NEW PROTOTYPES FOR THE ISOLATION OF THE ANODIC CHAMBERS IN MICROBIAL FUEL CELLS

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Abstract

This work has been focused on the assessment of new prototypes of MFC in which a more strict separation of the anode and cathode compartments is looked for, in order to attain strict anaerobic conditions in the anode chamber and hence, avoid lack of efficiency due to the prevalence of non-electrogenic competing microorganisms and to optimize composition of the anolyte and catholyte. Results show that the three prototypes tested perform as MFC from the electric point of view and they are efficient in the degradation of the COD contained in wastewater. However, the efficiencies in the production of electricity are very different and the greater the isolation of the anodic compartment, the lower are the current intensities produced. These results are explained because of the higher resulting ohmic losses.

Keywords: Microbial fuel cell, prototypes, double chamber, isolation; separated compartments.

Highlights

- The cell construction have a great influence on results obtained during the performance of a MFC.
- A cathode facing the two compartments of the cell allows to keep ionic and electric conductivity and to isolate completely the two compartments.
- Separation with a PEM membrane of anodic and cathodic compartments is the best choice from the viewpoint of efficiency.

29 - Non-balance consumption of COD and oxygen and production of electricity indicates
30 the co-existence of more complex processes.

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35 1. Introduction

36 With the increasing concern for alternative more sustainable energy sources, global climate
 37 change and waste management, the search for novel technological solutions becomes a
 38 crucial necessity (Bebelis et al., 2013). Amongst other technologies, microbial fuel cells stand
 39 up as an alternative and sustainable energy technology that nowadays is under development
 40 (da Costa Silva, 2014; Logan, 2005; Logan et al., 2006b; Quek & Balasubramanian, 2014).

41 A microbial fuel cell (MFC) is an electrochemical reactor that converts the chemical energy
 42 contained in organic substrates directly into electricity, by means of the metabolic abilities of
 43 microorganisms (Cercado-Quezada et al., 2010; Gonzalez del Campo et al., 2013b; Parot et al.,
 44 2008). In the anodic chamber, microorganisms oxidize substrates releasing carbon dioxide,
 45 protons and electrons, which are transported through the cellular respiratory chain to the
 46 solid anode. In this way, the anode acts as a solid external electron acceptor for the
 47 microorganisms. The electrons released in the oxidation of the organic matter are transported
 48 by an external electrical circuit to the cathode. While the electrons travel through the circuit,
 49 in conventional divided MFC the corresponding protons migrate to the cathodic compartment
 50 through a proton exchange membrane to maintain charge neutrality (Lu et al., 2008). At the
 51 cathode, an electron acceptor is reduced by the electrons transported from the anode via the
 52 external electrical circuit and the protons via the membrane. The kinetics of electrochemical
 53 reactions in MFC are comparable and they may vary depending on physical, chemical and
 54 biological operating condition (Logan & Rabaey, 2012; Lyautey et al., 2011; Rabaey &
 55 Verstraete, 2005). In literature, different MFC configurations have been proposed, all of them
 56 aiming to reach the highest performances, usually measured as exerted power or potential
 57 and coulombic efficiencies (Logan et al., 2006a).

58 The theoretical ideal potential, E_{thermo} (V), attainable from a MFC can be thermodynamically
 59 predicted by the Nernst equation as shown in eq. 1, where E° is the standard cell potential
 60 (V), R the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the temperature (K), n the number of electrons
 61 transferred in the reaction (dimensionless), F the Faraday's constant ($96,485 \text{ C mol}^{-1}$), and Π
 62 the chemical activity of products divided by those of reactant (dimensionless).

$$63 \quad E_{\text{thermo}} = E^{\circ} - \frac{RT}{nF} \ln(\Pi) \quad (1)$$

64 However, the actual potential exerted by a MFC is always lower than the thermodynamic one
65 due to irreversible losses. The three major irreversibilities are related to activation, ohmic and
66 mass transport losses (Villaseñor et al., 2013). Moreover, other irreversibilities such as the
67 presence of oxidants in the anaerobic compartment usually exist (Gonzalez Del Campo et al.,
68 2015). The extent of these inefficiencies depends also on adopted materials and configuration.
69 Thus, MFCs are being constructed using a variety of materials and configurations.

