress.

Our fuel cell fabrication is similar to many in the published fuel cell literature. Our fabrication is based on a wet etch of the substrate and deposition of metallic current collectors. Two major improvements to the process differentiate our process from others. First, we use laser ablation to drill through the substrate, allowing fluidic input and output through the substrate. Second, we use a liquid epoxy instead of gaskets to seal the MEA to the substrate.

2. Fuel Cell Fabrication

The fabrication of the fuel cell proceeds in two steps. The first step is a standard bulk micromachining process, which creates the flow channels and current collectors. The second step is post-processing, where the holes are drilled using laser ablation, and the membrane electrode assembly is sealed to the substrate. The channel etching process is shown in Fig. 3. A channel mask showing six separate cells is shown in Fig. 4. The process is summarized as follows.

1. A thermal oxide is grown on a silicon wafer. Both <100> and <110> wafers were processed.
2. A mask is etched in the thermal oxide, providing an etch mask for the substrate.
3. The substrate is etched for approximately 2.5 hours in EDP and TMAH.
4. The remaining oxide is removed and regrown to provide a protective coating.
5. Aluminium or gold is sputtered onto the channels and patterned so that only the collectors over the flow field risers remain.

The results are a set of flow fields made of oxide, with metallic bulk current collectors to channel electrons from the carbon supported anode on the membrane. The microfabricated component forms the electrode of the fuel cell.

The square edges of the mask were left uncompensated, so the EDP etchant rounded the flow field boundaries as shown in Fig. 5. This agreed with our fluidic intuition, which led us to believe that some rounding of the corners was desirable. The dimension of the flow fields in Fig. 5 is approximately 300 um.

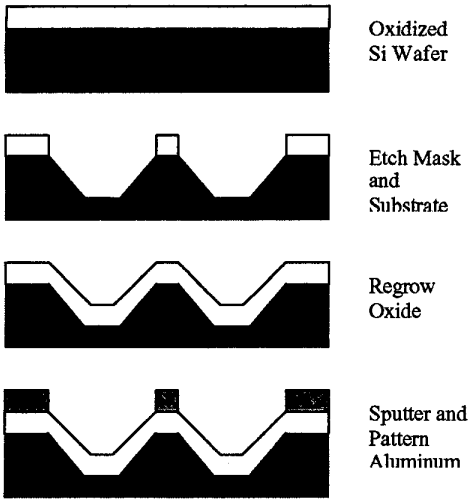

Figure 3: Fabrication process

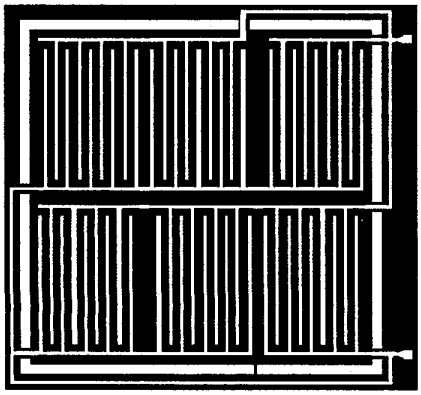

Figure 4: Interdigitated etch mask

Initially we intended to epoxy feed tubes to the top of the channels to provide an inlet and out put for the methanol solution. However, this approach led to leaky seals and blocked channels. As an alternative we examined laser post-processing of the substrate.

3. Post-processing and Assembly

We performed two major post-processing steps: laser ablation of fluidic vias, and assembly and sealing of the fuel cell. Laser ablation of fluidic vias allowed us to seal the feed tubes to the back of the wafer, simplifying the sealing process. Epoxy sealing attached the commercial MEA to the substrate and sealed the flow fields from short-circuiting from the anode to the cathode. The final assembly with the outer plexiglass supports gave the fuel cell additional mechanical strength for easy manipulation during cell during testing.

