

# On the Effect of Different Configurations in Air-Cathode MFCs Fed by Composite Food Waste for Energy Harvesting

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In this work, experimental results on the behavior of single chamber air-cathode microbial fuel cells, fed by composite food waste, are illustrated. Specific interest has been focused on the presence/absence of a Nafion membrane, the influence of horizontal/vertical cell layout and on the amount of water inside the cells, in order to evaluate the performances in different configurations. A remarkable increment of performances is observed when a Nafion membrane is used or when the composite food waste has a low Solid-to-Liquid ratio. Results showed that values of about 380-550 mV, for the open circuit voltage, and power density of 16-27 mW/m<sup>2</sup> are achieved when Nafion/Vertical or Nafion/Conditioned/Horizontal configurations are used. The most limiting factors to power generation can be attributed to the high water losses, when Nafion is absent, and to the high internal resistance, when a thick cathode is used instead of a thin carbon cloth.

## 1. Introduction

The large part of municipal solid waste is represented by organic matter, and its recovery for reuse is so challenging that an energy recovery process is often preferred, due to the chemical energy content (Karagiannidis and Perkoulidis, 2009). Actually, waste-to-energy technologies are used in large plants, with a wide number of processes and configurations (Bosmans et al., 2013). The most diffused and reliable technologies are represented by landfilling and composting, for biogas production with perspectives of carbon capture and storage (Cormos 2014) by means of anaerobic processes (Facchin et al., 2013), and gasification for syngas production (Ahmed and Gupta, 2010): all of them are characterized by production of tars and ash (Vivanpatarkij et al., 2014), greenhouse gas or pollutants emissions (Pavlas et al., 2010), making their management and control complex and expensive. In addition to these problems, collecting, logistic and social issues are also connected to waste-to-energy plant installation (Ng et al., 2013).

In this scenario, Microbial Fuel Cells (MFCs) can solve some of these problems, because they actually are a valid alternative for distributed and direct conversion of organic waste to electricity (Du et al., 2007; Wang et al., 2011). These systems are characterized by low environmental impact, low operating temperatures and can be realized with many architectures (Logan et al., 2006). The optimization of cell design and materials has led to a substantial increase in performance, as confirmed by many recent works in the literature (Rinaldi et al., 2008; Milner et al., 2014). However, it is worth noting that the cost of parts associated with electrochemical components, membranes and sealing elements to the anode chamber, accounts for about 60-70% of the overall costs (Mohan et al., 2014). Very interesting power densities can be obtained if some high energy electron mediators and pure substrate are fed to the cell, but their use is a not sustainable approach for profitability of this technology due to the high concentration required (Rossi et al., 2015). Recently, food waste fermentation has been considered eligible for MFCs applications (Mohan and Chandrasekhar, 2011; Mohan et al., 2014), but the use of this concept in real application is still at the beginning and research efforts are devoted to develop the optimal layout and to increase the feasibility of these systems (Di Palma et al., 2015). In this work, lab-scale MFCs with cost effective materials have been tested under different assembling and operative conditions, fed with a composite food waste. The data collection hardware was based on the Arduino board MEGA 2560 (Arduino LCC, 2014), which comprised a load array, for polarization curve

acquisition, composed by 6 resistors, ranging from  $\sim 10^6 \Omega$  to  $\sim 10 \Omega$ . The software for data acquisition was developed with LabVIEW Interface For Arduino (LIFA) package (National Instruments, 2013). The results were compared to the relevant literature to demonstrate feasibility and reliability of developed cells for scale-up.

## 2. Materials and methods

### 2.1 Anode and anodic chamber preparation

In its essential configuration, a single chamber MFC was composed by two electro-active elements (anode and cathode), an anaerobic volume for the organic substrate conversion (anodic chamber), and optionally a selective Cation Exchange Membrane (CEM). In this work, the anodic chamber was obtained from a standard 50 mL polypropylene Falcon testing tube, supplied by BD Corning Inc. (Tewksbury, USA), sterile and suitable for biological cultures (Kim et al., 2009). The anode was a brush of high-strength carbon fibres of the type FIDCARBON GRID 170, with a diameter of  $47 \mu\text{m}$ , supplied by FIDIA s.r.l. (Perugia, Italy). A bunch of 6 cm length was cut and the fibres were held together by means of a stainless steel wire, representing the external electrical contact. This brush, with an estimated surface area of  $0.22\text{--}0.21 \text{ m}^2$  (Logan et al., 2007) was housed in the conical-shaped bottom of the Falcon testing tube and the steel contact came out through a small hole in the tube wall. Anode was fixed and sealed by using a silicone adhesive, to prevent oxygen penetration and short circuits. In the horizontal layout, anode and cathode are aligned, while in the vertical layout the cathode represents the upper part of the cell and the anode is the bottom part. Finally, a smaller test tube, connected and sealed to the anodic chamber, was used as port for water refilling. By design, the distance between electrodes was fixed to about 2 cm, in accordance with literature.