70 Regarding to MFC configuration, an ever increasing diversity of configurations is shown in
71 literature ranging from the simple batch H-shape systems used for preliminary lab-scale tests
72 to the continuous single chamber MFC (Logan & Regan, 2006). In relation to configuration of
73 the systems in one or two chambers, it must be stated that single-chamber MFCs design avoids
74 the need for a membrane, thus avoiding the ohmic losses given by the separator (Rozendal et
75 al., 2006). However the spacing of the electrodes is a critical factor for achieving high
76 performance MFCs. Indeed, decreasing the distance between the electrodes can improve
77 power output because it reduces the ohmic losses (Logan & Regan, 2006). Close electrode
78 spacing could be especially important for domestic wastewater treatment as its conductivity
79 is very low (1 mS cm^{-1}), and therefore widely spaced electrodes would result in high ohmic
80 losses. Unfortunately, when electrodes are very close the presence of electron acceptors near
81 the anode reduce the efficiency in the electron transfer and therefore the performances of
82 the MFC (Lobato et al., 2012a; Rodrigo et al., 2009). In literature, it has been reported that
83 very closely spaced flat electrodes have been shown to decrease MFCs performance, despite
84 a reduction in ohmic resistance, due to oxygen crossover from the cathode to the anode (Ahn
85 et al., 2014). Very close spacing of the electrodes can be obtained by placing a separator
86 between the electrodes to avoid electrode contact and short-circuiting. This membrane
87 electrode assembly (MEA) configuration also enables both more compact packing of
88 electrodes and reduces oxygen crossovers into the anodic compartment. Adding a separator,
89 however, increases ohmic resistance (Zhang et al., 2009), which can decrease power
90 generation as well as create pH gradients, due to the limitations imposed to the protons
91 transfer to the cathode, that can decrease performance. The effect of ohmic resistance on the
92 performance becomes more important when solutions with low conductivity, such as
93 wastewater, are used as fuels, and the importance of the pH gradients became important
94 when a significant amount of protons are generated in the system but not consumed.

Because of that, it is clear that the possibility of a stricter separation of the anodic and cathodic processes could enhance the performance of the MFC, because it may help to optimize both compartments separately and hence to obtain higher efficiencies (Gonzalez del Campo et al., 2013a; Rodrigo et al., 2007). This is particularly important in miniaturization of MFC, which for sure will become a challenge for the next years. In this context, the aim of this work was to assess three prototypes based on the same primary reactor design, in order to study the feasibility of an effective separation of the anodic and the cathodic chambers of a MFC in order to prevent oxygen transfer and to help to optimize composition of the anolyte and catholyte.

2. Experimental

2.1 Setup and MFC configuration

A schematic view of the setup used in this work is shown in Figure 1. The main element of the setup is the biological reactor, the MFC, which presents a special design with two concentric chambers: the inner chamber with graphite bars acting as anodes and the outer one with a stainless steel tube, acting as cathode, which separates the two chambers.

The anode chamber included 40 graphite bars, each with a diameter of 0.2 cm and length of 10 cm. The graphite bars were fixed to two perforated plastic plugs with a metal adhesive (Silver Loaded Epoxy Adhesive RS). Copper wires and the conductive metal adhesive were used to connect the graphite bars with the electrical circuit. The anodic compartment (113 cm³) was connected to a reservoir of 600 cm³.

The cathode was a stainless steel tube. The external side of the cathodic chamber was made with a concentric plastic tube, being the cathodic volume 74 cm³. This chamber was also connected to a reservoir, 600 cm³, from which an aqueous solution of HCl was fed. During operation, the anode and cathode were connected by means of copper wires and a resistance (120 Ω).

In this work, three different prototypes were taken from this base design. They were the following:

- R1: base design with no modifications; the stainless steel cylinder is in direct contact with the anodic (inner surface) and cathodic (outer surface) chambers but no electrolyte flow is allowed between the two compartments.
- R2: inner surface of the stainless steel (in contact with the anodic chamber) is isolated with a polymeric layer coating (previously painted) preventing, or at least strongly limiting, the exchange of electrons between the steel tube and the anodic solution. Initially, this prototype is not expected to perform as a MFC because the ionic circuit is virtually detached.
- R3: holes made in the surface of the stainless steel and a cationic exchange membrane (Sterion) separating the anodic and cathodic compartments and preventing the mixture of both electrolytes.

Figure 1. a) Set up used in the experiments. b) Layout of the base MFC prototype.

To start-up the process, the anodic compartment was inoculated with 300 cm³ of activated sludge from the biological reactors of a conventional municipal wastewater treatment plant (WWTP) located in Ciudad Real (Spain). More information about this facility can be found elsewhere (Rodrigo et al., 2007; Rodríguez Mayor et al., 2004). The characteristics of the actual wastewater and of the activated sludge employed in this work in terms of chemical oxygen demand (COD), pH, phosphates (P_T), nitrates (N_T) and total suspended solids (TSS) are given in Table 1.

