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A New Design Improves Performance of a Single Chamber Microbial Fuel Cell

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Abstract: *A new design of MFC (MFC-A) whose main features were the assemblage or sandwich' arrangement of the anode-PEM-cathode and the extended surface area of electrodes (higher electrode surface to cell volume ratio, ξ) exhibited a performance significantly superior to that of a similar cell (MFC-B, standard cell) where the electrodes were separated. The characterization experiments showed that the new design lead to a significant 70% reduction of cell internal resistance (R_{int}) compared to the standard cell. During the batch operation of the cells loaded with a model extract typical of hydrogenogenic fermentation of organic solid wastes and a sulphate-reducing inoculum, the maximum, open circuit potentials were 0.5 and 0.3 V whereas the average voltages were 0.21 y 0.18 V for MFC-A and MFC-B, respectively. Maximum volumetric power P_V and anode density power P_{An} of the MFC-A were superior to those of the MFC-B by factors of 13.2 and 8.4, respectively. The experimental improvement factor was almost double of the expected (algebraic) factor 6.5. The P_V of the MFC-A (922 mW/m^3) was in the middle to high side of the range of P_V reported in the literature whereas P_{An} was in the low range of published results (38.4 mW/m^2). Finally, this work points out to the usefulness of the approach of increasing x and reducing R_{int} for improving MFC performance.*

Keywords: microbial fuel cell; batch tests; electricity production; internal resistance; leachate; ratio surface area to volume; solid waste; sandwich electrode

1. INTRODUCTION

At present, the energy needs of our societies are mainly met with fossil fuels, whereas renewable energy plays only a marginal role. Fossil fuels use present several disadvantages such as high costs, increasing scarcity in the near future, and adverse impacts on the environment and human health due to combustion products, spills and leaks during exploration, production and transport [1,2]. Furthermore, energy experts [3,4] advocate a near future technological transition where fossil fuels importance will progressively decrease and renewable energy contribution will become more significant. Renewable energies, such as wind, solar, hydraulic, and biological-based energy represent an interesting alternative because of their potential lower costs and minimum environment negative impact [5,6]. However, renewable energy availability depends on the type and geographic localization of such systems. In this regard bioenergy production from biomass and organic wastes is an attractive alternative.

Among the energy systems based on biomass, the biological processes that use microorganisms display significant advantages over the others, because they use biomass or wastes as raw material and they may attain the double goal of waste treatment and bioenergy production. Renewable bio-energies usually look for the most complete conversion of waste to energy [7]. Sometimes this is not possible, such as in the hydrogen production from fermentation of organic wastes. In this type of processes, there is just a partial biodegradation of waste to hydrogen, with the consistent production of organic metabolites remaining in the spent solids [8,9]. These metabolites can be used to yield additional bioenergy by a methanogenic system, by phototrophic bacteria capable of

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ABBREVIATIONS

A	surface area of electrode (usually the anode)
A_{an}	surface area of the anode
AMC	'sandwich' arrangement anode-PEM-cathode
b_{COD}	number of moles of electrons harvested from one mol of COD (4)
CE	Coulombic efficiency
COD	chemical oxygen demand
CRS	actual amount of charge (electrons) produced from the substrate
CTS	maximum amount of charge (electrons) that could be produced from the substrate
COD_i	initial COD
COD_f	final COD
E_{MFc}	MFC voltage
F	Faraday's constant
HRT	hydraulic retention time
I_{An}	current density normalized per surface area of the anode
I_{MFC}	current intensity
L	length of separation between anode and cathode
M_{COD}	COD's molecular weight (32 g/mol)
MFC	microbial fuel cell
MFC-A	new design of microbial fuel cell in this work
MFC-B	standard microbial fuel cell in this work
O_t	operation time
$P_{An\text{-}ave}$	average power density
$P_{An\text{-}max}$	maximum power density
P_{MFC}	MFC power
$P_{V\text{-}ave}$	average volumetric power
$P_{V\text{-}max}$	maximum volumetric power
PEM	proton exchange membrane
R_{elec}	electronic resistance
R_{ext}	external resistance
R_{int}	internal resistance
R_{ion}	ionic resistance
R_{ohmic}	ohmic resistance
V_{MFC}	MFC operation volume

Greek characters

η_{COD}	chemical oxygen demand removal
η_{Coul}	columbic efficiency
η_{ohmic}	ohmic overpotential
ξ	ratio surface-of-electrode to cell volume
κ	specific conductance or conductivity
ρ	specific resistance or resistivity

producing hydrogen as a fuel, or by a microbial fuel cell [7,10].