### 2.2 Cathode and cation exchange membrane

A standard Nafion 117 thin film, provided by DuPont Inc. (Richmond, USA), was used as CEM. The thickness of the membrane is  $183 \mu\text{m}$  and the percentage of swelling is 4-5%, according to its water uptake. For the MFC reactors prepared with the Nafion membrane, a square portion of the thin film of about  $30 \times 30 \text{ mm}$  was cut and previously saturated in water to prevent swelling. The membrane was thus placed between the cathode and the cylindrical top part of the anodic chamber (Kim et al., 2009).

The cathode material was a graphite/cement composite, with a 50 % on dry weight basis of graphite, type GK 2 Ultra-fine by AMG Mining AG (Hauzenberg, Germany). The composite material had an open porosity of 59.97 %, a density of  $0.965 \text{ g/cm}^3$ , a pore surface area of  $60.75 \text{ m}^2/\text{g}$  and an electrical conductivity of  $1.88 \text{ S/m}$ . The cathode was fabricated in the form of a disk, with a diameter of 28 mm, equal to the internal one of the anodic chamber. In this way, the cathode acted as a plug to seal the anodic chamber and to avoid leaching of liquids, from the inside, and oxygen diffusion, from the external environment. A stainless steel wire again was used as external contact.

### 2.3 Composite food waste preparation

In order to mimic the organic fraction of municipal solid waste, a mix of different vegetable and fruits residues was used. Four common types of solid organic waste were selected, and in particular: apples, chickpeas, pumpkins and zucchinis. Equal quantities by weight of the four wastes, for a total of 400 g, were shredded at a speed of 230 rpm for 20 s and mixed with 400 g of sterile distilled water, in order to obtain a homogeneous suspension. Subsequently, to obtain a suspension with a Solid-to-Liquid ratio (S/L) of 1/3, additional water was added and the suspension mixed again for 20 s. To promote the formation and growth of anaerobic bacteria, the obtained slurry was pre-incubated under anaerobic conditions at  $22 \text{ }^\circ\text{C}$  for 24 h. The substrate resulting from this preparation was used as the initial inoculum for the different MFCs (Mohan and Chandrasekhar, 2011; Mohan et al., 2014).

### 2.4 Experimental tests

In order to study the influence of different configurations on the performance of MFCs, 3 identical cells were prepared and monitored in parallel during a batch test of 30 days, under the same environmental conditions ( $26 \pm 2 \text{ }^\circ\text{C}$ , ambient pressure, relative humidity  $46 \pm 5 \%$ ). Current and power densities are calculated considering the cathode projected area. Differently from previous literature (Mohan and Chandrasekhar 2011; Kim et al., 2009) an eventual deionized water refilling was performed to retain the initial S/L ratio instead of the use of a buffer solution amendment. The amount of refilled water was considered in order to estimate the water losses from the cells. Finally, some attempts to use a poised potential to enhance electrical output during MFC operation were carried out: an external voltage of 700 mV was pre-applied to some cells for 7 days before normal operation. So, the parameters considered in this work were: the presence (Naf) or absence (NoNaf) of the Nafion membrane, the application of a poised potential (Cond), and the horizontal (Hor) or vertical (Vert) layout of the cell. Therefore, 6 types of MFCs were realized and their characteristics are summarized in Table 1. Unfortunately, not all the possible combinations of parameters produced significant results for the present study. For example, the case of poised potential with vertical layout was not reported.

Table 1: Type of MFCs tested for comparative study

Cell #	Naf	NoNaf	Hor	Vert	Cond
A	X		X		
B	X		X		X
C		X	X		
D		X	X		X
E	X			X	
F		X		X	

During each batch test, the best performance, in terms of output voltage and power density, was achieved after 16-18 days of operation. Therefore, all the comparisons below were referred to the day of maximum electricity generation.

