



## PARALLEL CONNECTION AND SANDWICH ELECTRODES LOWER THE INTERNAL RESISTANCE OF A MICROBIAL FUEL CELL

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### ABSTRACT

The internal resistance ( $R_{int}$ ) is one of the main factors that have an impact on microbial fuel cell (MFC) performance. The objective of this work was to design and characterize a novel, multiface parallelepiped MFC in the perspective of decreasing the  $R_{int}$  and increasing the volumetric power ( $P_v$ ) output. The cell was fitted with a ‘sandwich’ cathode-membrane-anode assemblage, and possessed a ratio electrode surface area-to-volume  $\xi$  (csi).

The  $R_{int}$  was determined by the polarization curve method. MFC-P characterization was first carried out with the five faces connected in series and second with faces connected in parallel. Microbial fuel cell was loaded with sulfate-reducing inoculum and the substrate was a stock of short-chain organic acids and solvents representative of the leachate generated in dark fermentation of organic wastes.

When the 5 faces of the MFC-P were connected in series, the  $R_{int}$  was 600  $\Omega$  with a voltage of 0.52 V. Characterization of the cell with the 5 faces connected in parallel gave a  $R_{int}$  of 60  $\Omega$  with a voltage of 0.5 V. This result was ascribed to the changes in cell architecture, decrease of the





inter-electrode distance as well as the parallel connection. The  $P_v$  of the new MFC-P achieved values of 62 and 570 mW/m<sup>3</sup> for series and parallel connection, respectively.

*Keywords: internal resistance, microbial fuel cell, parallelepiped, parallel, sandwich electrodes, series.*





## 1. INTRODUCTION

A microbial fuel cell (MFC) is a promising technology for generating electricity directly from biodegradable compounds using bacteria under anaerobic conditions [1-2]. 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 [2]. 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 [3-4]. The actual voltage output of an MFC is less than the predicted thermodynamic ideal voltage due to irreversible losses. The three major irreversibilities that affect MFC performance are: activation losses, ohmic losses, and mass transport losses. These losses are defined as the voltage required to compensate for the current lost due to electrochemical reactions, charge transport, and mass transfer processes that take place in both the anode and cathode compartments [4-5]. The extent of these losses varies from one system to another [6]. The electrochemical limitations on the performance of MFC are due to the internal resistance ( $R_{int}$ ). The primary component of  $R_{int}$  is ohmic resistance, which can be further divided into the electrolytic resistance and ohmic resistance of electrodes, and the transfer resistance electrodes.

The  $R_{ohmic}$  is dominated by the  $R_{ion}$  associated to the electrolyte(s) resistance [5-6]. The  $R_{ion}$  due to electrolyte is given by the following expression [7].

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

where  $\rho$ : specific resistance or resistivity of the electroyte, L: distance between electrodes; A: electrode surface area;  $\kappa$ : specfic conductance or conductivity of the electrolyte. Inspection of Eq. 1 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  $\kappa$ ). 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.

The influence of electrode spacing on performance of MFCs has been shown in several works [4,8-12]. Another variable that may lead to lower  $R_{ohmic}$  is the electrode area. The latter can be expressed in terms of a variable  $\xi$ , the ratio of surface area of electrode to the cell volume, as follows:

$$\xi = A/V_{MFC} \quad (2)$$

where  $V_{MFC}$ : volume of the MFC. Several works have investigated the use of electrode materials with high  $\xi$ , such as granular and reticulated graphite and granular activated carbon [3,13]. Regarding the use of flat electrodes, the  $\xi$  of the cell can still be increased if more walls of the cell are fitted with electrodes.

The aim of this work was to design and characterize a novel, multiface parallelepiped MFC in the perspective of decreasing the  $R_{int}$  and increasing the volumetric power ( $P_v$ ) output. The cell was fitted with a ‘sandwich’ cathode-membrane-anode assemblage, and possessed a high ratio electrode surface area-to-volume  $\xi$  (csi).

## 2. MATERIALS AND METHODS

### 2.1 Microbial fuel cell architecture

The new design MFC-P consisted of a parallelepiped built in plexiglass with a liquid volumen of 1 000 mL (Figure 1A). Five faces of this cell were fitted with ‘sandwich’ cathode-membrane-anode assemblages (CMA). Each CMA (from inside to outside) consisted of an anode made of Toray carbon cloth, the proton exchange membrane (Nafion 117), and the cathode made of flexible carbon-cloth containing 0.5mg/cm<sup>2</sup> Pt catalyst (Pt 10 wt%/C-ETEK, and a perforated





plate of stainless steel 1 mm thickness.

On the other hand, a standard cell of 150 mL MFC-S 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 painted with Pt catalyst, and a perforated plate of stainless steel 1 mm thickness. Separation between electrodes was 7.8 cm (Figure 1B).