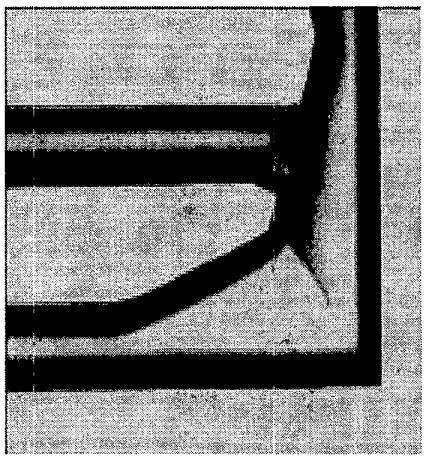

Figure 5: Rounded flow fields from no corner compensation

The laser ablation of the fluidic vias was performed at the NRC Integrated Manufacturing Technologies Institute. Using a 1064 nm, 7W diode pumped solid-state laser holes were drilled in the feed channels in approximately 1 minute using 6 ns pulses. The results of drilling are shown in Fig. 6 and Fig. 7. The holes in the image are approximately 500 um in diameter. It should be apparent from the image that the holes are of a very high quality, with little damage to the surrounding substrate. laser ablation is an excellent method for introducing high quality fluidic vias in chips.

The assembly process occurs in three-phases. First, the MEA is mounted to the plexiglass support and current collecting wires are bound to the aluminum pads using a silver epoxy, shown in Fig. 8. Second, the commercial MEA and silicone rubber feed tubes are sealed to the plexiglass and substrate. The seal was created using Industrial Formulators Inc. Cold Cure liquid epoxy, applied with a syringe around the exterior of the flow fields on the plexiglass support. The epoxy is allowed to dry overnight with 5 kg of weight applied to the sealed area by means of a metal weight and a corrugated plastic gasket. Third, the cathode, a stainless steel mesh, is secured to the fuel cell mechanically by securing the top plate. The final fuel cell assembly is shown in Fig 9.

The epoxy worked moderately well as a sealant; however, in pre-stressed locations it did have a tendency to yield if the pressure was too high. In addition, the epoxy had to be applied very carefully or it would leach into the fuel cell and block flow fields. The entire assembly process was successful, but tedious.