### 3. Results and discussion

#### 3.1 Effect of Nafion membrane

The remarkable effect of the Nafion membrane is clearly visible in Figure 1, where the cells with Nafion, i.e. cell A and E, are compared to the cells without Nafion, i.e. cell C and F, confirming the positive effect of the membrane on both layouts used. In fact, considering Figure 1a, both cells A and C show a polarization curve with a similar slope, thus indicating that the internal resistance is the same, but the use of Nafion in the cell A allows an Open Circuit Voltage (OCV) 2 times higher, namely  $300 \pm 25$  mV instead of  $151 \pm 15$  mV. The maximum power density of cell A is  $18.22 \pm 0.72$  mW/m<sup>2</sup> at a current density of 116 mA/m<sup>2</sup>, while cell C is limited to  $3.36 \pm 0.49$  mW/m<sup>2</sup> at 49 mA/m<sup>2</sup>. During operations, the cell C without Nafion shows high water losses and requires the highest amount of water for refilling, estimated to be  $12.5 \pm 3.5$  mL per day, compared to the  $7.2 \pm 1.5$  mL of cell A. A similar trend is observed for cells with vertical layout in Figure 1b. In particular, the maximum power density of  $16.59 \pm 1.00$  mW/m<sup>2</sup> is achieved by cell E at 69.4 mA/m<sup>2</sup>. The behaviours of cell F and cell C are quite similar, with estimated water losses higher than that of cells with Nafion.

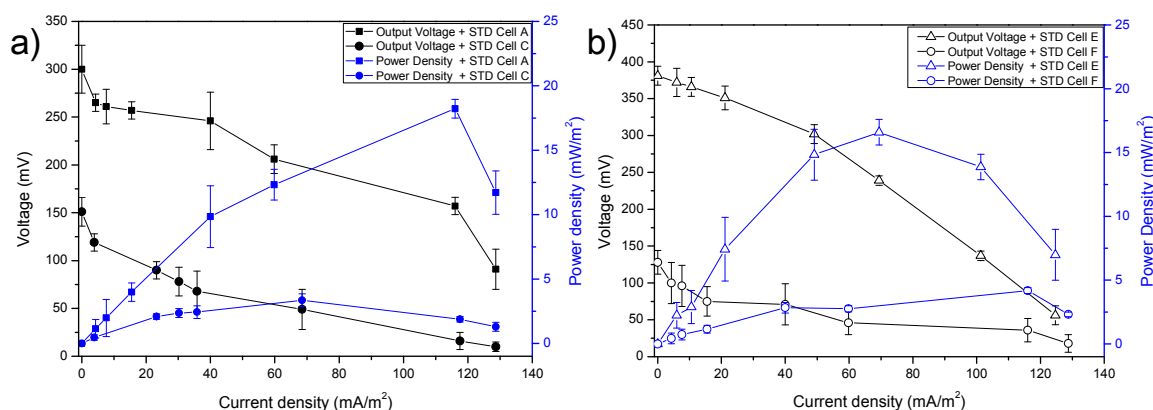


Figure 1: Polarization curve and MFC power density in presence and absence of Nafion: a) Horizontal layout; b) Vertical layout.

In order to confirm this results, a third comparison is carried out in Figure 2 between pre-conditioned cells B and D, with horizontal layout. Polarization curves show similar slopes, i.e. same internal resistance, but the OCV of cell B with Nafion is confirmed to be quite 2 times higher than that of cell D without Nafion,  $520 \pm 15$  mV and  $285 \pm 7.5$  mV respectively. In addition, maximum power density of cell B is the highest value achieved in these experiments, i.e.  $26.83 \pm 0.71$  mW/m<sup>2</sup>, while cell D is  $10.29 \pm 0.54$  mW/m<sup>2</sup>. The average water refill per day of cell B is estimated as  $5.4 \pm 1.5$  mL while for cell D is  $8.5 \pm 2.5$  mL, thus confirming that when the Nafion membrane is used water losses decrease. The essential role of the Nafion membrane is to selectively transport cationic species from anode side to the cathode side, without leakages from anodic chamber, and this transport phenomenon is of fundamental importance to electrically close the MFC circuit. The homogeneous suspension in the anode chamber is in contact with the membrane and during transport only some positive ions, e.g.  $H_3O^+$ , can migrate through the membrane together with water molecules by electro-osmotic drag (Kim et al., 2009; Chae et al., 2008). In this work, the use of deionized water and of a pre-saturated Nafion membrane reduces water losses and drag of alien cation, as confirmed by Chae et al. 2008. Adversely, when Nafion membrane is missing, the homogeneous suspension is in direct contact with the

cathode and all types of ions can freely migrate. Thus, water losses due to capillarity and natural evaporation increase (Kim et al., 2009) due to the high open porosity (59.97 %) of the cathode and the absence of a selective membrane.