Table 1. Characteristics of wastewater and activated sludge used.

	COD (mg·dm⁻³)	pH	P_T (mg·dm⁻³)	N_T (mg·dm⁻³)	TSS (mg·dm⁻³)
Wastewater	320	7.1	0.9	11.1	280
Activated sludge	1643	6.9	5.1	19.1	1105

A peristaltic pump was used to recirculate the activated sludge and actual wastewater from the reservoir through the anodic chamber at 0.5 cm³ s⁻¹. Once the anodic chamber was completely filled, 125 cm³ of actual wastewater were added to the reservoir. In order to ensure the presence of organic substrates in the wastewater fed to the anodic chamber, 50 cm³ of liquid was removed from reservoir and replaced by actual wastewater every day. By working in this way, the system was fed in a semi-continuous mode, being the hydraulic and sludge residence time 14.5 days.

Because several experiments were performed isolating anodic and cathodic chambers, the reservoir of the cathode compartment was fed with a solution of hydrochloric acid (pH 3.5) to ensure protons availability. A fisheries compressor and pore stones were used to supply the oxygen to the acid solution and a peristaltic pump was employed to recirculate the solution through the cathodic chamber of the MFC at 0.75 cm³ s⁻¹.

2.2 Electrochemical and chemical measurements

A digital multimeter Kethley 2000 was connected to the system to continuously monitor the value of the cell potential (V). This potential is directly related to the current flowing between the electrodes by the Ohms Law. The polarization and power density curves were obtained by

varying the external resistance used in the circuit and measuring the potential. Volumetric power (mW m^{-3}) was calculated by relating the power with the volume of the electrolyte in the anodic chamber.

Chemical Oxygen Demand (COD) and concentration of phosphorous were determined using a HACH DR2000 analyser. The total nitrogen was monitored using a Multi N/C 3100 Analytik Jena analyzer. Dissolved oxygen and pH were measured using an Oxi538 WTW oxy-meter and a GLP22 Crison pH-meter, respectively. Total suspended solids were gravimetrically determined. All the measurements were performed according to Standard Methods (American Public Health Association. et al., 1989).

3. Results and discussion

3.1 Potential exerted during standard operation and polarization curves

Figure 2 shows the changes in the electricity production observed for the three MFC prototypes tested in this work during the lifetests. These lifetests consisted of standard operation of the MFC fed with the same wastewater during 11 days, period which was found to be long enough to observe a steady state value in the monitored operation parameters.

Figure 2. Time course of the current density produced in the three prototypes: ■ prototype R1 (with no electrode isolation) ◆ prototype R2 (with electrode isolation) ▲ prototype R3 (compartments separated by PEM).

The electricity produced strongly depended on the type of cell, in spite of the fact that the three prototypes were fed with the same wastewater and operated under the same operating conditions. In comparing the volumetric current density, differences of more than one fold in the production of electricity can be observed. These differences become higher with the increase in the isolation of the compartments. Hence, current intensity produced with the lower level of isolation (prototype R3 in which the separation between compartments is carried out with a PEM membrane) is around 10 times higher than that produced with prototype R1 and 100 times higher than that obtained with prototype R2. A significant point is that even in the cell R2 (with the highest isolation level) electricity was produced and the biological reactor performs as a typical MFC, in spite of having detached the ionic circuit from the electrical circuit of the cell. In order to understand this result, it is useful to mention that, according to the literature, water molecules, ions and other specie could slowly penetrate through the coatings to the metallic interface (Fernandez-Perez et al., 2014; Grundmeier et al., 2000). Thus, the transport of these species can occur through small pores or at local defects within the coating. Obviously the electricity produced is very low, because of the very high resistance given by the coating, and it advices against its use. Another important observation is that less than 100 hours (4 days) was enough to attain a steady state electricity production in the three prototypes and transient time constants seems to be equal in the three cases (the 63.2% of the response was obtained in around 3 days for the three setups).

In order to further study the electrochemical performance of the system, polarization curves were carried out for the three setups studied. Results are shown in Figure 3 that compare the polarization curves obtained in the three prototypes during the startup and once the steady state was met. From these polarization curves it must be stated that the three cells perform in a very different way. However, a common key point in all the polarization curves is the clear behavior as MFC of the three configurations studied in this work, in spite of the non-conventional design of cells R1 and specially of R2. The ohmic contribution seemed to be the most important lose in all cases and the E vs I plot was close to a straight line for the six polarization curves shown (with the exception of few data recorded at very low values of current densities). This observation can be explained in terms of the masking effect of a very

high value of resistance towards the activation and the mass transport limitation regions of the polarization curves.

