

# Micro Direct Methanol Fuel Cell Utilizing Silicon Supported Ionomer Membrane

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**Abstract:** This paper reports the design, fabrication, and IV-characteristics of pump-free micro direct methanol fuel cells, based on silicon technology. The fuel cell design features a rigid silicon support with micropores containing the proton conducting ionomer Nafion®. This design intends to limit the effects of methanol cross-over by constraining the hydrophilic conducting channels of the ionomer. The IV characteristics of the cells are evaluated and the device is shown to be able to deliver 4 mW/cm<sup>2</sup> using ambient air and 3M methanol at room temperature. The performance limiting characteristics are investigated and indicate that large cavity defects in the ionomer membranes are formed during fabrication.

**Keywords:** Fuel Cell, DMFC, Methanol, Crossover

## INTRODUCTION

In many small scale low power devices rechargeable battery technology cannot meet the power requirements without breaking the size constraints of the system. This is, for example, the case in most modern hearing aids. Today, such devices are often powered by non-rechargeable zinc-air batteries. A potential alternative to these batteries are micro fuel cells, which can be refuelled in seconds. For such systems pump-free (i.e. passive) operation is desirable due to size constraints which do not allow for active components such as pumps and heaters, without lowering the achievable total device power density significantly.

Our candidate for such a micro fuel cell is the direct methanol fuel cell (DMFC)[1]. The performance of DMFC's however, are limited by the direct permeation (crossover) of fuel through the proton exchange membranes (PEM) [2], which greatly limits the efficiency, and maximum power output. DMFC's lifetimes can also be limited by the mechanical stability of the cell membrane. The PEM expands when hydrated which can delaminate the catalyst layers. Therefore improving mechanical stability should enhance the total device lifetime.

### Methanol crossover

Fuel crossover in DMFCs is the main limiting factor in performance. One effect of this crossover is a loss of useful fuel, which reduces the overall efficiency. The other performance limiting effect is oxidation of methanol on the cathode which greatly increases the polarization loss of the cell. For typical cells this loss can lead to more than a 50% reduction in open circuit potential (OCV), where the crossover is mainly due to diffusion. At positive currents, the concentration of methanol at the anode electrode, and thus the diffusion flux, will decrease. However, for

increasing currents convection through the membrane will increase and becomes a relevant factor in the crossover.

Nafion® is a solid ionomer, consisting of fluorinated hydrocarbon backbone, with sulfonic acid groups. This structure leads to formation of hydrophilic and hydrophobic regions in the solid polymer. Due to the high acidity of the acid groups the hydrophilic regions become highly proton conductive. Methanol is miscible in water and can therefore diffuse through the liquid phase of the hydrophilic regions. Reducing water content will therefore reduce proton conductivity[4].

## FABRICATION AND CHARACTERISATION

Our fuel cell design is intended to investigate the effects of crossover. It constrains both the proton and liquid flow channels by employing a porous silicon membrane as support for the proton conducting ionomer membrane. This allows for a detailed study of the influence of the hole-sizes and spacing on proton conductivity.

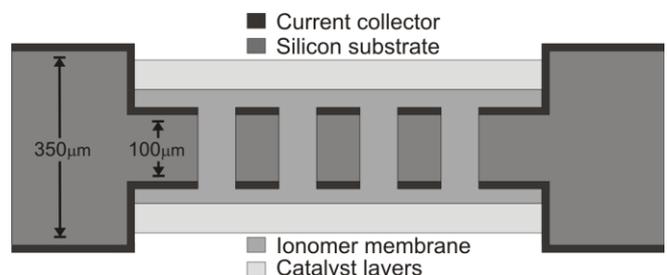


Fig. 1: Schematic illustration of the fuel cell. Aspect ratios are not to scale.

