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## Batch operation of a microbial fuel cell equipped with alternative proton exchange membrane

G. Hernández-Flores <sup>a</sup>, H.M. Poggi-Varaldo <sup>a,\*</sup>, O. Solorza-Feria <sup>b</sup>,  
T. Romero-Castañón <sup>c</sup>, E. Ríos-Leal <sup>d</sup>, J. Galíndez-Mayer <sup>e</sup>,  
F. Esparza-García <sup>d</sup>

<sup>a</sup> Environmental Biotechnology and Renewable Energies R&D Group, Dept. of Biotechnology and Bioengineering, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, Delegación Gustavo A. Madero, México D.F., C. P. 07360 Apartado Postal: 14-740, 07000 México, D.F, Mexico

<sup>b</sup> Dept. of Chemistry, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, Delegación Gustavo A. Madero, México D.F., C. P. 07360 Apartado Postal: 14-740, 07000 México, D.F., Mexico

<sup>c</sup> Electric Research Institute, Reforma 113, Col. Palmira, C. P. 62490, Cuernavaca, Morelos, Mexico

<sup>d</sup> Dept. Biotechnology and Bioengineering, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Av. Instituto Politécnico Nacional 2508, Col. San Pedro Zacatenco, Delegación Gustavo A. Madero, México D.F., C. P. 07360 Apartado Postal: 14-740, 07000 México, D.F., Mexico

<sup>e</sup> ENCB del IPN, Division of Basic Sciences, Escuela Nacional de Ciencias Biológicas, ENCB, Unidad Profesional Lázaro Cárdenas, Prolongación de Carpio y Plan de Ayala s/n, Col. Santo Tomas, C. P. 11340, Delegación Miguel Hidalgo, México, D.F., Mexico

### ARTICLE INFO

#### Article history:

Received 30 December 2014

Received in revised form

6 May 2015

Accepted 10 June 2015

Available online 23 July 2015

#### Keywords:

Proton exchange membrane

Low cost membrane

Batch operation

Microbial fuel cell

Leachate

### ABSTRACT

We compared the effect of membrane type on the performance of microbial fuel cells (MFC) fed with an actual leachate and operated in batch for 15 days. The tested proton exchange membranes (PEMs) were Nafion 117 (NF) and a low cost membrane (LCM). The cell equipped with LCM outperformed the one equipped with NF. In the first period of the batch, 0–8 d, average volumetric powers ( $P_v$ ) were 9000 and 4000  $\text{mW/m}^3$  for the MFC equipped with LCM and NF, respectively. In the second period (8–15 d) when the external resistances were adjusted, the average  $P_v$ s were 20 000 and 6800  $\text{mW/m}^3$  for LCM and NF, respectively. At the end of the batch, deposits of dry salts appeared on the external side of the cathode carbon cloth of the cell equipped with NF. Likely, this could be related to the decrease of power output in the last days of the batch (11–15 d) in the cell equipped with NF.

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\* Corresponding author. CINVESTAV del IPN, Environmental Biotechnology and Renewable Energy Group, Dept. Biotechnology and Bioengineering, Apartado Postal 14-740, 07000, México D.F., Mexico. Tel.: +52 (55) 5747 3800x4321, +52 (55) 5747 3800x4324.

E-mail address: [r4cepe@yahoo.com](mailto:r4cepe@yahoo.com) (H.M. Poggi-Varaldo).

<http://dx.doi.org/10.1016/j.ijhydene.2015.06.057>

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## Introduction

Nowadays the human-kind depend heavily on the use of petroleum oil as well as other fossil energy sources, and consequently faces at least two great risks: the inevitable depletion and the environmental pollution caused during exploration, transport, combustion of fossil-based fuels. Thus, the investigation to develop novel, renewable energy sources, particularly bioenergies, has notably increased in the last years [1–3].

Microbial fuel cells (MFCs) constitute a promising technology that generates electrical power from a wide range of soluble substrates (organic or inorganic), wastes included. The MFCs has become an interesting alternative to produce electrical energy and provide wastewater treatment simultaneously [4–8].

In order to increase the MFC efficiency, several conditions of MFC operation and components have been the subject of intensive research such as the type of biocatalysts, membrane (electrolyte) or separators, temperature, pH, substrates, the type and materials of electrodes, electrode catalysts, cell configuration and architecture, among others [2,8a–12].

