Characteristics of a Single Chamber Microbial Fuel Cell Equipped with a low cost Membrane

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ABSTRACT

Currently, Nafion is the most common membrane used due its good transport properties; however its cost is very high and it determines about 40% of the *MFC* total cost. Thus, the aims of this research were: *(i)* to test a new organic membrane (*NOM*) in an air-cathode, single chamber *MFC*, and *(ii)* to compare its characteristics with those of an *MFC* equipped with a Nafion® 117 membrane (*NF*). The *MFC* consisted of a horizontal cylinder built in Plexiglas 80 mm long and 57 mm internal diameter. The anodic chamber was packed with graphite flakes as anodic material The *MFC* was seeded with a sulfate-reducing inoculum. The *MFC* performance was determined using the polarization curve method. The internal resistances (R_{int}) were 112.0 and 110.1 Ω using *NOM* and *NF*, respectively, whereas the maximum volumetric powers ($P_{V,max}$) were 2146 and 14246 mW/m^3 for *NOM* and *NF*, respectively. The relatively low value of R_{int} of the *MFC* equipped with *NOM* was encouraging. Furthermore, the value of the R_{int} *NF*-equipped *MFC* was in the same order. Yet, the power delivered with *NOM* was 15% of that with *NF*. However, the cost ratio *NOM*/*NF* was quite low, (\$14/m^2)/(\$1733/m^2) ~ 1/120 ~ 0.8%. These results point out to a trade-off between sacrificing some power output of the cell (85%) but achieving outstanding savings on membrane costs (99.2%).

Keywords: New Organic Membrane; Nafion 117 Membrane; Microbial Fuel Cell

1. Introduction

Petroleum oil is the main energy source in our modern societies. However, their adverse effects on the environment and its imminent depletion have arisen the interest in bioenergies as well as other renewable energy sources [1-3]. Microbial fuel cells

(*MFC*s) constitute an interesting technology for simultaneous wastewater treatment and energy recovery [4,5]. A *MFC* is a bioelectrochemical system that can generate electricity utilizing anaerobic microorganisms as the biocatalysts and effluents as substrate (or "fuel"); it converts chemical energy stored in organic and inorganic matter into electricity [6-8]. A *MFC* is a device with at least two electrodes (anode and cathode) commonly divided by a separator such as proton exchange membrane (*PEM*). In the anodic chamber, the microorganisms anaerobically oxidize the organic or inorganic matter and release electrons and protons. The electrons are transferred to the anode in order to flow to the cathode through an external connection under a load to be powered. On the other hand, the protons diffuse through the liquor of the *MFC* and the separator *PEM*, until they reach the cathode. Finally, at the cathode, the electrons react with protons and molecular oxygen from the air producing water in what is known as the oxygen reduction reaction (*ORR*).

A membrane is an important piece in the configuration of the *MFC*s. The main features and purpose of the membranes in *MFC*s are listed below [9-11]:

- to separate the anodic from the cathodic chamber (Fig 1.) in order to reduce the substrate flux from the anode to cathode, to avoid the back-diffusion of the electron acceptor, and to isolate the catalyst from the cathode in single-chamber *MFC*s
- to perform as a barrier to the transfer of other ions between the chambers
- to increase the Coulombic efficiency (*CE*) reducing the flux of the oxygen from the cathode chamber to the solution in the anode chamber
- to ensure an efficient and sustainable operation along time

However, there are disadvantages related to the *PEM* use. The main one is the high cost of standard membranes [9-11]. Logan (2008) reported that Nafion® can cost up to $1400/m^2 [10]. Currently the cost has increased to $1733/m^2 [12]. Furthermore, its use negatively affects the power generated by the *MFC* due to the increase of the internal resistance (R_{int}) [10,11,13]. Nafion® 117 (*NF*), a perfluorinated membrane, due to their good properties, is the most common used as *PEM* in *MFC*s, however is very expensive and their cost is reflected in the production cost of the *MFC* [8,10,14,15]