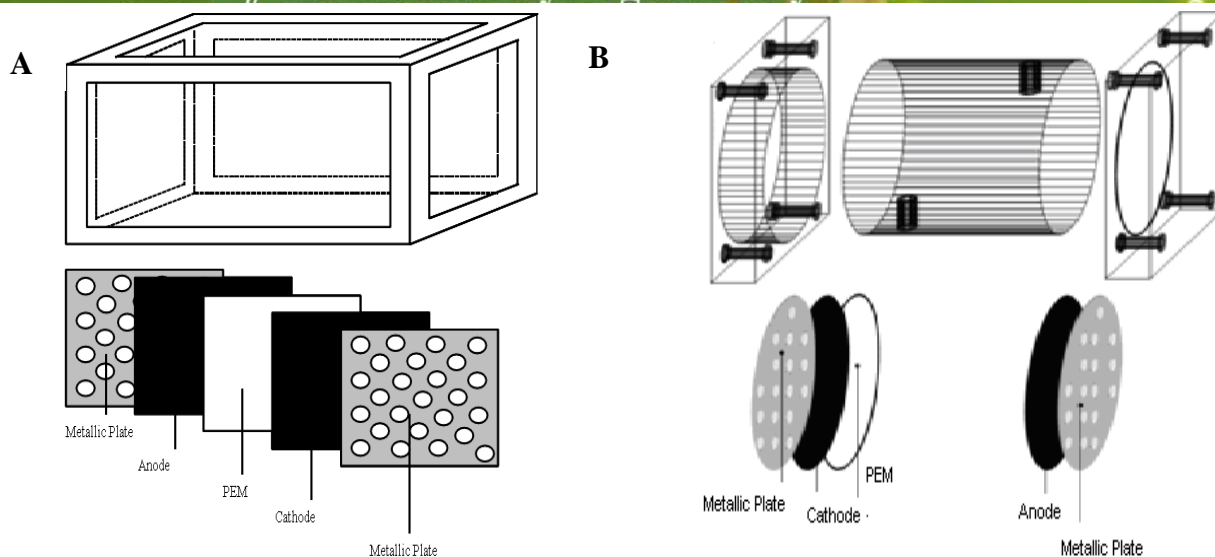
The MFC-P had a ratio  $\xi = 19.1$  (1/m) whereas the corresponding value of the standard MFC-S was 12.9 (1/m).

## 2.2 Model extract and biocatalyst

The cells, MFC-S and MFC-P, were loaded with 7 and 46 mL, respectively, from a model extract [14-16]. 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  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  (3 each) and  $\text{K}_2\text{HPO}_4$  and  $\text{NH}_4\text{Cl}$  (0.6 each). Organic matter concentration of model extract was ca. 25 g COD/L. The cells, MFC-S and MFC-P, were loaded with 143 and 954 mL, respectively, 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 150 mL/d with an influent whose composition was (in g/L): sucrose (5.0), Acetic acid (1.5),  $\text{NaHCO}_3$  (3.0),  $\text{K}_2\text{HPO}_4$  (0.6),  $\text{Na}_2\text{CO}_3$  (3.0),  $\text{NH}_4\text{Cl}$  (0.6), plus sodium sulphate (7.0). The initial COD and biomass concentration in the MFC-S liquor were ca. 1 450 mg  $\text{O}_2$ /L and 1100 mg VSS/L, the concentration and biomass in the MFC-P liquor were ca. 1600 mg  $\text{O}_2$ /L and 1400 mg VSS/L.







**Figure 1.** Schematic diagrams of microbial fuel cells: (A) type P (new design), and (B) type S (standard design).

## 2.3 Determination of internal resistance of the cells

The internal resistance of cells was determined 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 [1,17]. For the MFC-P, characterization was first carried out with the five faces connected in series and second with faces connected in parallel. In brief, each MFC was loaded with substrate and inocula as described above. Each MFC was batch-operated for 8 h at room temperature. The circuit of the MFC was fitted with an external variable resistance. In this regard, we carried out the polarization curve of the MFC, relating mathematically the cell voltage ( $E_{MFC}$ ) and current intensity ( $I_{MFC}$ ) 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 100  $\Omega$  to 1 M $\Omega$  and viceversa. 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. The current was calculated by the Ohm's Law as indicated below.

## 2.4 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 [18]. The current intensity  $I_{MFC}$ , the power  $P_{MFC}$  and the power density  $P_{An}$  were determined according to [2].

The power per unit volume or volumetric power  $P_V$  was calculated as follows:

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

where  $R_{ext}$  is the external resistance,  $E_{MFC}$  is the voltage, and  $V_{MFC}$  is the cell volume.

