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Influence of current collectors design on the performance of a silicon-based passive micro direct methanol fuel cell

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ABSTRACT

In this paper, the influence of current collector open ratio on the performance of a passive micro direct methanol fuel cell is evaluated. The device is based on a hybrid approach consisting of two microfabricated silicon current collectors assembled together with a commercial membrane electrode assembly. The characterization was performed by measuring polarization curves of the fuel cell using current collectors with different open ratios on anode and cathode. Results show that the way in which the open ratio of current collectors is combined has an effect not only on the output power but also on the repeatability of polarization curves. This study allows the setting of some general design rules for current collectors of passive micro direct methanol fuel cells.

1. Introduction

In recent years, direct methanol fuel cells (DMFC) have proven to be a promising solution as portable power sources due to their high energy density and ease of fuel handling. These same reasons make them particularly attractive for the microsystems field, where the energetic needs of complex smart integrated systems have encouraged an intensive search for a suitable power source. Among the several alternatives that have arisen as possible solutions at small scales – such as vibration, magnetism and thermoelectric harvesters, microbatteries, microreactors – direct methanol fuel cells stand out for their capability to deliver high power densities. In particular, methanol fuel cells with passive fuel delivery have the advantage over active systems of not requiring any external pumps or auxiliary devices [1,2]. Although most of the parameters regulating the performance of passive methanol micro fuel cells are common with active devices, the fact that passively-fed cells rely on diffusion as fuel transport mechanism lead to the necessity of using higher methanol concentrations to enhance fuel distribution [3,4]. In this sense, the microfluidic structures implemented in the fuel cell current collectors have to be designed carefully as they must ensure an effective methanol distribution and at the same time, avoid the accumulation of both carbon dioxide and water in the electrodes. Whereas the influence of the fluidic structures geometry on active micro fuel cells performance – either in single-cell or fuel cell stacks – has been widely explored in the past, only a few works about this subject have been published in passive micro fuel cells literature [5,6]. Particularly, it has been shown that in this type of devices, the most influential parameter is the current collector open ratio (i.e. the electrode area exposed to the fuel). Up to now, the effect of the open ratio on fuel cell performance has been explored through experimental studies [7–9], as well as through analytic and computer-based models [10–16]. However, these studies report on current collectors with geometrical features in the millimeter range, whereas there is a lack of experimental results concerning passive fuel cells in micro-scaled technologies.

This work evaluates the influence of the current collector geometries on the operation of a passive microDMFC by measuring the fuel cell performance using silicon microfabricated current collectors with the same and different open ratio on anode and cathode. Characterization of the devices is performed by obtaining their polarization curves and these results are compared in terms of power density and repeatability.

2. Device description and assembly

The micro fuel cell under study consists of two silicon microfabricated plates and a commercial membrane electrode assembly (MEA) made of a thin Nafion® 117 layer coated with a Pt–Ru $4\,g\,cm^{-2}$ anode and a Pt $4\,g\,cm^{-2}$ cathode. In this device, the silicon plates act as current collectors and at the same time, deliver the reactants to the catalyst layers that reach both sides of the MEA by diffusion. Fuel delivery to the electrodes takes place through grids of $80\,\mu m \times 80\,\mu m$ cross-section channels obtained

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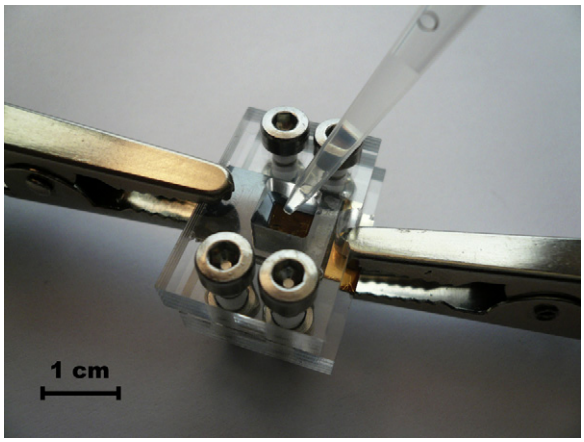

Fig. 1. Picture of the micro fuel cell being filled with a micropipette.