Microbial fuel cells (MFC) constitute a promising technology for sustainable production of alternative energy and waste treatment. A microbial fuel cell is an electro-biochemical reactor capable of directly converting organic matter into electricity. In the anodic chamber the microorganisms anoxically oxidize the organic matter and release electrons and protons. Electrons are transported to the anode that acts as an intermediate, external electron acceptor. The electrons flow through an external circuit where there is a resistor or a device to be powered, producing electricity and finally react at the cathode with the protons and oxygen producing water [11]. The corresponding protons released during the oxidation of organic compounds migrate to the cathode through the electrolyte (liquor) contained in the cell and a proton exchange membrane; in this way charge neutrality is kept [12].

The reversible or ideal voltage delivered by a MFC at a given temperature of operation, that is, the maximum voltage attainable, can be estimated by the Nernst equation [13]. Yet, the actual voltage of an MFC is lower than the predicted by the Nernst equation due to irreversible losses or overpotentials [12,14,15]. The most significant losses associated to poor MFC performance are the following: activation losses, ohmic losses, and mass transport losses. These irreversibilities are usually defined as the voltage required to compensate for the current lost due to electrochemical reactions, charge transport (also known as ohmic loss), and mass transfer processes that take place in the cell; these voltages substract from the potential calculated by the Nernst equation [15,16]. So, much of the current research on MFC is devoted to overcome the limitations imposed by these irreversibilities.

Ohmic potential η_{ohmic} is the ohmic loss from ionic and electronic resistances; it collectively represents the voltage lost in order to accomplish electron and proton transport in the cell. The η_{ohmic} is usually described by the Ohm's law, that is

$$\eta_{ohmic} = I_{MFC}\, R_{ohmic} \quad (1)$$

The ohmic resistance is the result of the resistances of electrodes, electrolyte(s), membrane (if any), junctions, and connections. In other words, R_{ohmic}, in turn, combines the ionic and electronic resistances (R_{ion} and R_{elec}) given by the equation

$$R_{ohmic} = R_{ion} + R_{elec} \quad (2)$$

In most cases the resistance associated to electrodes and connections is relatively low. So the R_{ohmic} is dominated by the R_{ion} associated to the electrolyte(s) resistance [12,16]. The R_{ion} due to electrolyte is given by the following expression [17]

$$R_{ion} = \rho * L/A = (1/\kappa) * L/A \quad (3)$$

where ρ: specific resistance or resistivity of the electroyte, L: distance between electrodes; A: electrode surface area; κ: specfic conductance or conductivity of the electrolyte.

Inspection of Eq. 3 draws our attention to the ways to lower ohmic losses, i.e., by reducing the distance that separates the electrodes (decreasing L), increasing the electrode surface area (increasing A), and increasing the conductivity of the electrolyte and materials of the proton-exchange membrane (increasing κ). A plausible physical picture of the effect of inter-electrode separation would be that the protons have less distance to travel, and consequently the ohmic resistance is lowered. Thus, electrode separation

has been investigated by several researchers as one way to improve MFC performance [12].

The influence of electrode spacing on performance of MFCs been shown in several works [18 - 22]. Liu et al. [22] in experiments with a membrane-less MFC, observed that decreasing the distance between the electrodes from 4 to 2 cm significantly reduced the ohmic resistance and resulted in a 67% increase in the power output. Reduction of electrode spacing in membrane-less MFC, however, should be taken with caution. Indeed, if the electrodes are placed very close, then the oxygen back diffusion from the cathode to the anode may increase. Dissolved oxygen can become inhibitory to anaerobic respiration and promote aerobic respiration; both effects may reduce the coulombic efficiency because divert a significant fraction of substrate electrons from electricity generation to microbial metabolism.

Relatively high power outputs have also been achieved in MFCs with a 'sandwich' membrane-electrodes arrangement (AMC, for anode-membrane-cathode setup) [23 - 26] that minimized the inter-electrode distance and significantly reduced the R_{ohmic}. In another research, the internal resistances of two air-cathode MFCs, one with an AMC design and the other one with a 4-cm electrode spacing were compared Liang et al. [26]. It was reported a significant decrease of internal resistance and a 3-fold improvement in power delivery with the MFC equipped with the AMC arrangement compared to a standard MFC where electrodes were separated 4 cm.