### 3. RESULTS AND DISCUSSION

The polarization curves and the power variation with current intensity of the MFC-P connected in series and parallel, are shown in Figure 2A and Figure 2B, respectively. The polarization curves and the power variation with current intensity of the MFC-S are shown in Figure 3.

The internal resistences were calculated as the slopes of the sets of aligned points of the corresponding polarization curves; the values were 600 and 60  $\Omega$  for the MFC-P connected in series and parallel, respectively, and 4 600  $\Omega$  for MFC-S. The new design connected in series and parallel, lead to significant reductions of cell internal resistance, compared to the standard cell (by 60 and 98.7%). This effect may be ascribed to the ‘sandwich’ assembly of the CMA. 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 [8-12]. In particular, the proportion of  $R_{int}$  decrease in our work was similar to that reported elsewhere [4]; it was found a 70% reduction in  $R_{int}$  value in a single chamber MFC fitted with a ‘sandwich’ CMA, compared to a second cell where the electrodes were separated 7.8 cm.

Table 1 shows the maximum and average main response variables of the MFC-P and MFC-S in this work. All response variables showed a better performance in the new design MFC-P than in the MFC-S. Maximum volumetric powers  $P_V$  in MFC-P connected in series and parallel were 62



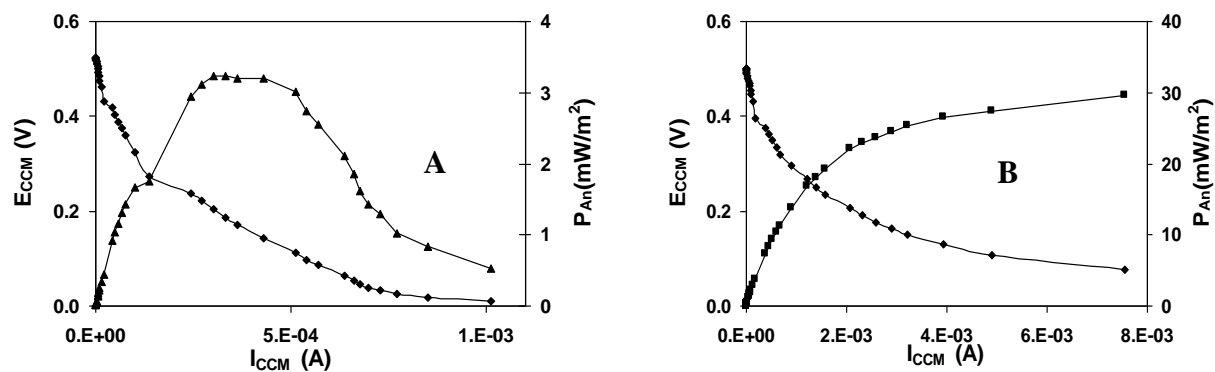
and  $570 \text{ mW/m}^3$ , respectively, and anode density powers  $P_{An}$  of the MFC-P connected in series and parallel were  $3.2$  and  $29.6 \text{ mW/m}^2$ , respectively, those response variables were superior to those of the MFC-S ( $4.34 \text{ mW/m}^2$  and  $52.07 \text{ mW/m}^3$ ). The improvement in  $P_V$  was probably due to the combined effects of increased  $\xi$  and decrease of  $R_{int}$ .

The parallel connection substantially lowered internal resistance, this decrease could be attributed to the increased cross section area of the ion flow path due to parallel connection. Also, calculations using the Ohm's law for parallel resistance connection closely agrees with the the total experimental value of  $63 \text{ ohms}$ . In effect,

$$1/R_{int \text{ total}} = \sum (1/R_{int,j}), j = 1, \dots, 5 \quad (4)$$

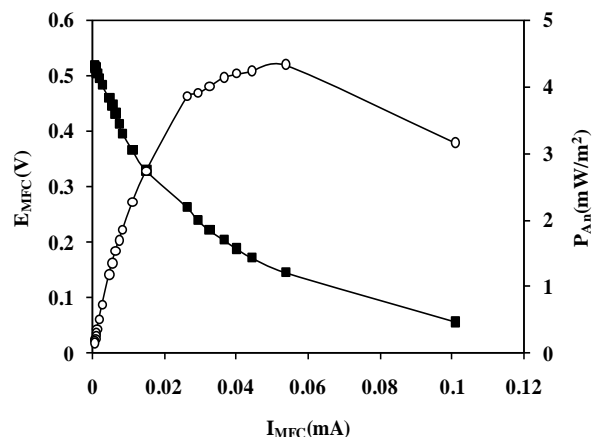
When substituting the  $R_{int,j}$  of each face, Eq. 4 gives  $R_{int \text{ total}} = 63 \text{ ohms}$

Parallel connection decreased not only the internal resistance by increasing the cross sectional area for ion flow, but also possibly diminished the electrode overpotential by increasing the total electrode surface area.