Nowadays, one of the challenges of the *MFC*s is the scaling up, but it depends of the performance *MFC* and cost materials [11,16]. In order to replace the Nafion® as *PEM*, in recent years, several polymeric membranes has been studied, such as ultrafiltration and microfiltration membranes, sulphonated polyether ether ketone membrane, anion and cation exchange membranes, bipolar membrane, forward osmosis membrane [1,6,8,10,11,15,16,17]. However, these polymeric membranes are also expensive. Recently, Sivasankaran and Sangeetha (2011) developed a sulphonated polyether ether ketone (SPEEK) to use in a *MFC* instead of *NF* [15]. The $P_{V,max}$ produced by their system, using dairy wastewater and domestic wastewater as influent were 5.7 ± 0.2 and 3.2 ± 0.2 W/m^3, respectively. The SPEEK was compared with *NF* and they report that the SPEEK membrane produced 55.2% higher power density than *NF*.

On the other hand, in order to reduce the costs there are some alternatives for instance:

- Membraneless *MFC*s
- New alternative materials

Membrane-less *MFC*s have been studied because of a membrane is not strictly necessary in a *MFC*. The water conducts the protons by itself, however, the most of the works operated without a membrane, the *CE* is low [6,8-11]. Liu and Logan (2004) explored the bioelectricity generation in a membrane-less *MFC*, in order to increase the energy output and reduce the cost. They reported a power density of 146 ± 8 mW/m^2 and 20% of *CE* for their membrane-less *MFC*. In contrast, their *MFC* equipped with *NF* membrane displayed a power density of 28 ± 3 mW/m^2 and 28% of *CE* [9].

Regarding new materials as *PEM*s, to reduce costs but to keep the *CE* and obtain an still attractive volumetric power (P_V), a few studies with glass fibers or glass wool, salt bridge, as well as other materials and configurations such as assemblies have been reported [10,11,18,19].

Yet, the efforts to find a low cost and effective separator or membrane to replace *NF* are still scarce. Thus, the aims of this research were *(i)* to test a new organic membrane (*NOM*) in an air-cathode, single chamber *MFC*, and *(ii)* to compare its characteristics with those of an *MFC* equipped with a Nafion® 117 membrane.

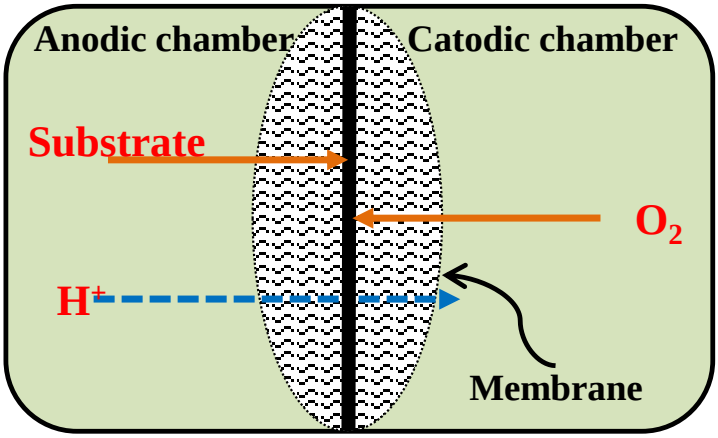

Fig 1. A *MFC* divided by a membrane

2. Experimental

2.1. Experimental design

The experiment consisted of the characterization of the *MFC*s packed with graphite flakes (*GF*) as anode and loaded with a sulfate-reducing inoculum (S*R-In*). The *PEM*s tested were a *NOM* and *NF* as reference. The experiment was carried out in two replicates. The main response variables were the maximum volumetric power ($P_{V,max}$) and the R_{int} of the *MFC*s. The *MFC*s were single compartment, air-cathode cells. They were operated at ambient temperature, with no mechanical mixing not heating.