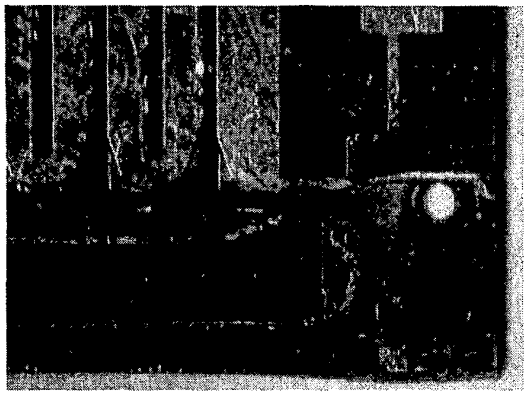

Figure 6: Hole drilling with context

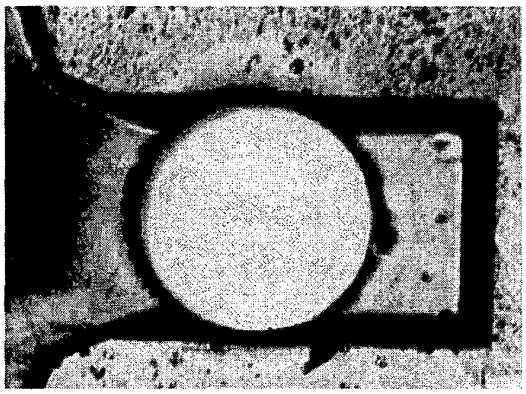

Figure 7: Hole at 5x magnification

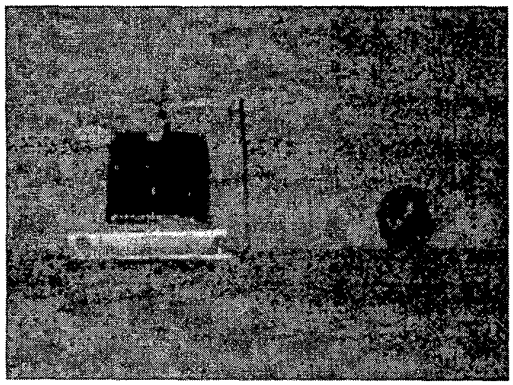

Figure 8: Assembly: flow fields and plexiglass backing

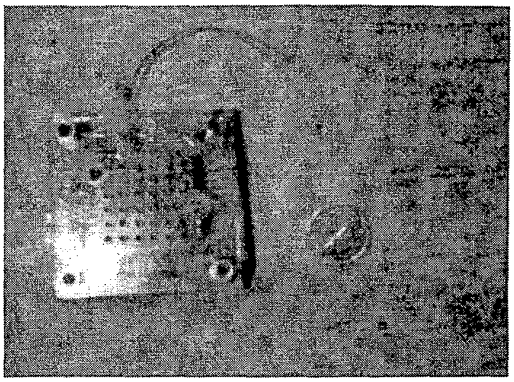

Figure 9: Final fuel cell assembly

4. Results

We ran a finite element analysis simulation of the fuel cell to determine the amount of pressure that would be required to drive the methanol through the microchannels. The simulation was run using ANSYS on a Sun machine. Results for a single element of the serpentine channel are shown in Fig. 10. The simulations were run for both 1 cm/s and 1 mm/s flow rates through the cell. Pressure drop across a single channel element was calculated as 76.2 Pa for 1 cm/s flow and 7.62 cm/s for a 1 mm/s flow. Assuming the pressure drops sum linearly across the cell, the total pressure loss is approximately 5500 Pa or 0.82 psi. This was anecdotally confirmed, as liquid could be driven through the cell by directly blowing in the feed tube. The maximum blowing pressure the average human can exert is approximately 2 psi. More accurate measurements were planned, but the appropriate gauged pumps had not arrived at the writing of this paper. The simulations are encouraging, as they show that little effort will be required to pump the fuel cell, increasing the total system efficiency.

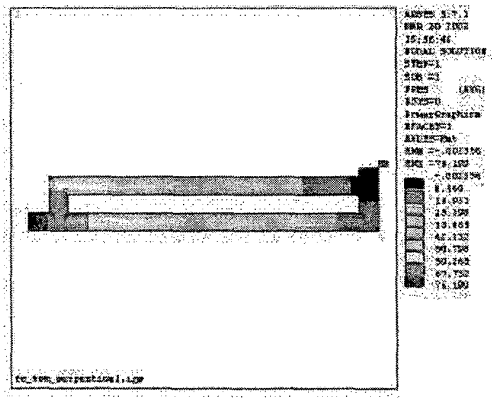

Figure 10: A Single Serpentine Flow Element Simulation

We also obtained preliminary voltage-current responses for the fuel cell. Fuel cells have a non-linear V-I characteristic because of polarization of the anode and cathode and limiting effects of reaction rate and mass transfer. To test the G-I characteristics, we used a 2 kΩ potentiometer as the load, and by varying the load, changed the current and voltage drawn. A 5% by vol. methanol-water solution was used as fuel. The results are shown in Fig. 11.