Another variable that may lead to lower R_{ohmic} is the electrode area. The latter can be expressed in terms of a variable ξ, the ratio of surface area of electrode to the cell volume, as follows:

$$\xi = A/V_{MFC} \quad (4)$$

where V_{MFC}: volume of the MFC.

Since ξ is proportional to A (Eq. 4) and the R_{ohmic} is inversely proportional to A (Eq. 3), it follows that R_{ohmic} would be inversely proportional to ξ. Beyond the math, intuitively, it is plausible that a high ξ would be desirable, since more active electrode area is available for bioelectricity generation in a given volume of the cell, that is, the exploitation of cell volume is maximized. In this regard, flat electrodes had an inherent relatively low ξ. Thus, several works have investigated the use of electrode materials with high ξ, such as granular and reticulated graphite and granular activated carbon [14,27]. Regarding the use of flat electrodes, the ξ of the cell can still be increased if more walls of the cell are fitted with electrodes. In this way, the MFC fitted with a 'sandwich' ACM as reported by Liang et al. [26] might have an increased performance if the ***two*** circular surfaces of the cylindrical shell of their MFC were fitted with AMC arrangements.

Therefore, the aim of our research was to evaluate the performance of a new design of a single chamber microbial fuel cell (MFC-A) for the processing of a model extract similar to the one generated in the hydrogenogenic fermentation of organic solid wastes. Results were compared with the performance of a standard single chamber cell (MFC-B). The MFC-A consisted of a cylindrical cell equipped with 'sandwich' AMC electrode arrangement in each of the two circular faces of the cylindrical shell. The MFC-B consisted of an identical shell equipped with the anode fitted to one circular face and the cathode to the opposing face, separated by distance of 7.8 cm. A sulphate-reducing inoculum was used as biocatalyst [28] whereas the fuel was a model extract similar to leachates from the hydrogenogenic fermentation of organic solid wastes [8, 29,36].

2. MATERIALS AND METHODS

2.1. Microbial fuel cell architecture

Both MFC consisted of a horizontal cylinder built in Plexiglass 78 mm long and 48 mm internal diameter . In the MFC-A (new design), the two circular, opposing faces of the cylindrical shell were fitted with corresponding sets of an assemblage or circular 'sandwich' arrangement that consisted (from inside to outside) of an anode made of Toray carbon cloth, the proton exchange membrane (Nafion 117), the cathode made of flexible carbon-cloth containing 0.5 mg/cm2 platinum catalyst (Pt 10 wt%/C-ETEK), and a perforated plate of stainless steel 1 mm thickness (Fig. 1a). This 'sandwich' arrangement is referred to as AMC for the anode-membrane (PEM)-cathode.

On the other hand, the standard cell MFC-B (Fig. 1b) was fitted with a circular anode made of stainless steel plate 1 mm thickness with a Toray flexible carbon-cloth sheet placed in one circular face and a cathode in the opposing face made of (from inside to outside): proton exchange membrane (Nafion 117), a Toray flexible carbon-cloth containing 0.5 mg/cm2 platinum catalyst (Pt 10 wt%/C-ETEK), and a perforated plate of stainless steel 1 mm thickness. All the cathodes in both cells MFC-A and MFC-B were in direct contact with atmospheric air on the perforated metallic plate side.

It is worth highlighting that the MFC-A had a ratio ξ (electrode surface area to cell volume, Eq. 4) two-fold greater than the MFC-B. Also, the separation between electrodes in MFC-A was null or minimal ('sandwich' arrangement) whereas the inter-electrode distance in MFC-B was 7.8 cm.

2.2. Model Extract and Biocatalyst

The cells were loaded with 7 ml from a model extract similar to the produced metabolites profile found in the biological hydrogen production from the organic fraction of the municipal solid wastes [8], [30], [31]. The model extract was concocted with a mixture of the following substances (in g/L): acetic, propionic and butyric acids (4 each) as well as acetone and ethanol (4 each) and mineral salts such as $NaHCO_3$ and Na_2CO_3 (3 each) and K_2HPO_4 and NH_4Cl (0.6 each). Organic matter concentration of model extract was ca. 25 g COD/L. The cells were loaded with 143 mL of mixed liquor from a sulphate-reducing, mesophilic, complete mixed, continuous bioreactor. The bioreactor had an operation volume of 3 L and was operated at 35°C in a constant temperature room. The bioreactor was fed at a flow rate of 120 mL/d with an influent whose 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), plus sodium sulphate (7.0). The initial COD and biomass concentration in the cell liquor were *ca*. 1 250 mg O2/L and 890 mg VSS/L, respectively.