The proton exchange membrane (PEM) is an important part of MFCs. The main features and purposes of the membranes in MFCs are listed below [13–15]:

- to separate the anodic from the cathodic chamber 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 MFCs
- 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

Yet, there are disadvantages related to the PEM use, such as the high cost of standard membranes such as those made of the polymer Nafion [13–15]. For instance, Nafion cost has increased up to \$1733/m<sup>2</sup> [16]. Furthermore, its use might affect negatively the power generated by the MFC due to the increase of the internal resistance ( $R_{int}$ ) [14,15,17].

Presently, one of the challenges of the MFCs is their scaling up; this mainly depends on the performance of MFC and cost of materials [15,18]. So, in order to replace the Nafion 117 (NF), several polymeric membranes have been studied, such as ultrafiltration and microfiltration membranes, sulphonated polyether ether ketone membrane, anion and cation exchange membranes, bipolar membrane, forward osmosis membrane [2,9,14,15,18–21]. However, these polymeric membranes can also be expensive.

Membrane-less MFCs have also been tested, where the water conducts the protons by itself. However, in most of the works operated without a membrane, the CE is low or falls down to unfeasible values [9,13–15,19]. Liu & Logan explored the bioelectricity generation in a membrane-less MFC, in order to increase the energy output and reduce the cost [13]. They reported a power density of 146 mW/m<sup>2</sup> and 20% of CE for their

membrane-less MFC. In contrast, their MFC equipped with NF membrane displayed a lower power density of 28 mW/m<sup>2</sup> but a higher CE of 28%.

Regarding the use of new materials for PEMs that could reduce costs there are few studies that have focused on glass fibers or glass wool, salt bridge, as well as assemblies membrane-cathode [14,15,22,23]. Yet, results so far indicate that either high  $R_{int}$  were found or low power was delivered by the cells or both. For instance, Li et al. indicated that some coarse-pore filters (i.e., glass fiber, nylon mesh, and porous fabrics) can be more economic than ionic exchange membranes used in MFCs [15]. Yet, the first ones show the disadvantage of large pores that, in turn, would detract from the effectiveness of the separator for decreasing the flux of oxygen to the anodic chamber [24]. Glass fiber mats show better performance: they are resistant to biodegradation and biofouling, they exhibit a low O<sub>2</sub> permeability, and relatively high CEs can be achieved (81%) [15,24]. Indeed, it has been reported that glass wool can also serve as a low cost separator in MFCs [25,26]. Yet, the power was low, with a maximum of 10.1 mW/m<sup>2</sup>. Besides the open circuit potential (OCP) was only 0.36 V with a resistance as high as 4000  $\Omega$ .

In another work, Min et al. [22] determined the power output in a MFC equipped with a salt bridge that replaced the Nafion membrane; the inoculum was a pure culture of *Geobacter metallireducens*. The power density was very low, 2.2 mW/m<sup>2</sup>, whereas the  $R_{int}$  was nearly 20 k $\Omega$ . The authors ascribed the low power output to the higher  $R_{int}$  of the salt bridge system. In contrast, the  $R_{int}$  of a similar device equipped with Nafion membrane was 1286  $\Omega$ . Kargi & Eker worked with a two-chamber MFC separated by a salt-agar slab. A low power density ca. 3 mW/m<sup>2</sup> and current intensity of 0.24 mA were obtained [23]. The authors claimed that these values were comparable with those reported in the literature for MFC utilizing salt bridge, i.e., a work by Min et al. [22].

Therefore, the purpose of this work was to compare the effect of membrane type on the performance of MFC operated in long batch process, using actual leachates from Mexico City sanitary landfill and inoculum previously enriched (*E-In*) in electrochemically-active bacteria (EAB). The tested separators were a low cost membrane (LCM) and NF as reference.

## Materials and methods

### Experimental design

The experiment consisted of the operation in a long batch process of the MFCs equipped either with a LCM or NF (as control). The MFCs were packed with graphite flakes (GF) as anodic material and loaded with a mixture of inoculum previously enriched in EAB and a very recalcitrant, actual leachate from Mexico City sanitary landfill. The mix was in a proportion 80% inoculum and 20% actual leachate. The MFCs were operated for 15 d.

The long batch process was divided in two periods, a first one from 0 to 8 d, and a second one from 8 to 15 d. In the first period the cells were fitted with external resistances ( $R_{ext}$ ) defined by the first electrochemical characterization of the  $R_{int}$  at time 0 d. After a second electrochemical characterization

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