2.2. Microbial fuel cell

The *MFC*s consisted of a horizontal cylinder built in Plexiglas 80 mm long and 57 mm internal diameter. The anodic chambers were packed with *GF* as anodic material with surface area of 0.28 m^2. For *GF*, we screened a large sample of material and collected the fraction between meshes 10 and 6 (diameters 2 mm and 3.55 mm, respectively). We took and weighed five 20 g subsamples of this fraction; the mass values were annotated. Afterwards, the number of particles in each subsample were determined and annotated. An average number of particles was estimated. With this number, we estimated the average weight of particle of each material. By using the equations shown below, it was possible to calculate the surface area of the mass of material loaded into the *MFC*. The shape factor of the material (also called sphericity factor in other textbooks) was taken into account as described in Perry [20]. For instance, we chose 0.43 for *GF*.

On the other hand, the net volume of the only chamber in our *MFC*s was calculated as the geometric volume of the chamber minus the physical volume of the anodic material. With the surface area of the anodic material and the net volume *V*, the specific surface area of the anode A'_s was finally calculated with Eq. 1 below

$$A'_s = \frac{\frac{M}{\Phi_s}\left(\frac{6^2 m_p{}^2 \pi^3}{m_p{}^3 \pi^2 \rho^2}\right)^{1/3}}{V} = \frac{\frac{M}{\Phi_s}\left(\frac{36\pi}{m_p \rho^2}\right)^{1/3}}{\left(V_{cell} - \frac{M}{\rho}\right)} \qquad (1)$$

where

$\bar{D}_p$ average particle diameter, defined as the diameter of a sphere of the same volume as the particle
Φ_s shape factor of the particle defined as the quotient of the area of a sphere equivalent to the volume of the particle divided by the actual surface of the particle
m_p average weight of a particle of the given size fraction
M total mass of anodic material loaded into the *MFC*
ρ actual density of the material

V_{cell} geometric volume of the cell chamber

The net volume of the *MFC* necessary for the denominator in the calculation of A'_s was estimated as described above in the denominator of Eq. 1.

The cathode of our *MFC* was a flexible carbon-cloth containing 0.5 mg/cm^2 platinum catalyst (Pt 10 wt%/C-ETEK). On the air side, the cathode was limited by a perforated plate of stainless steel 1 mm thickness. In the liquid side, the cathode was in contact with the *PEM* (*NF* or *NOM*) [12,21].

The *NF* was pretreated to activate and to remove impurities before to use in the *MFC*. We describe a modified technique from Oh and Logan (2006) [22]. The membrane was soaked first in H_2O_2 (3% v/v), followed by soaking in deionized water, in 2 M H_2SO_4 , and again in 1 h and deionized water, each stage for 1 h and at temperature of 80 °C. The *NOM* was fabricated and pretreated as reported elsewhere [12].

2.3. Sulfate-reducing inoculum SR-In

The *MFC*s were seeded with a *SR-In* sampled from a sulphate-reducing complete mix reactor. The biomass concentration in the inoculum was *ca*. 1280 mg VSS/L. The complete mix bioreactor was operated at 37°C in a constant temperature room. An influent containing sucrose as carbon source was fed at a flow rate of 120 mL/d to the complete mix sulphate-reducing bioreactor. Its composition was (in g/L): sucrose (5.0), acetic acid (1.5), $NaHCO_3$ (3.0), K_2HPO_4 (0.6), Na_2CO_3 (3.0), NH_4Cl (0.6), Na_2SO_4 (11.0).

2.4. Leachate

The *MFC* was loaded with 6 mL of a leachate similar to that produced in the hydrogen fermentation of the organic fraction of the municipal solid wastes [23]. The model leachate was concocted with a mixture of simple organic acids and solvents (in g/L): acetic, propionic and butyric acids (4 each) as well as acetone and ethanol (4 each) and mineral salts like $NaHCO_3$ and Na_2CO_3 (3 each) and K_2HPO_4 and NH_4Cl (0.6 each) [24,25].