Table 1
Summary of the microfabricated current collectors.

Design	d (μm)	Open ratio (%)
A	40	40
B	80	23
C	160	10

by a deep reactive ion etching process and defined over areas of 5 mm × 5 mm. Electrical conductivity is achieved by sputtering a thin Ni–Au layer. Once fabricated, the silicon current collectors are cut in chips of 10 mm × 14 mm. Finally, the device is assembled between two methacrylate pieces that also serve as fuel reservoirs (a picture of the device can be seen in Fig. 1). More details about the microfabrication process can be found in a previous work [17].

In order to study the influence of channel density on the fuel cell performance, three different current collector designs were fabricated by setting the distance between consecutive channels d to A = 40 μm, B = 80 μm and C = 160 μm. Since the arrays of channels are all defined in the same chip area, this distance determines the number of channels in the chip, hence the open ratio of the plates. In this way, open ratio is set to 40% for the current collectors with distance A, to 23% for distance B and to 10% for distance C. These geometric features are summarized in Table 1. A set of optical microscope images of the microfabricated current collectors of different channel density is shown in Fig. 2.

3. Fuel cell characterization

The device mounted with the same current collector with an intermediate open ratio (type B) in anode and cathode was set as reference configuration. The influence of the variation of the area exposed to reactants was tested by comparing the performance obtained when using one of this B-type collectors with another using a current collector with larger (type A) or smaller (type C) open ratio. As it has been summarized in Table 2, these tests were performed subsequently for the anode and the cathode sides (allowing in this way the discrimination between the cases when the performance of the device is being limited by the supply of methanol – anode – or oxygen – cathode –). The effect of a highly unbalanced open ratio was evaluated by measuring the performance of fuel cells mounted with a combination of A and C current collector types.

Table 2
Fuel cell configurations measured.

Fuel cell label	Current collector design	
	Anode	Cathode
fc-BB (reference)	B	B
fc-AB	A	B
fc-CB	C	B
fc-BA	B	A
fc-BC	B	C
fc-AC	A	C
fc-CA	C	A

The polarization curves of the micro fuel cell were obtained with a Keithley 2400 Sourcemeter using an in-house LabVIEW program. Passive fuel cells are usually operated at higher fuel concentrations than active fuel cells because mass transport mechanism is driven mainly by diffusion. Therefore, the characterization of the micro fuel cells was done at room temperature for methanol concentrations of 2 M and 4 M, as generally these values lay within the concentration range that yields optimal fuel cell performance [4,17,18].

The experimental results are reported in the following two sections. In the first one, the polarization curves obtained from the different fuel cells configurations are presented and discussed in terms of the obtained power densities. In the second one, the same configurations are subjected to consecutive characterizations to evaluate the repeatability of the measurements.

3.1. Influence of current collector geometry on power density

This section reports on the influence of the current collector open ratio on the power density delivered by a ready-mounted micro fuel cell. The performances of the measured configurations are compared to the reference device fc-BB.

3.1.1. Influence of the anode open ratio

The effect of anode open ratio on the power density delivered by a fuel cell was evaluated by testing fc-AB, fc-BB and fc–CB fuel cell configurations at methanol concentrations of 2 M and 4 M. Fig. 3a shows that at 2 M concentration, the obtained maximum power density of the fuel cell is enhanced at larger anode open ratios