2.3. Determination of internal resistance of the cells

The internal resistance is one of the main characteristics of a MFC, because according with the Theorem of Jacobi of maximum power delivered by an electromotive force, an MFC fitted with an external resistance equal to its internal resistance will give a maximum power output [32]. The internal resistance of cells was deter-

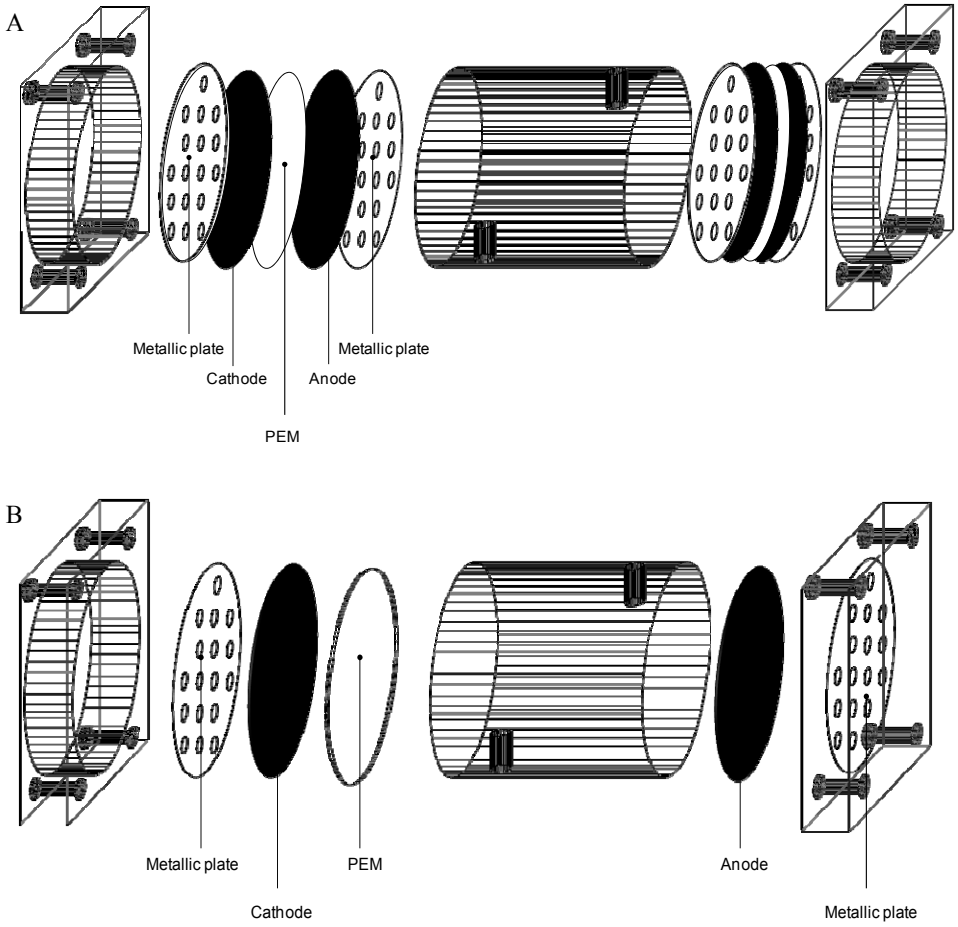

Figure 1. Schematic diagrams of single chamber cells: (a) type A (new design), and (b) type B (standard design).

mined using the polarization curve method, by varying the external resistance (R_{ext}) and monitoring both the voltage and the current intensity, according to procedures suggested by Clauwaert et al. [33] and Logan et al. [11]. In brief, each MFC was loaded with substrate and inocula as described in section 2.2. Each MFC was batch-operated for 7 h at 35°C. The circuit of the MFC was fitted with an external, variable resistance device. In this regard, we carried out the polarization curve of the MFC, relating mathematically the cell voltage (EMFC) and current intensity (IMFC) against the external resistance value, forwards and backwards regarding the R_{ext} values. *Ab initio*, the MFC was operated at open circuit for 1 h. Afterwards, the R_{ext} was varied from 1000 Ω to 10 kΩ and vice-versa. 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 as indicated below in Section 2.5.

2.4. Batch operation of microbial fuel cells

The MFCs were loaded with substrate and inoculum as described in section 2.2. The cells were batch-operated for 50 h at 35°C, without mixing. The circuit of each MFC was fitted with a corresponding external resistance equal to the R_{int} determined in section 2.3, in order to be consistent with the Theorem of Jacobi [32]. Cell voltage (E_{MFC}), current intensity cell (I_{MFC}) and power cell (P_{MFC}) were recorded against time.