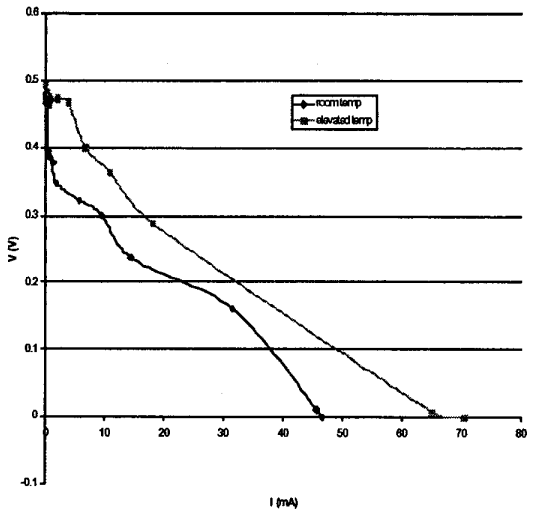

Figure 11: Voltage-Current Characterisitcs

The lower, dark curve represents the behavior of the cell at room temperature. The upper curve represents the behavior of the cell at an elevated temperature. The elevated temperature reading has some error associated with the measurement because we were indirectly controlling the temperature of the fuel cell by initially heating the fuel. Because our hotplate was operating open loop, the actual output temperature of the cell varied over a ±5 C range around 47 C. Our voltage performance was similar to the voltage reported by Kelly, Deluga and Smyrl. However, our current performance was approximately half of their reported values. We feel this difference is primarily due to the catalytic loading of our cells compared to theirs.

The seals performed well, except for an area which had been previously distressed, and resealed while the anode current collecting wire was attached. This leak may have also impeded the performance of the cell.

5. Conclusion

Significant work has been done at the NRC and SFU on the microfabrication of fuel cells. While the V-I characteristics of the fuel cell were not as good as hoped, we have made considerable progress on the fabrication of the fuel cells. The fabrication of the fuel cell proved that it was possible to micromachine a fuel cell in a hybrid manner. The low-pressure difference required, and the ease of fabrication were encouraging. Through this work, we identified two key problems with current fuel cell designs: sealing and assembly. While our assembly and sealing processes were effective, they were tedious and prone to error. Further work on the current design could yield an effective micro fuel cell. However, we believe that tackling the two key problems directly will result in better overall performance. In particular we will investigate injectable seals and the development of assemblyless processes for micro fuel cells.

Acknowledgements

The authors would like to acknowledge Eva Czyzewska and Bill Woods for help in fabrication and Simon Liu for the simulations. The authors would like to thank the NRC National Fuel Cell program for funding and support.

References

1. G. McLean, N. Djilali, M. Whale, T. Niet, "Application of Micro-scale Techniques to Fuel Cell Systems," *10th Canadian Hydrogen Association Conference*, Quebec City, 2000, pp. 760-768.

2. S. C. Kelly, G. A. Deluga, W. H. Smyrl, "A Minature Methanol/Air Polymer Electrolyte Fuel Cell," *Electrochemical and Solid-State Letters,* 3 (9) 2000, pp. 407-409.

3. W. Y. Sim, G. Y. Kim, S. S. Yang, "Fabrication of Micro Power Source (MPS) Using a Micro Direct Methanol Fuel Cell (uDMFC) for the Medical Application," *14th IEEE International Conference on Micro Electro Mechanical Systems* IEEE, Piscataway, NJ, p.341-4

4. X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, "Recent advances in direct methanol fuel cells at Los Alamos National Laboratory," *Journal of Power Sources,* 86, 2000, pp. 111-116.

5. R. Hockaday, M. DeJohn, C. Navas, P. Turner, H. Vaz, L. Vazul, "Development of Micro-Fuel Cells™ for Cellular Telephones," *Fuel Cell 2000*, Lucerne, Switzerland, 2000, pp. 37-44.

6. G. A. Tompsett, M. S. Brown, C. Finnerty, N. M. Sammes, K. Kendall, "Design of a Tubular Micro-SOFC Demonstration System," *Fourth European Solid Oxide Fuel Cell Forum,* Lucerne, Switzerland, 2000, pp. 13-18.

7. J. Larminie, A. Dicks, *Fuel Cell Systems Explained,* John Wiley and Sons, New York, 2000.

8. G. Kovacs, *Micromachined Transducers Sourcebook,* McGraw-Hill, Boston, 1998.