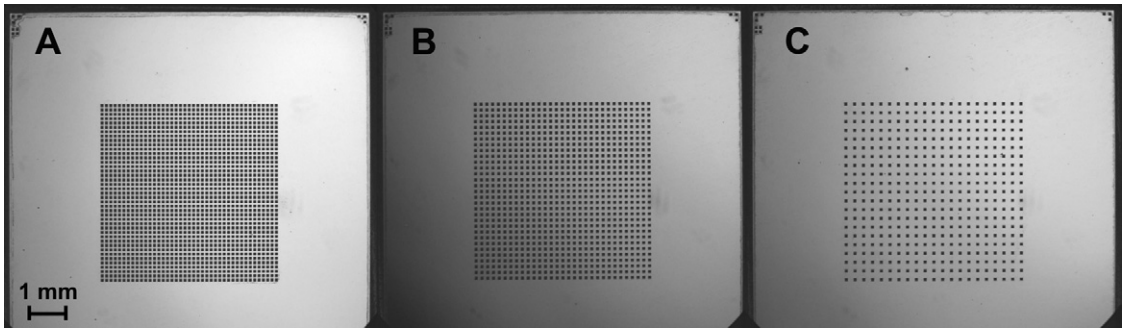

Fig. 2. Detail of the three silicon current collectors with different open ratio.