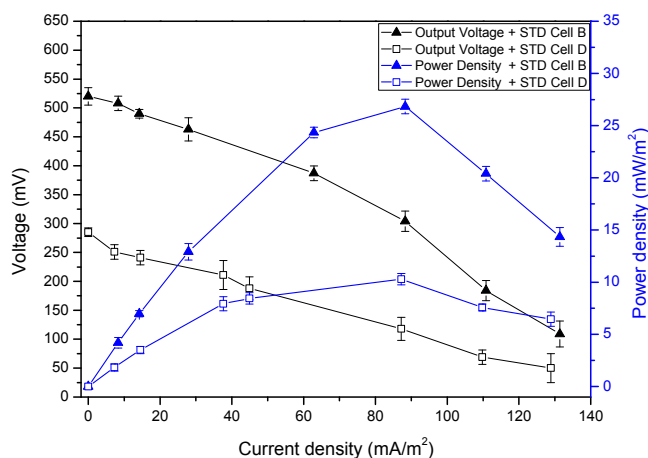


Figure 2: Polarization and power density curves of MFCs at poised potential of 700 mV with/without Nafion.

### 3.2 Effect of cell layout

Considering the cells reported in Figure 1, a crosscutting comparison in term of the layout effect on output voltage and power generation of these four cells is shown in Figure 2. In Figure 2b, even though cell C and cell F without Nafion had different layouts, horizontal and vertical respectively, their polarization curves are quite identical and maximum power densities are in general limited to 3-4 mW/m<sup>2</sup>. Thus, the layout seems to have no effect on performance when the membrane is missing. As concern cells with Nafion, only a slight difference in the slope of polarization curves can be noticed, indicating an increase in the internal resistance of cell E at high value of current density. This change in the slope of the vertical cell explain the lower value of its power density even though the OCV value of cell E is  $381 \pm 12.8$  mV, higher than the  $300 \pm 25.0$  mV of cell A.

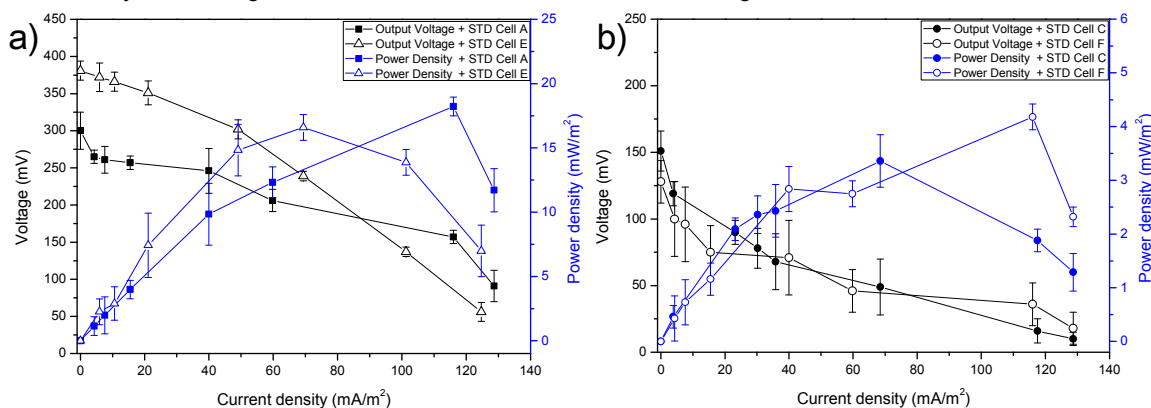


Figure 3: Polarization curve and power density with Horizontal or Vertical MFC's layout: a) Nafion; b) NoNafion.

At high current density, a pH check in Cell E reveals different values at the bottom and the top of the anodic chamber. Near the bottom (anode) pH is around 4, while at the top (membrane) pH is 4.5-5 so that a  $H_3O^+$  gradient is observed. The uneven distribution of  $H_3O^+$  indicates a net accumulation near the anode, probably due to a slow mass transport inside the chamber compared to a fast cations transport near the membrane (Kim et al., 2009), so that the output voltage must decrease when operating at high currents. However, in the case of cell with Nafion, the layout effect on power generation is marginal even if a little increment in the OCV can be achieved using a vertical layout.