The voltage was determined with a Multimeter ESCORT 3146A. The current intensity as well as other response variables were calculated as indicated below in section 2.5.

2.5. Analytical methods and calculations

The COD and VSS of the liquors of sulphate-reducing seed bioreactor and cells were determined according to the Standard Methods [34]. In addition, the individual concentrations of volatile organic acids and solvents in the model extract were analyzed by gas chromatography in a chromatograph Perkin Elmer Autosystem equipped with a flame ionization detector as described elsewhere [8].

The current intensity I_{MFC} was calculated by the Ohm's law:

$$I_{MFC} = \frac{E_{MFC}}{R_{ext}} \tag{5}$$

The delivered power was obtained as the product of the current intensity times the voltage, that is:

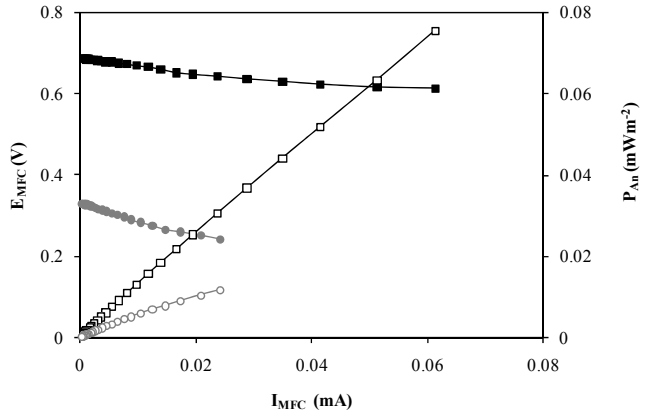

Figure 2. Curves of polarization (■, new design MFC-A; ●, standard MFC-B) and power densities (□, new design MFC-A; ○, standard MFC-B) of microbial fuel cellsusing a sulphate-reducing inoculum.

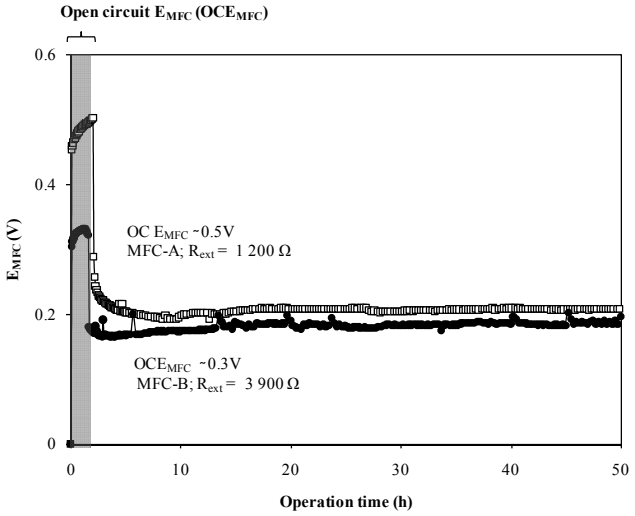

Figure 3. Time course of voltage outputs of new design cell MFC-A (□) and standard cell MFC-B (●) using a sulphate-reducing inoculum and fed with a model extract.

$$P_{MFC} = I_{MFC} \cdot E_{MFC} \tag{6}$$

With the purpose to get values comparable with the works already published, the power was normalized by the anode surface area (Eq. 3) and the cell volume (Eq. 4)

$$P_{An} = \frac{E^2{}_{MFC}}{A_{An} \cdot R_{ext}} \tag{7}$$

$$P_V = \frac{E^2_{MFC}}{V_{MFC} \cdot R_{ext}} \tag{8}$$

where A_{An} is the anode superficial area, R_{ext} is the external resistance, and V_{MFC} is the cell volume. It is worth noting that other researchers sometimes use the volume of the anodic chamber in Eq. 4 instead of the cell volume; there is no difference when Eq. 4 is applied to a single chamber MFC, but a significant difference may result when the MFC is a two-chamber model.

