

INFLUENCE OF METHANOL CONCENTRATION AND TEMPERATURE IN A PASSIVE AND SILICON-BASED MICRO DIRECT METHANOL FUEL CELL

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Abstract:

This paper presents a passive and silicon-based micro direct methanol fuel cell. The microdevice is based on a hybrid approach composed of a commercial Membrane Electrode Assembly (MEA) sandwiched between two microfabricated silicon current collectors. It was found that methanol concentration had low impact in the fuel cell maximum power density, which reached a value around 10 mWcm^{-2} and is comparable to values reported in the literature for larger passive and stainless-steel fuel cells. Temperature measurements were performed and it was seen that the fuel cell temperature did not change significantly and was independent of the methanol crossover rate.

Key Words: micro-DMFC, silicon microsystem, methanol concentration, passive fuel cell

1. INTRODUCTION

The increasing presence of sensing and actuating MEMS in different application fields (automotive, food industry, security...) in the last decade has generated an increasing demand of light and efficient power sources. Regarding both functionality and cost, the integration of these power sources within the devices to be powered arises as the optimal solution and opens interesting opportunities in future advanced MEMS-based devices. Compared with other approaches such as energy harvesting devices, microfuel cells have shown the capability of providing higher power densities and in particular, those fuelled with methanol are very attractive due to the high density, low cost and easy storage of this fuel.

A lot of research has been performed in the study of active methanol fuel cells, in which usually the liquid fuel and the oxidant are pumped externally [1,2]. However, the application of this kind of cells as portable power sources has lead to simpler approaches that give up ancillary devices such as pumps or gas compressors and in consequence, the parasitic power losses associated to them [3-5]. In this way, this passive fuel cell approach offers the advantage of a simpler and compact design, which is very adequate regarding MEMS integration. In this work, we present the main features of a passive

silicon direct methanol fuel cell. The microDMFC is based on a hybrid approach, which means in this case that a commercial MEA has been assembled with two silicon micromachined components. The device yields one of the highest power density values reported up to date in a MEMS-based DMFC operating at room temperature.

2. EXPERIMENTAL

The presented device is based on a hybrid approach composed of a commercial Membrane Electrode Assembly (MEA) consisting of a Nafion® 117 membrane with 4.0 mg/cm^2 Pt-Ru catalyst load on the anode side and 4.0 mg/cm^2 Pt on the cathode (E-TEK ELAT®) sandwiched between two microfabricated silicon current collectors. Nafion® 117 was chosen due to its higher efficiency at high methanol concentrations [6]. The silicon plates have been provided with an array of vertical squared channels of 300 micrometers depth that covers an area of $5.0 \times 5.0 \text{ mm}$. These channels allow fuel transport to the electrodes and their dimensions have been set to 80×80 micrometers in order to ensure the prevalence of the capillary force versus gravity regardless of device orientation in the anode side [7]. The silicon components have been covered with a sputtered layer of Au in order to ensure good electrical conductivity. A detailed

explanation of the fabrication process is reported elsewhere [8]. In order to guarantee uniform pressure over the active area of the cell, two micromilled methacrylate pieces tightened with four bolts were used as external casing. In addition to acting as a mechanical support while testing, these pieces provide the cell with a 100 μl methanol reservoir. Figure 2 shows a photograph of the assembled device.

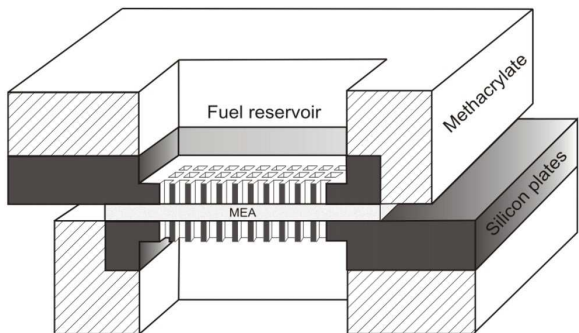


Fig.1: Schematic view of the microfabricated fuel cell

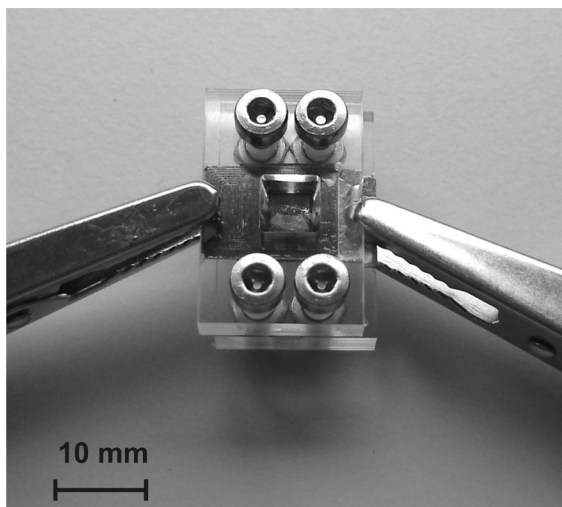


Fig.2: Photograph of the mounted device

The microfuel cell was tested at room temperature and the characteristic I-V curves were obtained by applying different current loads with a Keithley 2400 Sourcemeter.