2.5. Electrochemical characterization of the microbial fuel cells

The *MFC* characterization was performed by duplicate. The internal resistance of the cell was determined by using the polarization curve method, i.e., varying the external resistance and recording both the voltage and the current intensity [10, 21]. The *MFC*s were operated at open circuit for 1 h; afterwards different resistors were varied, 10 to 1 MΩ and viceversa, to determine the power generation an another response variables as a function of load. After this, the cell was set to open circuit conditions for 1 h in order to check the adequacy of the procedure (values of initial and final open circuit voltages should be close). The voltage was measured and recorded with a Multimeter ESCORT 3146A.

The current was calculated by the Ohm's law (Eq. 2) and the R_{int} was calculated as the slope of the linear section of the curve voltage versus the current intensity [8,21].

The volumetric power (P_V) was calculated according the Eq. 3:

$$I_{MFC} = \frac{E_{MFC}}{R_{ext}} \quad (2)$$

$$P_V = \frac{(E_{MFC})^2}{V_{cell} \times R_{ext}} \quad (3)$$

where I_{MFC} is the current intensity of the *MFC* in A, E_{MFC} is the voltage delivered by the cell in V, R_{ext} is the external resistance connected to the cell in Ω and V_{cell} is the net volume of the anodic chamber.

The initial chemical oxygen demand (*COD*) and biomass concentration in the cell liquor were *ca*. 3334 ± 106 mg O_2/L and 920 ± 71 VSS/L respectively. The pH and the electrical conductivity were 7.63 ± 0.03 and 16.75 ± 0.07 mS/cm respectively. The *COD* and VSS of the liquors of sulphate-reducing seed bioreactor and cells were determined according to the Standard Methods [26].

3. Results and discussion

3.1. *Assessment of the NOM as PEM in MFCs*

The *NOM* and *NF* were used as *PEM* in the corresponding *MFCs;* the *MFCs* were operated under the same conditions. Table 1 exhibits some properties of the anodic material (*GF*) used to pack the *MFCs*. The net working volume used to obtain the $P_{V,max}$ was 7.22×10^{-5} m^3.

Table 1. Selected physical characteristics of graphite flakes

Characteristics	Values
Working net volume (m^3)	$7.22\times10^{-5} \pm 5.05\times10^{-6}$
Anodic actual surface (m^2)	0.28 ± 0.08
A'_s [a] (m^2/m^3)	1302 ± 91
Conductance (S)[b]	0.13 ± 0.04

[a] Relationship between the anode surface area to cell volume, also known as specific surface area of the anode.
[b] Electrical conductance of the materials, expressed in Siemens.

Fig. 2 shows the electrochemical characterization of both *MFCs*. The R_{int} and $P_{V,max}$ for the *MFC* equipped with *NOM* were 112 Ω and 2146 mW/m^3, respectively (Fig. 2b). On the other hand for the *NF*-equipped *MFC* (Fig. 2a), the R_{int} and $P_{V,max}$ were 110 Ω and 14,246 mW/m^3 (Table 2). Regarding the R_{int} the values obtained were in the same order for both membranes in *MFC*. These results were very encouraging.

The power delivered with *NOM* was 15% of that with Nafion® 117 as *PEM*. However, the cost ratio *NOM*/Nafion was quite low, ($14/$m^2$)/($1733/m^2) ~ 1/120 ~ 0.8% (Table 3). These results point out to a trade-off between sacrificing some power output of the cell (85%) but achieving outstanding savings on membrane costs (99.2%).

Comparing our results with other works, Min *et al*. (2005), using a pure culture of *Geobacter metallireducens* and domestic wastewater, examined the power produced by their *MFC* equipped with a salt bridge as separator. The performance displayed by their *MFC* was 2.2 mW/m^2 with a high R_{int} of 19920 ± 50 Ω. Their maximum voltage recorded was 22 mV using a resistance of 1000 Ω, whereas in our system using the *NOM*, 124 mV was recorded with a resistance of 110 Ω [18]. Their *MFC* performance was too low compared with our system (61 mW/m^2 and R_{int} 112 Ω, Table 2).