The porous silicon membrane is fabricated using conventional cleanroom silicon fabrication techniques. There are three defining etch steps, two openings and one hole etch. All three etch steps are carried out using deep reactive ion etching. Initially the holes are etched through the entire 350 μm thick wafer. After the holes

have been defined a large opening is etched in both sides of the wafer, defining a 100  $\mu\text{m}$  thick membrane with a 350  $\mu\text{m}$  thick border as illustrated in Figure 1. The membrane contains a triangular lattice of holes with diameters ranging from 2  $\mu\text{m}$  to 100  $\mu\text{m}$ . The use of this technique also allows structures to be defined on the membrane, such as pillars which could improve the electrical contact of the catalyst layer. A scanning electron microscope (SEM) image of such a structure can be seen in Figure 2.

After definition of the membrane structure, a thermal oxide is grown to insulate the two sides of the membrane from each other. Then a 200 nm layer of gold is deposited on both sides to act as current collectors. Sputter deposition is used to ensure coverage of the frame sidewalls which connect the collector with the surface of the frames. The device is briefly etched with aqua regia to remove any gold contacts between the current collectors. A SEM image of the resulting membrane can be seen in Figure 3. The final device measures 10 mm x 7.5 mm with a 1 mm frame, such that the total active area is 8 mm x 5.5 mm (0.44  $\text{cm}^2$ ).

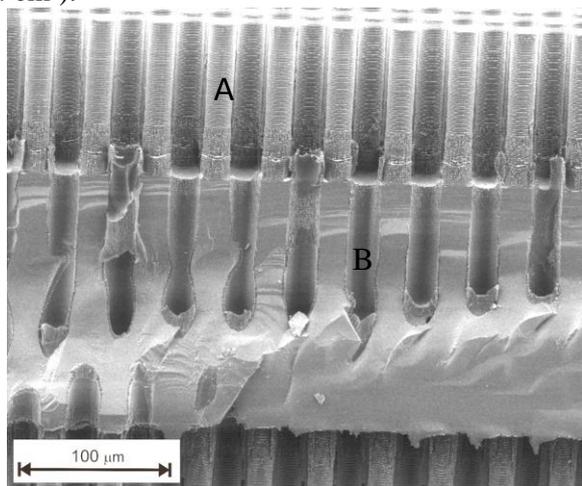


Fig. 2: SEM image of a cross-sectional fracture of a membrane with pillars (A) defined around the pores (B). The characteristic scallops of the Bosch process are visible on the pillars.

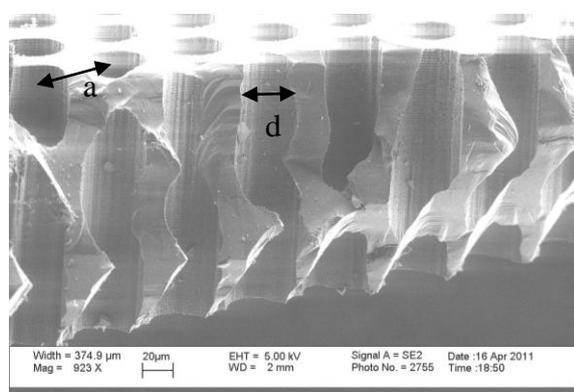


Fig. 3. SEM image showing a cross-section of the membrane prior to Nafion® treatment. The holes are approximately 20  $\mu\text{m}$  in diameter (d) with 30  $\mu\text{m}$  spacing (a)

Nafion® is soluted in a water and isopropylalcohol (IPA), mixture, and inserted into the membrane pores using capillary forces. The water and IPA is then slowly evaporated casting solid Nafion® in the pores.

After the membrane has been fabricated, the two catalysts layers are applied. Figure 4 shows a cross-sectional SEM image of the anode catalyst layer. The layer is a spray coated porous layer of Nafion® and PtRu on carbon black (80 wt.% catalyst loading on Vulcan-XC72) on the anode side, and Nafion® and Pt on carbon black on the cathode side. The loadings are approximately 4  $\text{mg}/\text{cm}^2$  on the anode and 2  $\text{mg}/\text{cm}^2$  on the cathode side.