The performance of an MFC can be also assessed in terms of two essential parameters, the first one is the organic matter removal (chemical oxygen demand removal, η_{COD}) and the coulombic efficiency CE (η_{Coul}). The η_{COD} it is a method widely distributed to analyze the organic matter removal in waste treatment [34,35]. In batch processes, it is calculated as

$$\eta_{COD}(\%) = \frac{COD_{initial} - COD_{final}}{COD_{initial}} \times 100 \tag{9}$$

The coulombic efficiency η_{COD} is the ratio between the produced electrons in reality (CRS) and the electrons that could be produced from the substrate (CTS), as it follows:

$$\eta_{Coul}(\%) = \frac{CRS}{CTS} \cdot 100 \tag{10}$$

$$CRS = \int_0^t I_{MFC} dt \tag{11}$$

$$CTS = \frac{F_i \cdot b_{COD} \cdot (COD_i - COD_f) \cdot V_{MFC}}{M_{COD}} \tag{12}$$

where F: Faraday's constant (96 485 Coulombs mol^{-1} e^-), b_{COD}: number of moles of electrons harvested from the COD (4 mol e^- per mol of COD), COD_i: initial COD (g L^{-1}), COD_f: final COD (g L^{-1}), V_{MFC}: MFC operation volume (L), M_{COD}: COD's molecular weight (32 gmol^{-1}).

3. RESULTS AND DISCUSSION

3.1. Internal resistance of the cells

The polarization curves and the power variation with current intensity of the cells are shown in Fig. 2. It can be seen that both polarization curves were reasonably linear. Internal resistances were calculated as the slopes of the corresponding polarization curves; the values were 1 200 y 3 900 Ω for the MFC-A and MFC-B, respectively.

The new design lead to a significant 70% reduction of cell internal resistance compared to the standard cell. This effect may be ascribed to the 'sandwich' assembly of the ACM. The significant decrease of R_{int} with decrease of inter-electrode distance is consistent with previous experiments on the effect of electrode spacing on internal resistance of MFC [18,19,21,22]. In particular, the proportion of R_{int} decrease in our work was similar to that reported elsewhere [26]; it was found a 68% reduction in R_{int} value in a single chamber MFC fitted with a 'sandwich' AMC, compared to a second cell where the electrodes were separated 4 cm.

3.2. Performance of cells during their batch operation

Figure 3 shows the time course of voltage of the two MFCs loaded with sulphate-reducing inoculum during the 50 h of operation. In general, voltage output was higher in MFC-A than in MFC-B. The gray area shows that the maximum, open circuit potential (the two first hours and without a resistance in the external circuit) of the cells were 0.5 and 0.3 V for the MFC-A and MFC-B, respectively. The average voltages of cells were 0.21 y 0.18 V for MFC-A and MFC-B, respectively.

Table 1. Average performance of microbial fuel cells in this work.

Parameter	MFC-A	MFC-B
$P_{An\text{-}max}$ (mWm^{-2})	38.4	4.6
$P_{V\text{-}max}$ (mWm^{-3})	922.2	69.8
$E_{MFC\text{-}max}$ (V)	0.29	0.20
$I_{MFC\text{-}max}$ (mA)	0.24	0.05
$P_{MFC\text{-}max}$ (mW)	0.14	0.01
$P_{An\text{-}ave}$ (mWm^{-2})	20.0 ± 1.9	4.6 ± 0.4
$P_{V\text{-}ave}$ (mWm^{-3})	479.6 ± 23.1	55.6 ± 4.7
$E_{MFC\text{-}ave}$ (V)	0.21 ± 0.01	0.18 ± 0.01
$I_{MFC\text{-}ave}$ (mA)	0.17 ± 0.03	0.04 ± 0.002
$P_{MFC\text{-}ave}$ (mW)	0.07 ± 0.003	0.01 ± 0.0007
η_{COD} (%)	35	38
η_{Coul}(%)	4.23	0.91

Notes: MFC-A: new design microbial fuel cell; MFC-B: standard microbial fuel cell; $P_{An\text{-}max}$: Maximum power density; $P_{An\text{-}ave}$: Average power density; $P_{V\text{-}max}$: Maximum volumetric power; $P_{V\text{-}ave}$: Average volumetric power; η_{COD}: Chemical oxygen demand removal; η_{Coul}: Columbic efficiency.