On the other hand, Kargi and Eker (2007) used a *MFC* equipped with a salt-agar slab (salt bridge) to treat a synthetic wastewater composed of diluted molasses [19]. The electrodes were copper and gold-covered-copper wires as anode and cathode, respectively. The salt-agar slab used as separator depicted a low cost for their system, nevertheless, the electrodes cost is high.

The *MFC* performance reported was too poor, the maximum power density reached was only 2.9 mW/m^2, a maximum power density 20-fold lower than our results shown in Table 2.

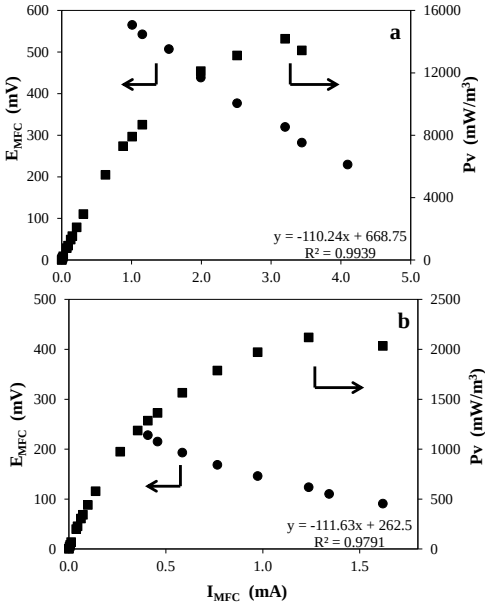

Fig 2. Characterization of the microbial fuel cell equipped either with (a) Nafion® 117 and (b) New organic membrane

Table 2. Results of characterization of the microbial fuel cells

Parameters	**Nafion® 117**	***NOM***
Inoculum	SR-In [a]	SR-In [a]
Anodic material	Graphite flakes	Graphite flakes
R_{int} (Ω)	110.1 ± 0.1	112.0 ± 5.0
$P_{s,max}$ (mW/m^2)[b]	403.0 ± 58.0	61.0 ± 14.0
$P_{V,max}$ (mW/m^3)[c]	14246.0 ± 2051.0	2146.0 ± 506.0
P_{max} (mW)	1.03 ± 0.15	0.15 ± 0.04
I_{max} (mA)[d]	3.20 ± 0.23	1.24 ± 0.15
$E_{MFC,max}$ (mV)[e]	320.0 ± 23.0	124 ± 15.0
$E_{MFC,OC}$ (mV)[f]	724.0 ± 23.0	363 ± 37.0

[a] Sulphate-reducing inoculum.
[b] Maximum power density based on surface area of electrode (cathode).
[c] Maximum volumetric power.
[d] Current intensity value at the maximum power.
[e] Potential value at the maximum power.
[f] Open circuit potential.

Table 3. Membrane cost analysis, costs in US dollars per square meter of membrane

Membrane	**Cost/m^2 ($)**
NF	1733
NOM	14

4. Summary and perspectives

The *NOM* tested in this work is a promising alternative to use as *PEM* in *MFC*s. It is the first report of *NOM* as *PEM*. The results obtained cost savings up to 99.2% in the cost of the membrane could be achieved compared to *NF*, although some power output by the *MF* had to be sacrificed (85%). The cost of *NOM* is the lowest reported in literature. Furthermore, it is worth highlighting that the *NOM* did not require any pretreatment; in contrast the *NF* typically had to be treated with hydrogen peroxide and sulfuric acid that in turn generated hazardous wastes, besides the increased costs of membrane fabrication and conditioning.

Finally, our work shows that it is possible to use our *NOM* as an alternative of *PEM* in *MFC*s.

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