Figure 3. Polarization curves obtained during the startup (●○) and during the steady state (▲△) stages of the three MFC prototypes. Empty points stands for power density while full points for cell potential. A) prototype R1; B) prototype R2; and C) prototype R3.

It is also interesting to compare the polarization curves obtained for the three prototypes during the first stage (starting up) and under steady state conditions: a very significant improvement is found for R1 and R3, while no significant differences are observed for configuration R2, which corresponds to the virtually completely isolated MFC.

In the three cases, a maximum in the power density is clearly observed, which obviously shifted from the startup to the steady state conditions for R1 and R3. It is obtained for different current intensities (0.012, 0.005 and 0.250 mA for R1, R2 and R3, respectively) and the differences in the maximum power density that can be attained are even higher, in particular in between R3 and the other two prototypes (0.75, 0.55 and 300 mW m⁻³ for R1, R2 and R3, respectively). The lower range of intensity observed for R1 and especially for R2 can be explained in terms of the very high ohmic losses. Slope of the V/I increases drastically in the sequence R3, R2, R1. These slopes were not significantly modified during the lifetests in prototypes R1 and R2. Opposite in prototype R3 value of the resistance decreases during the operation of the cell, being much lower at the steady state.

Hence, it is possible to run a MFC with the three prototypes tested, obtaining electricity by conversion of organic matter through bioelectrogenic microorganisms. The main challenge is the large ohmic losses obtained, which become huge, as expected, for the almost complete

isolated cell. These large ohmic drops mask the potential advantage which could be attained by the stricter anaerobic conditions in the anodic chamber. Anyhow, the production of electricity means that these alternatives are feasible from the technical point of view and next sections will try to give more light about performance of the prototypes.

3.2 Cathodic oxygen consumption

In order to evaluate the cathode performance, the oxygen consumption in the catholite was evaluated. This consumption is important because in the cathode oxygen is supplied for being used as the final electron acceptor for the electrochemical oxidation of the organic matter contained in wastewater by electrogenic microorganisms contained in the anodic chamber. Thus, it is converted into water, consuming therefore the electrons released during the organic matter oxidation which took place in the anode. It is important to take in mind that the cathode compartment is abiotic and contains a strongly acidic solution (hydrochloric acid), so that the consumption of oxygen can only be explained in terms of its electrochemical reduction. To assess this consumption, simple respirometric assessment tests were carried out periodically (Rodrigo et al., 2007). In those tests, aerator was stopped and oxygen was monitored in the three setups studied in this work. Results obtained in one of these tests, carried out at steady state conditions, are shown in the Figure 4.

Figure 4. Oxygen consumption in the cathodic chamber and influence of this parameter on the cell potential measured across a resistance of 120 ohm which connect anode and cathode in the three prototypes assessed. a) prototype R1; b) prototype R2; and c) prototype R3.

As it can be observed in Figure 4, there is a clear oxygen consumption at the cathode. This oxygen consumption was directly related to the cell potential measured across the 120 ohm resistance used as external load. The depletion rate of oxygen and the coulombic efficiency,

ε_{O_2} , expressed as the the ratio between the electrons recovered as current and that involved in oxygen depletion, were reported in Table 2. Worth mentioning, both these values depended on the cell configuration.

Table 2. Oxygen consumption rate (O.C.R.) in the cathodic compartment and coulombic efficiency ε_{O_2} .

	R1	R2	R3
OCR (mg O ₂ /d)	3.5	3.9	26.4
ε_{O_2} (%)	0.85	3.82	9.05

As expected, the maximum oxygen consumption rate was obtained when using the R3 cell that gave the highest current intensity. As predictable, the oxygen consumption in the two isolated reactors was lower due to the limitations imposed to the electricity production. However, it must be highlighted that the difference in the oxygen consumption rate between R3 and the other two reactors, R1 and R2, was not as high as expected on the bases of the electricity generation data. Because of that, coulombic efficiencies ε_{O_2} were not as extremely different as the maximum power densities. This difference could be explained in terms of three different processes: a) the existence of other processes that generate electricity in the cell without oxygen consumption (Gonzalez del Campo et al., 2013b); b) other reductions reactions in which oxygen are consumed (Mateo et al., 2014) or c) because of the corrosion of the cathode. Although the three processes can contribute, once finished the tests a visual inspection showed that the inner face of the stainless steel electrode (in contact with the anode compartment) of reactor R1 was slightly corroded, while this face remained completely clean in the other 2 prototypes, even if it is not possible to exclude that some small corrosion phenomena masked by the coating could take place also in the case of R2 (Fernandez-Perez et al., 2014; Grundmeier et al., 2000).