Table 1 displays the maximum and average main response variables of the MFC in this work. All response variables showed a better performance in the new design MFC-A than in the MFC-B. Maximum volumetric power P_V and anode density power P_{An} of the MFC-A were superior to those of the MFC-B by factors of 13.2 and 8.4, respectively (Table 1). The improvement in P_V was probably due to the combined effects of increased ξ and decrease of R_{int}. Yet, it is interesting to note that the expected (algebraic) enhancement due these two features would be in the order of 6.5 ((2/1)*(3 900 W/1200 W) = 6.5), that is, the experimental improvement factor was almost double of the mere algebraic one. It seems that there was a synergistic effect between the architecture of the cell (ξ) and the lower internal resistance of the 'sandwich' AMC arrangement on the volumetric power of the MFC that it is difficult to explain. A similar trend was found for P_{An}, where the expected improvement due to R_{int} reduction was a factor of 3.2 (3 900/1 200 = 3.23) whereas the actual improvement factor was 8.4 (38.4 ($mW\ m^{-2}$)/4.6 ($mW\ m^{-2}$) = 8.4), Table 1.

Liang et al. [26] in comparative experiments with a 'sandwich'-AMC MFC and a MFC with separated electrodes, reported a 3-fold increase in density power P_{An}; their improvement factor 3 was lower than the factor 8.4 determined in the present research. Yet, their density power values were much higher than those found in the present work. Values of P_{An}, P_V, and CE of MFC-A in this work were superior by factors of 3 to 6 (depending on the response variable) to those reported by Poggi-Varaldo et al. [28] who carried out

Table 2. Results from published works on microbial fuel cells.

Cell Type	Inoculum	Substrate	Conditions	Performance	Membrane	Reference
Dual	*G. sulfurreducens*	Acetate [5mM]	T=30ºC, O_t = 960h, pH=6.8	P_{An}=16 mW m^{-2}, P_V = 87 mW m^{-3}	membrane-less	[44]
Concentric Cathode	*G. metallireducens*	Wastewater	T=30ºC; HRT=33d	P_{An}=26 mW m^{-2}; ηCoul=12%	Nafion 117	[46]
Upflow	Anaerobic sludge	Sucrose	T=35ºC; TRH=1d	P_{An}=170 mW m^{-2}; η_{Coul}=8,1%	CMI-7000	[47]
Dual	Anaerobic sludge	Acetate	T=30°C, O_t=100h	P_{An}=70 mWm^{-2}	Nafion 117	[37]
Dual	Anaerobic sludge	Modified wastewater	T=30ºC; O_t=50h	P_{An}=8 mW m^{-2}; η_{Coul}=40%	Nafion 117	[48]
Air-Cathode	Anaerobic sludge	Modified wastewater and glucose	T=30ºC; O_t=120h	P_{An}=262 mW m^{-2}; η_{Coul}=55%	Nafion 117	[38]
Air-Cathode	Wastewater	Acetate modified wastewater	T=32-20ºC	P_{An}=1200 mW m^{-2}; η_{Coul}=61,4%	membrane-less	[49]
Air-Cathode	Wastewater	Wastewater	T=30ºC; O_t=120h	P_{An}=28 mWm^{-2}, P_V=706 mWm^{-3}	Nafion 117	[38]
Air-Cathode	Wastewater	Wastewater	T=30ºC; O_t=60h	P_{An}= 483mWm^{-2}, P_V=12000mWm^{-3}	membrane-less	[39]
Air-Cathode	Wastewater	Modified wastewater	T=30°C, O_t=60h	P_{An}= 160mWm^{-2},P_V=369 mWm^{-3}	membrane-less	[21]
Air-Cathode	Wastewater	Acetate or butyrate modified wastewater	O_t=60h	P_{An}=500 mW m^{-2}; η_{Coul}=30%	membrane-less	[50]
Air-Cathode Separated electrodes	Methanogenic consortium	Mixture of organic acids and solvents	T=37°C, O_t=50h	P_{An}=1.04 mW m^{-2}; P_V=13.4 mWm^{-3}, η_{Coul}=0.12%	Nafion 117	[28]
Air-Cathode Separated electrodes	Sulphate-reducing consortium	Mixture of organic acids and solvents	T=37°C, O_t=50h	P_{An}=12.3 mW m^{-2}; P_V= 158 mWm^{-3}, η_{Coul}=1.22%	Nafion 117	[28]
Air-Cathode Separated electrodes	Sulphate- reducing consortium	Mixture of organic acids and solvents	T=35°C, O_t=50h	P_{An}= 4.63 mWm^{-2}, P_V=69 mWm^{-3}, η_{Coul}=1%	Nafion 117	This work
Air-Cathode 'sandwich' electrodes	Sulphate-reducing consortium	Mixture of organic acids and solvents	T=35°C, O_t=50h	P_{An}= 38 mWm^{-2}, P_V=922 mWm^{-3}, η_{Coul}=4%	Nafion 117	This work

Notes: Dual: two-chamber MFC; Air-Cathode: single chamber MFC; P_{An}: Power density; P_V: Volumetric power; I_{An}: Current density; η_{Coul}: Coulombic efficiency; NS: Not shown; O_t: Operation time; HRT: Hydraulic retention time

experiments with a single chamber MFC fitted separated electrodes and loaded with sulphate-reducing inoculum and an influent similar to the used in the present research. Also, performance of our MFC-A was better than those reported by other researchers [28,36-38,44,46,48] (Table 2), probably ascribed to their high internal resistances and the use of two-chamber MFC in some cases.