**Figure 2.** Polarization curves of new design microbial fuel: (A) connection in series and (B) connection in Parallel.





**Figure 3.** Polarization curve of the standard microbial fuel cell.

**Table 1.** Average values of several variables in cell characterization in this work.

Parameter	MFC-S	MFC-P Series	MFC-P Parallel
$R_{int}$ ( $\Omega$ )	$4600 \pm 250$	$600 \pm 32$	$60 \pm 3$
$P_{An-max}$ (mW/m <sup>2</sup> )	4.3	3.2	29.6
$P_{V-max}$ (mW/m <sup>2</sup> )	52.1	62.1	570
$E_{MFC-max}$ (V)	0.52	0.52	0.50
$I_{MFC-max}$ (mA)	0.1	1.01	7.54
$P_{MFC-max}$ (mW)	0.008	0.063	0.585

Notes: MFC-B: Microbial fuel cell standard; MFC-P: Microbial fuel cell parallelepiped;  $P_{An-max}$ : Maximum power density.

On the other hand, series connection showed an inverse trend to those in the parallel connection, with one order of magnitude higher resistance. Energy loss in the series connection is known to be caused by lateral ion cross-conduction between electrodes [19].

The low values of  $P_{An}$  obtained in this work could be due to the reactor configuration, it based on the wet volumen MFC [20-24], our MFC design had a high wet volumen compared with other designs [25-26].



Other factor involved in low average  $P_{An}$  could be the surface area electrode material, the effect of the larger anode surface area on power was show with several material such as plain graphite, carbon cloth, graphite foam; this effect was relatively insignificant by adding graphite granules or using graphite fiber brushes in the MFC. Those material increased the surface area [24,27]. Another possible factor contributing to low average volumetric power in our work could be lack of an enriched exoelectrogenic biofilm-forming, consortium in our MFC. As it is known, presence and predominance of these microorganisms in MFCs are associated to high power outputs [28-31]. The enriched consortium in general have resulted in the increase power densities [32].

Parallel conection of multiple electrodes of MFC significantly increased  $P_{V-max}$  compared to  $P_V$  of both the MFC-P connected in series and MFC-S (Table 1).

#### 4. CONCLUSIONS

A new design of MFC whose main features were the assemblages or 'sandwich' arrangement of the cathode-membrane-anode and the extended surface area of electrodes (higher  $\xi$ ) 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 significant reduction of cell internal resistances compared to the standard cell. The improvement in  $P_V$  was ascribed to the combined effects of increased  $\xi$  and decrease of  $R_{int}$ .

When the 5 faces of the MFC-P were connected in series, the  $R_{int}$  was 600  $\Omega$  with a voltage of 0.52 V. Characterization of the cell with the 5 faces connected in parallel gave a  $R_{int}$  of 60  $\Omega$  with a voltage of 0.50 V. On the other hand, the standard MFC-S exhibited a  $R_{int}$  values of 4 600  $\Omega$  with a voltage of 0.52 V. Thus, the  $R_{int}$  of the new design MFC-P was significantly lower than that of the standard cell; this result was ascribed to both the changes in cell architecture and decrease of the inter-electrode distance. The  $P_V$  of the new MFC-P achieved values of 62 and 569





$\text{mW/m}^3$  for series and parallel connection, respectively, whereas the power delivered by the standard cell was much lower ( $52 \text{ mW/m}^3$ ).

Our results confirm the positive effect of  $\xi$  on  $P_v$ , show the advantages of the ‘sandwich’ assemblage of AMC over separated electrodes, and demonstrate the convenience of parallel connection of faces in multi-face MFC-P in order to further abate the internal resistance of the new design cell.

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## 6. ABBREVIATIONS

A	surface area of electrode (usually the anode)
CMA	‘sandwich’ arrangement cathode-membrane-anode
COD	chemical oxygen demand
$E_{MFC}$	MFC voltage
$I_{MFC}$	current intensity
L	length of separation between anode and cathode
MFC	microbial fuel cell
MFC-P	new design of microbial fuel cell in this work
MFC-S	standard microbial fuel cell in this work
$P_{An-max}$	maximum power density
$P_{MFC}$	MFC power
$P_{V-max}$	maximum volumetric power
PEM	proton exchange membrane
$R_{int}$	internal resistance
$R_{ohmic}$	ohmic resistance
$R_{ion}$	Ionic resistance
$V_{MFC}$	MFC operation volume
VSS	volatile suspended solids





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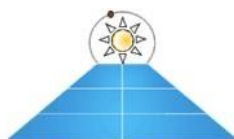
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**Greek characters**

$\xi$  ratio surface-of-electrode to cell volume

$\kappa$  specific conductance or conductivity

$\rho$  specific resistance or resistivity



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