### 3.3 Effect of poised potential

In Figure 4, poised and not poised cells are compared with respect to the presence of Nafion. In both cases, poised cells, namely cell B and cell D, have better performance than not poised cells. The major benefits from

the application of external voltage are related to NoNafion configuration but the performances are still lower than cells with Nafion, where a power density increase of 47 % is achieved.

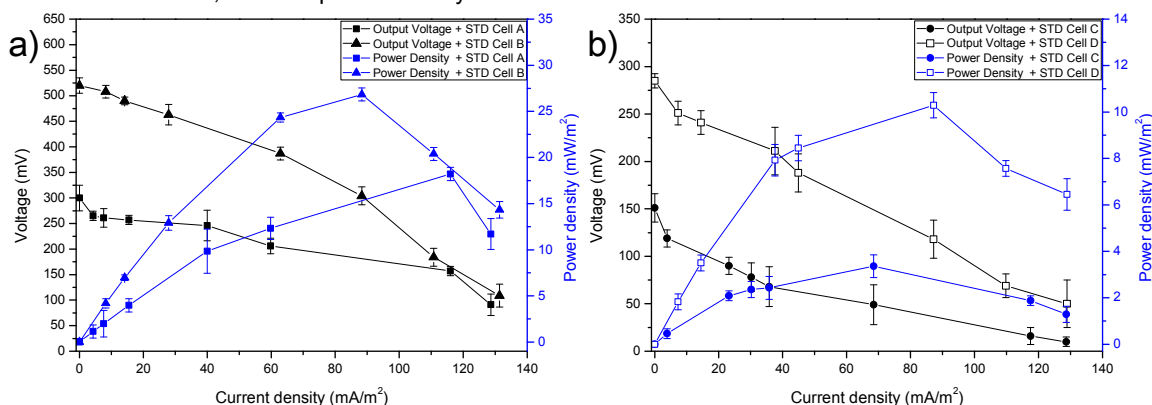


Figure 4: Effect of poised potential (700mV) on polarization and power density of MFCs: a) Nafion/Horizontal; b) NoNafion/Horizontal

Even if an attempt with available data was done in this work, the tricky effect of poised potential has an ambiguous and a not always clear interpretation because complex bacteria consortium and mixed electron transport mechanisms are involved (Mohan et al., 2014; Milner et al., 2014).

#### 4. Conclusions

The most appropriate benchmark is represented by the study of Mohan and Chandrasekhar on a MFC fed by a canteen waste (Mohan and Chandrasekhar, 2011). Comparing cells with similar electrode spacing and membrane type, they reported power densities in the range of 15-35 W/m<sup>2</sup> at a current density of about 300-500 mA/m<sup>2</sup>. These results are very close to those achieved by cell A and cell B with Nafion/Horizontal and Nafion/Horizontal/Conditioned layout, respectively. The major cause of the lower power density is the use of acetate and a buffer solution together with the substrate to amend pH during operations. Moreover, the use of a thin carbon cloth as cathode, rather than the present thick graphite/cement composite, represents a significant difference because the first has a low electric resistance compared to the second one. By the way, problem of carbon cloth is that it does not have the mechanical requirements for scale up while the graphite/cement cathode could be suitable to realize MFCs of different size. Thus, the optimization of cathode conductivity to reduce electrical resistance by retaining high mechanical strength is required.

Finally, the comparison shows that the approach used in this study is in agreement with the literature and there are concrete perspectives to achieve interesting power densities using solid food waste, without additional treatments or intensive amendment procedures. The comparative study on 6 different types of cells has pointed out that the presence of the Nafion membrane is of fundamental importance to obtain high OCV and power density values. In addition, it was observed that cells without Nafion had the highest water losses thus representing the cause of low power generation, together with a higher internal resistance. In general, in this work it was concluded that the cost effective components used are eligible to obtain interesting performance with different layouts but, in order to achieve higher current densities and thus higher power generation, an increase in the electrical conductivity of cathode or the addition of some electrolyte buffer solution to the solid waste is recommended.

#### Acknowledgments

This research has been funded by the Italian Government, with the PON project "Fuel Cell Lab – Innovative systems and high efficient technologies for polygeneration – PON03PE\_00109\_1/F12". The authors wish to thank Dr. Giovanni Erme and Dr. Enzo De Santis for their technical help.

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