The P_V of the MFC-A was in the middle to high side of the range of P_V reported in the literature (Table 2). Yet, the P_{An} of the MFC-A was in the low range of published results [11,21,26] that showed a predominance of studies using simple substrates (such as glucose, acetate), anaerobic inocula or seed from wastewater, and even use of Pt in the electrodes and connections [21,38,39].

Organic matter removal was low to moderate: 35% in the MFC-A and 38% in the MFC-B (Table 1). These results were consistent with low values of the CE. Both parameters could be increased by increasing the time of operation (since at the end of the batch run most of the organic substrate was still available) and by further lowering the internal resistance of the cell.

The relatively low values of PAn obtained in this work could be due to the fact that our MFC architecture relied on a cell design with a relative large volume compared to other designs [40 – 42]. In our study Pt as a low density catalyst was used only at the cathode to overcome the final reaction to produce water, the external circuit lacked platinum. Another possible factor contributing to low average power densities in this work could be lack of acclimation of the inoculum to the new substrate. In effect, microbial consortia used in our experiments were acclimated to a feed rich in sucrose and acetic acid, as well as sodium sulfate as electron acceptor, in the sulphate-reducing inoculating bioreactor. After transfer to the MFC, the substrate fed was a model extract that did not contain sucrose and sulphate, and was concocted with acetic, propionic and butyric acids as well as acetone and ethanol and mineral salts. The absence of acclimation to the new substrate could have played a negative effect on MFC performance. Moreover, the inoculum was not previously subjected to selective pressures that could lead to its enrichment in electrochemically-active bacteria (EAB, also known as anodophilic or exoelectrogenic bacteria). As it is known, most of those EAB are dissimilatory metal reducing microorganisms, and their presence and predominance in the consortia anchored in MFCs are associated to high power outputs [43 - 45].

4. CONCLUSIONS

A new design of MFC whose main features were the assemblage or 'sandwich' arrangement of the anode-PEM-cathode and the extended surface area of electrodes (higher ξ) exhibited a performance significantly superior to that of a similar cell (standard cell) where the electrodes were separated. The characterization experiments showed that the new design lead to a significant 70% reduction of cell internal resistance compared to the standard cell. During the batch operation of the cells loaded with a model extract typical of hydrogenogenic fermentation of organic solid wastes and a sulphate-reducing inoculum, the maximum, open circuit potentials were 0.5 and 0.3 V whereas the average voltages were 0.21 y 0.18 V for MFC-A and MFC-B, respectively.

Maximum volumetric power P_V and anode density power P_{An} of the MFC-A were superior to those of the MFC-B by factors of 13.2 and 8.4, respectively. The improvement in P_V was ascribed to the combined effects of increased ξ and decrease of R_{int}. The experimental improvement factor was almost double of the expected (algebraic) factor 6.5. This result points out to a synergistic effect between the architecture of the cell (ξ) and the lower internal resistance on the P_V.

The P_V of the MFC-A (922 mW m^{-3}) was in the middle to high side of the range of values reported in the literature whereas P_{An} was in the low range of published results (38.4 mW m^{-3}). Organic matter removal was low to moderate: 35% in the MFC-A and 38% in the MFC-B. These results were consistent with low values of the CE, i.e, 4 and 1% for MFC-A and MFC-B, respectively. Both parameters could be increased by increasing the time of operation (since at the end of the batch run most of the organic substrate was still available) and by further lowering the internal resistance of the cell.

Our results suggest that MFCs could be used to further tapping energy from leachates generated in solid waste bioenergy fermentation, thus increasing bioenergy yields (in the form of bioelectricity) using an easily available and cheap resource. Finally, this work points out to the usefulness of the approach of increasing ξ and reducing R_{int} for improving MFC performance. Future efforts in this direction should be accompanied by the development of enriched inocula in order to boost power output of the cells.

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