Worth mentioning, under adopted operating conditions, the corrosion was likely to cause a decrease of the performances of R1 cell but such kind of phenomena could be in perspectives investigated in order to evaluate the potential utilization of MFC prototype R2 for electrocoagulation processes.

3.3. COD consumption

Another very interesting point is the study of the organic load consumption. Table 3 shows the COD depletion rates calculated by mass balances in the three setups and the coulombic efficiencies ϵ_{COD} according to the anodic reaction defined as the fraction of electrons recovered as current versus that involved in the oxidation of the organic matter.

Table 3. COD consumption rate in the anodic compartment and coulombic efficiency ϵ_{COD} in the production of electricity.

	R1	R2	R3
OCR (mg O ₂ /d)	163.8	75.4	71.5
ϵ_{COD} (%)	0.018	0.198	3.339

As in the assessment of the oxygen consumption, the COD depletion rates were not very different from each other. This is easily explained in terms of the coexistence of electrogenic and non electrogenic microorganisms in the biological culture contained in the anodic chamber (Lobato et al., 2012b; Lobato et al., 2013). In fact, a higher COD consumption rate was obtained for R1 inspite of the fact that this prototype was less efficient in terms of current intensity production with respect to R3. This fact is reflected on the efficiency. In this case, differences are logarithmic and only for R3 a significant efficiency in terms of conversion of COD into electricity is obtained.

The comparison of the COD removal rates, measured in the anodic chamber, and the oxygen depletion rates, measured in the cathodic one, was also carried out in order to achieve other information on the process. Because of the anabolic reaction of the metabolism of microorganisms, ratio between COD converted into new biomass and into carbon dioxide is typically around 0.60 (De Lucas et al., 2007), meaning that 60% of COD is used for cells productions and only 40% in used in catabolic production of energy (transformation of COD into CO₂). This means that, from a theoretical point of view, for a balanced MFC consisting only of electrogenic microorganisms the maximum rate of oxygen depletion is expected to be around 0.4 r_{COD} . This relation is obtained in an approximate way for the R3 reactor (28.6 vs 26.4 mg O₂/d). However, the other two configurations are far away of the theoretical value. Please, consider, however, that the efficiency in the production of electricity ϵ_{COD} is very low

(3.3%) also in the case of R3. Hence, the oxygen in the cathode is not only reduced to oxidize COD but it is reduced in a much higher extension.

Protons consumption were observed in the cathodic compartment in all tests carried out. Because the pH in this compartment was clearly acidic (around 3.5), a proton mass balance was carried out without the need to apply further equilibrium calculations (rough approach). Because of that it will be interesting to highlight the relationship between the protons and the oxygen consumption rates. Theoretically, according to the reduction reaction taking place at the cathode, the ratio should be 4 mol of protons per mol of oxygen (Eq. 2).

However the ratio between proton and oxygen consumption was not kept in 4 (in molar units) as it could be expected from stoichiometry but it ranges from 0.24 to 6.50. In addition, and neglecting the effect of the reactor design, the higher the intensity produced, the lower is the value of this ratio. This is clearly observed in Figure 5, in which a clear relationship is defined.

Figure 5. Ratio proton consumption – oxygen consumption in the three prototypes as a function of the operating current density produced. ▲prototype R1; ■ prototype R2; ● prototype R3.

This fact suggests the existence of more complex processes happening in the cell in which oxygen and or protons are involved and that, in spite of the low production of electricity. Further research has to be carried out in order to clarify this point.

340

341 **4. Conclusions**

342 The three prototypes tested in this work:

343 - perform as MFC from the electric point of view with a well-defined production of electricity
344 and typical polarization curves.

345 - are efficient in the degradation of the COD contained in wastewater, although consumption
346 is not directly related to the production of electricity.

347 - exhibit very different efficiencies in the production of electricity: the greater the isolation of
348 the anodic compartment, the lower are the current intensities produced.

349 - exhibit a non-balanced consumption of oxygen and COD and production of electricity which
350 indicates the coexistence of more complex processes.

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