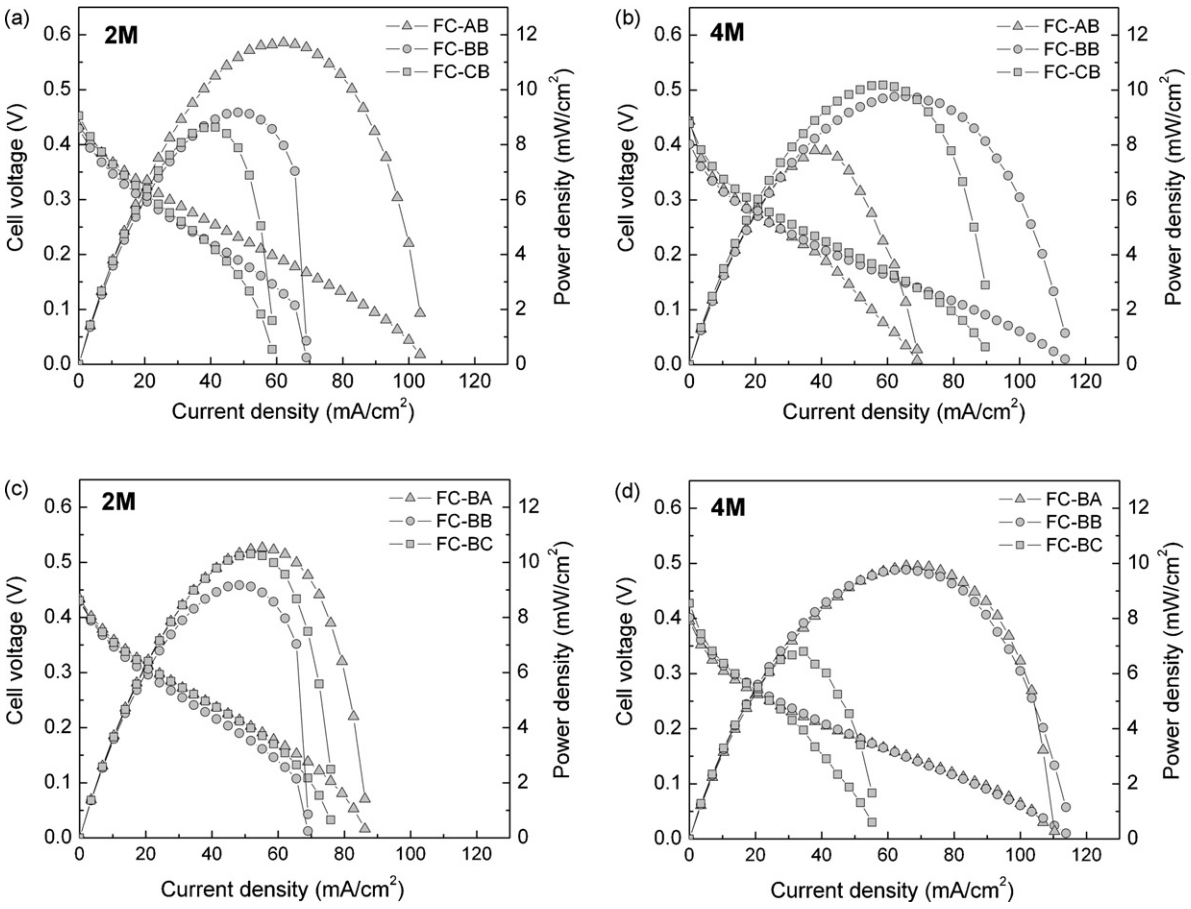

Fig. 3. Performance of micro FC when testing different silicon current collectors at the anode (a and b) and cathode (c and d) working with methanol concentrations of 2 M (a and c) and 4 M (b and d).

(values of 8.5 mW cm^{-2}, 9.0 mW cm^{-2} and 11.7 mW cm^{-2} were subsequently achieved when increasing the anode open ratio to 10%, 23% and 40%). The reason for this increase can be simply attributed to the enhancement of the mass transport mechanisms associated to a larger area of electrode exposed to methanol, as evidenced by the progressive extension of the limiting current region of the polarization curves.

However, a different trend was obtained when testing the same fuel cell configurations at a 4 M methanol concentration. Fig. 3b shows that in this case, although higher power densities than those achieved at 2 M concentration were obtained for configurations fc-BB and fc-CB (values around 10 mW cm^{-2} in both cases), the maximum power density of the fuel cell dropped to 8.0 mW cm^{-2} when setting the anode open ratio to 40% (configuration fc-AB). That is, when working at concentrations of 4 M, fuel cell performance gets worse at increasing anode open ratios. The reason for this behavior can be explained by taking into account the methanol crossover phenomena through the membrane [19]. As reported in the literature, concentrations of methanol up to 4–5 M enhance the mass transport rate of methanol to the anode which, depending on fuel cell design and catalyst load, generally results in a higher output power [4,20]. However, at the same time the amount of methanol crossing the membrane to the cathode becomes also significantly higher at 4 M than at 2 M – and in the present case, when the anode open ratio is higher than the cathode ratio it compromises the fuel cell operation. In this way, the abrupt voltage drop at current densities of 40 mA cm^{-2} observed for the fc-AB configuration is probably due to the blocking of cathode reaction sites by the crossovered methanol.

3.1.2. *Influence of the cathode open ratio*

The effect of the cathode open ratio was explored by testing fc-BA, fc-BB and fc-BC fuel cell configurations. Fig. 3c and d shows the polarization curves obtained at methanol concentrations of 2 M and 4 M, respectively. Measurements show that at a methanol concentration of 2 M, the maximum power output of the cell was placed at around 10 mW cm^{-2} and did not show any significant variation when the cathode open ratio was subsequently decreased down to 10%. These results proved that the reduction of the cathode open ratio did not cause any limitation in the oxygen transport required in the operation of the cell. The obtained power densities at 4 M methanol concentration show that the methanol concentration increase does not seem to improve the maximum power density values for configurations fc-BB and fc-BA (i.e. cathode open ratio ≥ anode open ratio) although higher limiting currents than those at 2 M are obtained. Moreover, when decreasing the cathode open ratio to 10% while maintaining the anode at 23% (configuration fc-BC) a clear deterioration of cell performance is observed. This decrease can be attributed to the effect of oxygen supply reduction associated to the cathode open ratio decrease. Compared to 2 M concentration, the oxygen limitation at 4 M is worsened by the fact that the crossovered methanol contributes to cathode blocking.