Prior to the performance test, the MEA was submitted to a pre-treatment procedure that consists on immersing it in methanol at 0.25 M for 2-3 hours and afterwards submitting the fuel cell to working conditions at a constant current for a short period of time [9].

3. RESULTS AND DISCUSSION

3.1 I-V microfuel cells characteristic curves and power output

Figure 3 shows the performance of the passive microdevice when filled with 100 μl of 2.0 M and 4.0 M methanol concentrations. It can be seen that the device reaches a maximum power density of 9.0 mW/cm^2 and an open circuit voltage (OCV) of 0.42 V when fed with 2.0 M methanol solution at room temperature. This maximum power density is higher than any of the values reported before in silicon-based methanol fuel cells without external fuel pumping [7] and close to the values reported in the literature for stainless-steel fabricated passive micro cells [10,11]. Note that the value of the OCV is below the values recorded in active silicon-based fuel cells, with typical values in the range of 0.5-0.7 V.

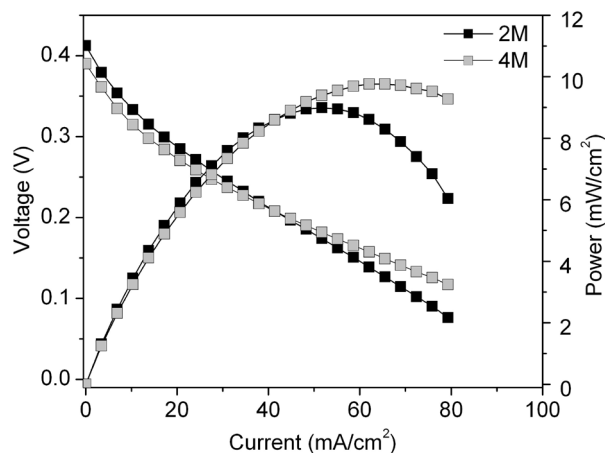


Fig.3: Device performance at room temperature at different methanol concentrations

According to Jiang et al, this could be due to the enhancement of methanol crossover that takes places due to the large pressure drop between the anode and cathode sides in air-breathing liquid-fed fuel cells [12]. Figure 3 also shows that when the methanol concentration is increased to 4.0 M, the OCV decreases to 0.39 V, whereas the maximum power density rises to 9.7 mW/cm^2 . The observed voltage drop at open circuit conditions is due to the increase of the methanol permeation rate from the anode to the cathode at a higher methanol concentration. These results

corroborate what has been extensively reported in literature, i.e. the methanol concentration yielding the maximum power in a passive cell is placed around 4.0-5.0 M, values that are significantly higher than in an active cell, which show optimal performance at concentration around 1.0 M [13]. In the case of the micro fuel cell presented in this work, using 4.0 M methanol instead of 2.0 M causes an improvement around a 7% in the maximum power density. Nevertheless, this increment is smaller than the obtained in passive macro devices, in which increases between 15-35% of maximum power density have been reported [10,13]. The reason of obtaining a better performance at higher concentrations has been attributed in the past to the compensation of the mass transport limitations arising in a diffusion-driven methanol distribution in this kind of cells. In fact, this effect can be observed in the differences shown in the high current region by the curves depicted in figure 3. However, they have low impact on the fuel cell performance because they lie at currents beyond the peak power point.

Recently, the temperature monitoring of a passive DMFC anode performed by Liu et al. showed that the better performance of the fuel cell at high methanol concentrations could be mainly attributed to a cell temperature increase caused by the exothermic reaction of the crossed-over fuel [10]. Therefore, the influence of methanol concentration on the temperature of our device was evaluated by placing a tiny thermistor in the anode current collector reservoir.

The temperature change of the cell at different electric loads was measured and depicted in figure 5. It was found that cell temperature at open circuit conditions depended on the methanol concentration. The evolution of fuel cell temperature at increasing current densities was also concentration dependent: with a methanol concentration of 2.0 M, the fuel cell temperature rises as it happens with active cells. This is due to the heat produced by the oxygen reduction reaction at the cathode [3]. However, at a concentration of 4.0 M, the temperature keeps constant around a value of 25.6 °C, probably due to a temperature compensation between the reduction of heat produced by methanol crossover as methanol starts to be consumed at the anode

and the heat produced by oxygen reduction at the cathode.