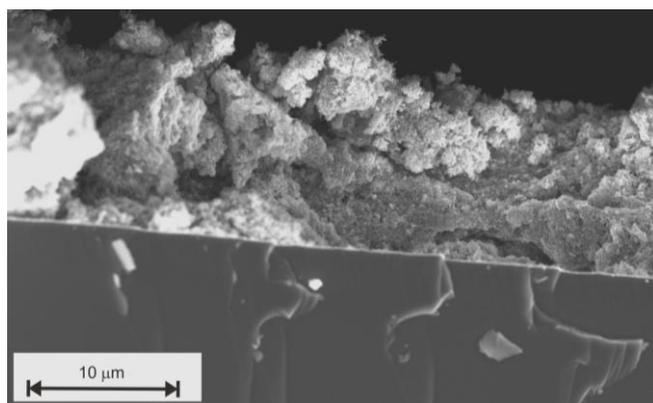


Fig. 4: SEM image of a membrane cross-section after catalyst layer deposition. The catalytic layer is a spray coated 10  $\mu\text{m}$  thick porous PtRu/carbon black/ionomer mixture.

### Device performance

The IV-characteristics three fuel cells (A, B and C) are shown in figure 5. The testing was conducted with 3M methanol on the anode side, ambient air on the cathode and room temperature and pressure conditions, and with a current scan rate of 0.3 mA/s. All three fuel cells have 20  $\mu\text{m}$  diameter hole sizes, but different lattice spacings. The results are tabulated in table 1. For fuel cells A and B the peak power density ( $P_{\text{max}}$ ) is in the 4  $\text{mW}/\text{cm}^2$  range, with OCVs of 500-600 mV. Fuel cell C has much lower OCV of only 160mV and a peak power of 0.42  $\text{mW}/\text{cm}^2$ . For fuel cell A and B the OCV is still well under the theoretical standard potential of 1.2V which indicates that as with typical DMFCs crossover loss is very large. For fuel cell A and B, the difference in lattice spacing leads to a difference in the pore area of 6.84  $\text{mm}^2$  for A and 4.36  $\text{mm}^2$  for B. Though A has the highest power output, B has the highest power output per active area. The IV-characteristics for these two devices are very similar, with almost identical ohmic regions, which suggests that the main difference in performance is caused by slight differences in the membrane quality, and not by the difference in pore area.

Table 1: Device performance parameters. All devices have 20  $\mu\text{m}$  holes

	Lattice spacing	OCV [mV]	Pmax [mW/cm <sup>2</sup> ]	Hole Area [mm <sup>2</sup> ]
A	40	636.68	4.63	6.84
B	50	500.25	3.69	4.36
C	50	159.61	0.42	4.36

We believe that the OCV and a low maximum power density of fuel cell C, is caused by increased fuel crossover, and lack of proton conducting pathways through the membrane, as the pores in its membrane contained cavities not filled with Nafion®, similar to the case shown in Figure 6. These cavities are currently believed to be the essential limiting factor in the device performance. When hydrated such cavities are filled with water and add significantly to the diffusion flow of methanol, but insignificantly to the proton conductivity. Through proper control the process it is possible to create membranes without these defects, such as the one shown in Figure 7. At the time of writing we are making a detailed study of the membrane formation but have none available for electric testing.

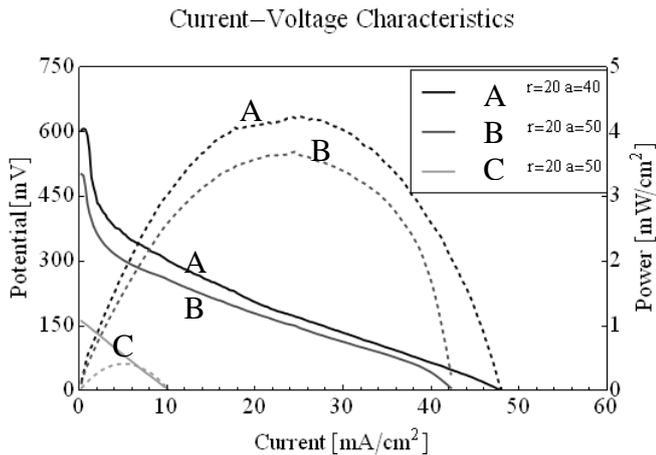


Fig. 5: Current-Voltage characteristics of three different devices, with two different membrane design specifications. Dashed curves are power curves (right axis). Full lines are potential curves (left axis). Data points are to closely spaced to be distinguishable.