3.1.3. *Effect of high open ratio unbalance on fuel cell performance*

In order to explore further effects of electrode open ratio asymmetry on the micro fuel cell performance, devices with both anode and cathode current collectors set to 10% and 40% (configurations fc-AC and fc-CA) were tested at 2 M and 4 M methanol concentrations. The obtained performance at 2 M methanol concentration is

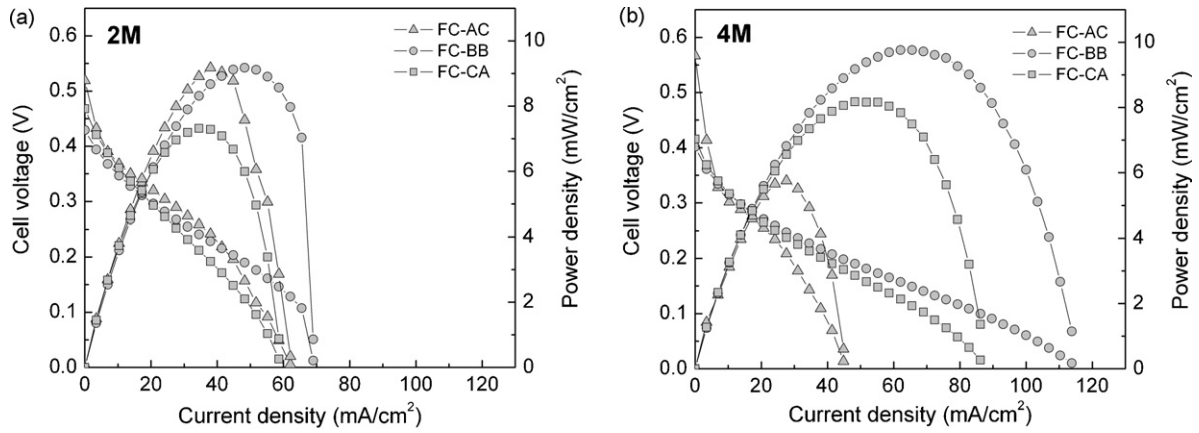

Fig. 4. Polarization curves for micro fuel cell configurations fc-AC and fc-CA, where very distinct current collectors are tested in anode and cathode sides, working at methanol concentrations (a) 2 M and (b) 4 M.

depicted in Fig. 4a. It can be seen that the maximum power density achieved with fc-AC is comparable to the reference fuel cell fc-BB (around 9 mW cm^{-1}). In this case, the hypothetical advantages of having a higher open ratio in the anode are compensated by the oxygen transport limitations taking place in the low cathode open ratio. Oxygen limitation hypothesis is supported by confirming that when the cathode is opened from 10% to 23% (configuration fc-AB, Fig. 3a) the maximum power density rises to ~12 mW cm^{-2}. On the other hand, fuel cell configuration fc-CA presents an overall lower performance due to the reduction of methanol contribution (7.2 mW cm^{-2}). The obtained power density is similar to the one obtained with fc-CB (Fig. 3a) and lower than fc-BA (Fig. 3c), confirming that when working at this concentration, the higher the open ratio in the anode current collector, the higher the obtained power density.

Finally, Fig. 4b shows the results obtained at 4 M methanol concentration. It can be seen that for fuel cell configuration fc-AC the maximum power density value falls to 6 mW cm^{-1}. As observed before, the reduction in fuel cell performance can be attributed to the blocking of cathode sites caused by the crossovered methanol. On the contrary, the configuration fc-CA shows an improvement (8.3 mW cm^{-2}) with regard to 2 M concentration performance. The