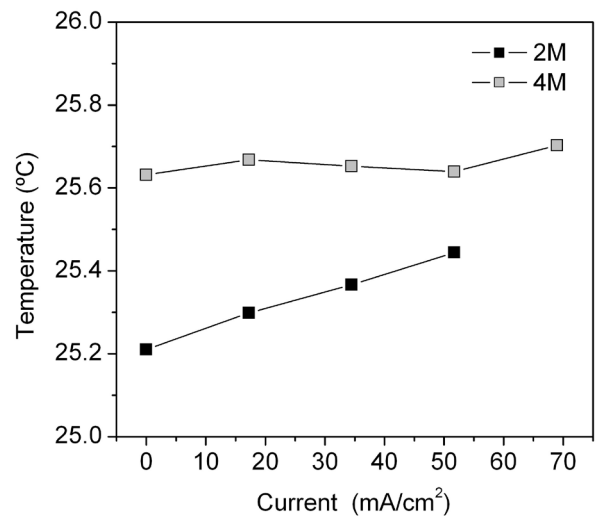


Fig.5: Fuel cell temperature at different operation points and methanol concentrations

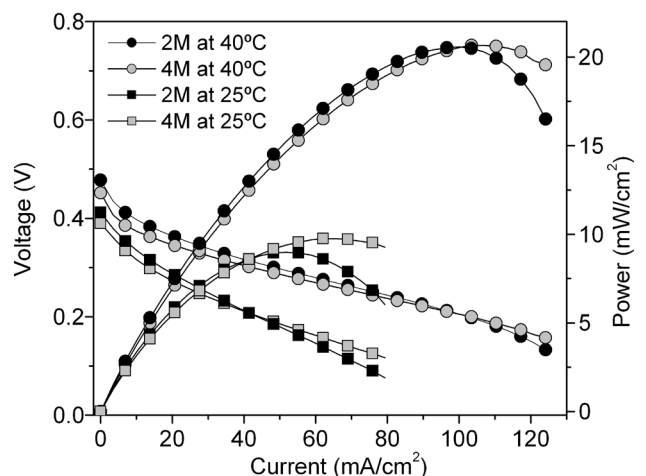


Fig.6: Microdevice performance at 25°C and at 40°C for 2M and 4M methanol concentrations

Despite the different temperature behaviour at the tested methanol concentrations, temperature difference between both cases did not exceed 0.5 °C. This could explain the low influence of the methanol concentration on the maximum power density provided by our device. The reason for such a small temperature increase can be found in the high thermal conductivity of the silicon current collectors of the device, value that exceeds by far the characteristic values of the materials typically used in macro devices. The

ability of silicon to dissipate heat has been reported extensively in different kinds of silicon thermal-based microdevices, in which the silicon is used as a heat sink [14].

Finally, the effect of temperature on the performance of our silicon microfuel cell was tested by submitting the device to a constant temperature of 40°C. Results are shown in figure 6. It can be seen that the maximum power density achieved at 40°C is significantly higher than at room temperature and reaches a value of 20mW/cm². However, it has to be noted that again, there are no visible differences in the maximum power density obtained with 2M and 4M methanol concentrations. These results show that temperature plays a main role in passive fuel cell performance whereas methanol concentration has an impact mainly in the concentration losses region that yields beyond the maximum power peak.

4. CONCLUSIONS

A passive silicon DMFC based on a hybrid approach consisting of a commercial MEA assembled with two silicon microfabricated current collectors is presented. When fed with methanol concentration of 2.0 M, the microdevice yields a power density of about 10 mWcm⁻², a value comparable to values reported for larger and stainless-steel microfabricated cells. This shows that in the present approach, miniaturization seems to affect performance negligibly. However, it was found that unlike in other reported devices, feeding the cell with a higher methanol concentration had low impact in the fuel cell performance. Temperature measurements showed that at a concentration as high as 4.0 M the temperature of the cell did not increase beyond 1°C. Accepting the hypothesis of Liu and co-workers who relate a better performance of passive fuel cells at high concentrations to the temperature increase caused by methanol crossover, the almost insignificant temperature increase registered in our cell would explain the small change in power density. This hypothesis is supported by a second experiment in which the temperature of the fuel cell was raised to 40°C by an external heater. Results showed an improved performance of the cell due

to the temperature increase but again, no differences were observed between 2M and 4M methanol concentrations.

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