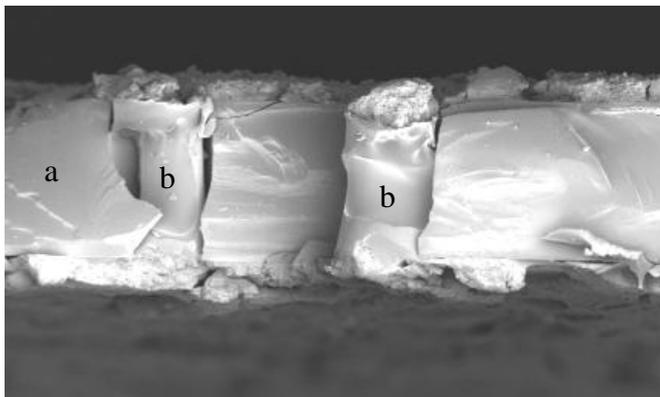


Fig. 6: SEM image of a cross-sectional fracture of a silicon membrane (a) after ionomer treatment. Cavities are visible in the center of the membrane filed pores

(b).

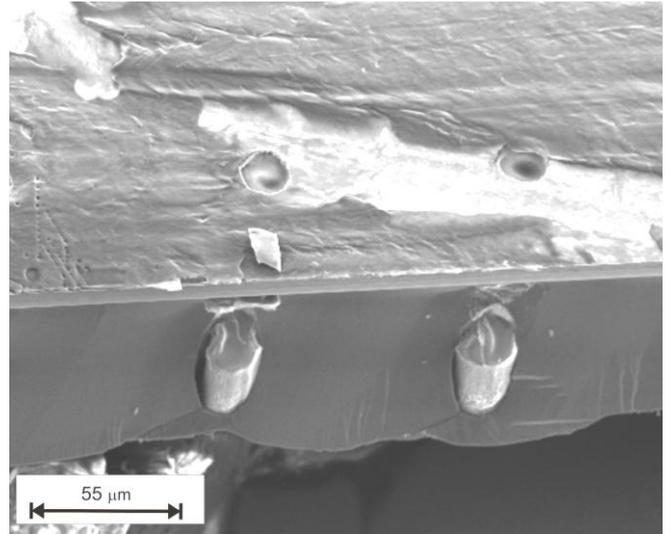


Fig. 7: SEM image of a cross-sectional fracture of a membrane after ionomer treatment. The fracture line is not perpendicular to the surface, and therefore exposes two ionomer filled columns.

## DISCUSSION

Ionomer membrane creation has proven to be a critical point of the fabrication, and improved control of the structure of the finished membrane is currently being investigated. Methods of further improving the membrane post insertion have yet to be considered, though for classical membranes both heat treatments as well as potential ramping methods have been reported to improve the proton conductivity.

Using silicon to reduce the active membrane area should, (1), reduce the ionic conductivity and, (2), fuel crossover of the membrane by the same fraction and, (3), slightly reduce electrode performance due to increased distances between reaction sites and the membrane.

IV-characteristics have shown that even though the active membrane area is 8-10 times lower than the total membrane area, the performance of the devices are comparable to all-Nafion® membranes. This suggests that it is not the ionic conductivity of the membrane, but rather the electrode performance and the fuel crossover that limits the fuel cell performance. Further testing will show if variations of the geometry can optimize the tradeoff between proton conductivity and crossover to the specific device needs. Reliability testing is still needed to determine if the membrane is capable of providing mechanical stability to reduce delamination problems in the catalyst layers.

## CONCLUSION

This work has resulted in small working direct methanol fuel cells, capable of operation within the power range of very low-power small scale portable systems. The full consequences of the design choices have yet to be characterized, especially regarding methanol crossover. The qualitative effects of membrane quality on performance have indicated that membrane formation is a critical point in the device fabrication and requires further optimization. Two fuel cells were capable of operation with peak powers of 4 mW/cm<sup>2</sup>, which is in the lower range of power requirements for small size portable electronics such as hearing aids or other medical devices. This shows promise that future improvements will increase the power into the range where batteries in such devices can be replaced with micro fuel cells.

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