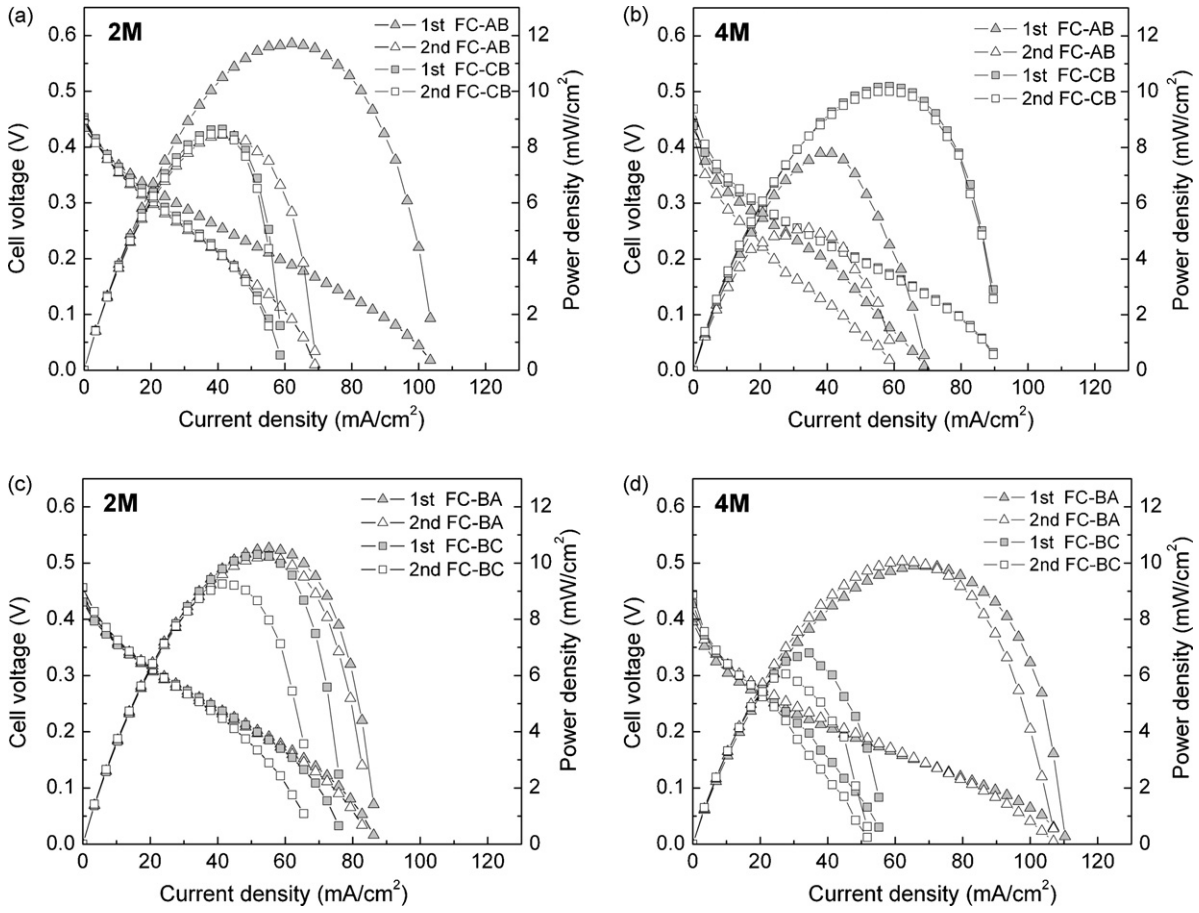

Fig. 5. Consecutive measurements of micro fuel cell with different current collector design in the anode (a and b) and in the cathode (c and d) working at methanol concentrations of 2 M (a and c) and 4 M (c and d).

low open ratio in the anode limits the methanol crossover whereas the high open ratio in the cathode side keeps it well ventilated avoiding any limitation in the oxygen supply.

3.2. Influence of current collector geometry on measurement repeatability

In addition to the impact on the output power density, some configurations of current collectors showed a clear effect on the repeatability of the measures. This was observed by performing a set of consecutive polarization curves to the previous fuel cell configurations at 2 M and 4 M methanol concentrations. After each of these measurements the concentration of methanol in the anode reservoir of the fuel cell was renewed. Results are presented by depicting pairs of I–V curves corresponding to polarization curves taken at the beginning of the experiment (labeled as 1st) and after having measured a set of polarization curves (between 10 and 15) with the same device (labeled as 2nd).

Fig. 5a and b shows the effect in repeatability when varying the open ratio of the anode at 2 M and 4 M methanol concentrations. These figures indicate that for both methanol concentrations, the polarization curves are repetitive when the open ratio in the anode is lower than in the cathode whereas for equal ratios at both sides (fc-BB), repeatability is only achieved at the lower methanol concentration. On the contrary, when the channel density in the cathode was lower than in the anode, fuel cell performance deteriorated considerably after some measurements.

The same trend can be observed in Fig. 5c and d, which shows the I–V curves obtained for different cathode open ratios i.e. repeatability is only achieved when the current collector in the anode has a

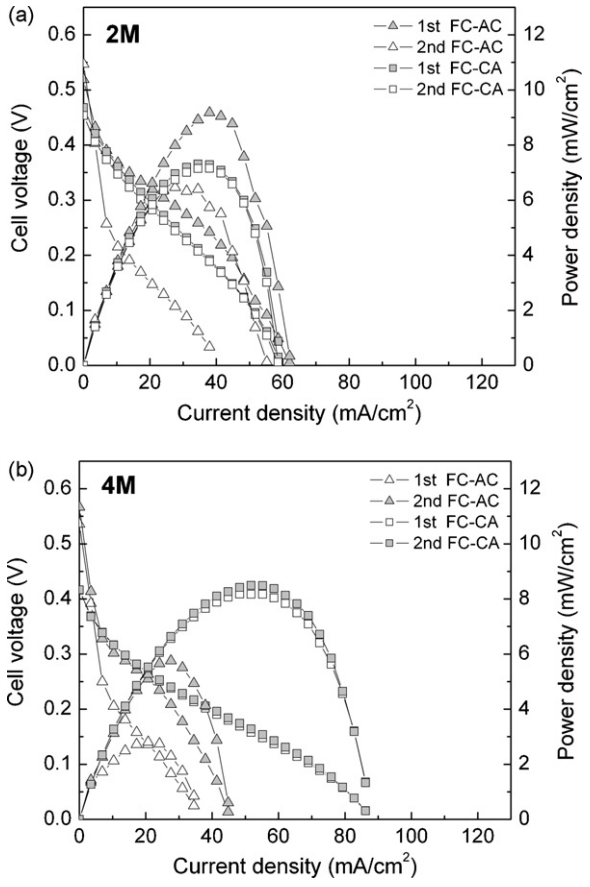

Fig. 6. Consecutive polarization curves for micro fuel cell configurations fc-AC and fc-CA, working at methanol concentrations (a) 2 M and (b) 4 M.

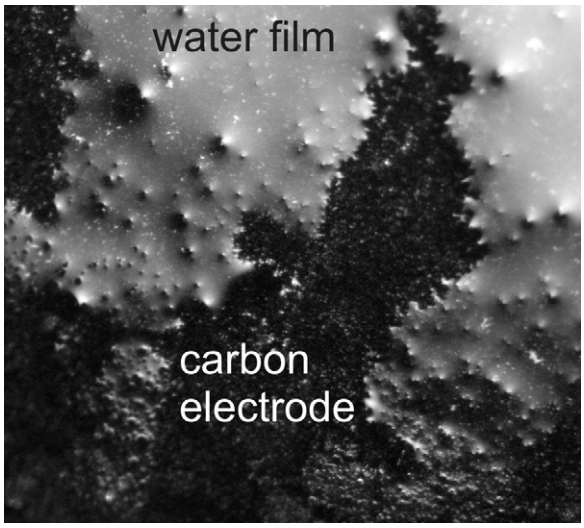

Fig. 7. Picture of a flooded cathode after performing a set of polarization curves.

smaller open ratio than the cathode. The deterioration observed on the polarization curves was attributed to the flooding of the cathode electrode [21–25]. When the cathode has a smaller open ratio than the anode, the amount of water generated during the subsequent polarization curves cannot be drained out efficiently, thus resulting in a partial cathode blockage.

These trends were confirmed again when measuring devices with a high open ratio unbalance (configuration fc-AC and fc-CA). Fig. 6a and b shows the polarization curves of these fuel cells working at the two tested methanol concentrations. The results from the figures make evident that when the anode open ratio is lower than the cathode (fc-CA), the measurements are quite repetitive for both tested concentrations. On the contrary, when fuel cells are operated with high open ratio on anode current collector and restricted oxygen supply (fc-AC), the performance degraded rapidly (sometimes even after the first measurement). As pointed out before, this behavior could be explained by considering the cathode flooding due to an inefficient water removal. In order to corroborate this, a picture of the cathode side of the MEA was taken just after the measurement of the last polarization curve in one of the configuration showing performance degradation. Fig. 7 shows that indeed, a water film had partially covered the electrode.

4. Discussion

The results obtained in the present study have been summarized graphically in Fig. 8. As it can be seen, our experiments allow to obtain a current collector design chart to be taken into account when determining the most adequate combination for achieving both high power density and stable operation. In the figure, power densities are shown in a gray-scale (darker tones representing higher power values) whereas non-repeatability is outlined with a white grid.

Results show that for some configurations of passive fuel cells, a dissimilar open ratio of the current collectors can yield better performance than a symmetric fuel cell arrangement. It has to be pointed out though, that the best choice regarding power density is strongly related to the methanol concentration of the fuel. That is, when the fuel cells are operated at 2 M methanol concentration, the maximum achieved power density increases with the anode open ratio, whereas no significant influence is observed when the cathode open ratio is varied. However, when the fuel cell is supplied with 4 M concentration, the anode open ratio must be reduced with regard to the cathode in order to keep a moderate methanol

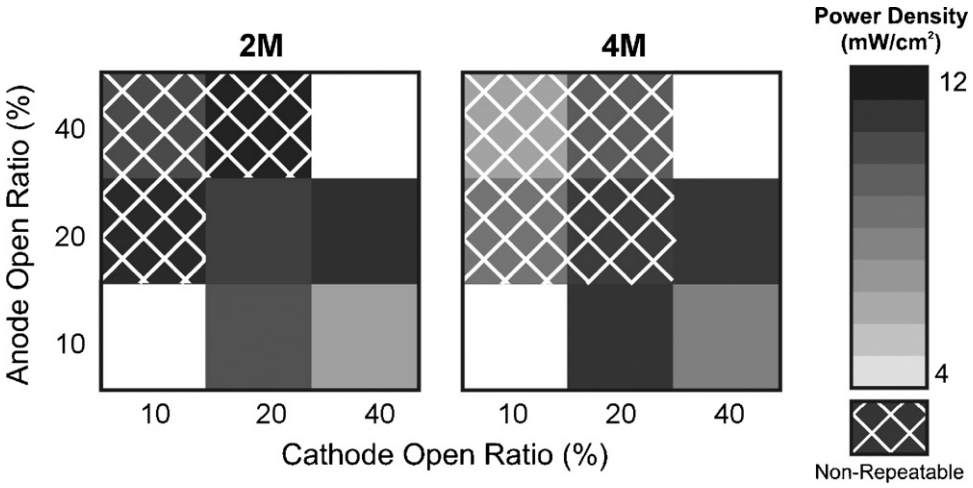

Fig. 8. Maximum power densities and repeatability of the different micro fuel cell tested configurations.

crossover. Another important result of our study concerns repeatability. It has been observed that some promising configurations turn to show unstable performance. As a general rule, it has been found out that if stability of the fuel cell is to be ensured, current collector open ratio in the cathode must be larger than in the anode so generated water can be effectively evaporated.

Finally, taking into account these recommendations, fuel cell fc-BA (consisting of an anode current collector with 20% open ratio and 40% in the cathode) would be selected by the authors as the optimal design, showing good stability and a maximum power density of around 10 mW cm^{-2} at the both tested methanol concentrations.

5. Conclusions

The present work shows that the ratio between the anode and cathode current collectors geometry affects significantly the performance of a passive micro direct methanol fuel cell not only regarding power output but also on its stability. The results obtained point out that a dissimilar open ratio of fuel cell current collectors can yield better performance than a symmetric fuel cell arrangement. Results have been assembled in a graphical chart that can help designers to set some general design rules for device optimization.

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