

Use of an Inoculum Enriched in Mn(IV)-reducing Bacteria for Bioelectricity Production from Municipal Leachates in a Microbial Fuel Cell

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ABSTRACT

The objective of this work was to evaluate the use of an inoculum enriched in Mn(IV)-reducing bacteria for bioelectricity production from municipal leachates in a microbial fuel cell. The cell *MFC-G* consisted of a horizontal cylinder built Plexiglass 90 mm long and 57 mm internal diameter. The opposing faces of the cylindrical shell were fitted with corresponding sets of an assemblage of (inside to outside) proton exchange membrane (Nafion 117), a Toray flexible carbon-cloth containing 1 mg/cm² Ru_xMo_ySe_z (20wt%/C), and a perforated plate of stainless steel 1 mm thickness. Each assemblage was corresponded with anodes made of graphite flakes and a graphite rod as collector.

The cell was loaded with an inoculum enriched for Mn(IV) reducing bacteria and leachate from Mexico City landfill as substrate. Faces I and II, when characterized by separate, showed internal resistance values (R_{int}) of 82 y 66 Ω , respectively. Afterwards, Faces I and II were connected in series and parallel with R_{int} of 98 and 44 Ω , respectively. A maximum volumetric power P_v of 1 239 mW/m³ was observed in the characterization of the *MFC* with Faces connected in parallel; this value was similar to high values reported in the open literature with cells using Pt as cathodic catalyst (Zhong *et al.*, 2011). After characterization, the *MFC-G* was operated in repeated batch mode. In each cycle, only the leachate was changed (spent leachate withdrawn and fresh leachate loaded) whereas the electrodes, membranes, and inoculum remained in the cell. It was observed that performance of the cell improved with consecutive periods of operation, which suggests that an additional in-cell enrichment of the inoculum could have occurred. In the 2nd and last cycle of operation, the following maximum values were observed: $E = 0.434$ V, $P_v = 1\,045$ mW/m³, and average values of COD removal efficiency = 70%; and coulombic efficiency = 14%. We conclude that it is feasible to produce electric energy from actual municipal leachates of Mexico City using a Mn(IV)-enriched inoculum in a cell that uses an alternative cathodic catalyst to Pt.

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1. Introduction

A microbial fuel cell (MFC) is an electro-biochemical reactor capable of directing converting organic matter into electricity [1]. Platinum has been commonly used as a catalyst of the oxygen reduction reaction (ORR) in *MFCs*. Yet the high cost of an *MFC* is mainly due to the high price of this noble metal. This, in turn, could deter the commercial *MFC* applications. So, the development of new materials with high catalytic properties to perform oxygen reduction is presently a task of great importance [2-5]. One of the challenges in microbial fuel cells research consists of the application of new electrochemically active catalytic materials (such as $\text{Ru}_x\text{Mo}_y\text{Se}_z$ [6]) as alternative electrocatalysts to replace the extensive use of the more expensive platinum.

On the other hand, municipal leachate is an aggressive effluent with relatively high concentration of organic matter. Leachate from sanitary landfills is of concern in Mexico City, since very recently the Bordo Poniente mega landfill has been closed and it is known that it generates large amounts of both fresh and aged leachates. We hypothesized that organic substances contained in leachates could be possibly recovered into electricity in a *MFC*. Thus, the objective of this work was to evaluate the use of an inoculum enriched in Mn(IV)-reducing bacteria for bioelectricity production from municipal leachates in a microbial fuel cell.

2. Materials and methods

2.1. Microbial fuel cell architecture

The *MFC-G* (Figure 1) consisted of a horizontal cylinder built Plexiglass 90 mm long and 57 mm internal diameter. The opposing faces of the cylindrical shell were fitted with corresponding sets of an assemblage of (inside to outside) proton exchange membrane (Nafion 117), a Toray flexible carbon-cloth containing $1 \text{ mg/cm}^2 \text{ Ru}_x\text{Mo}_y\text{Se}_z$ (20wt%/C) and a perforated plate of stainless steel 1 mm thickness. Each assemblage was corresponded with anodes made of granular graphite and a graphite rod as collector (80 mm long and 5 mm diameter). The average separation between cathode-anode in *MFC-G* was 17.5 mm. The anode chamber volume was 100 mL.

All the cathodes in cell were in direct contact with atmospheric air on the perforate metallic plate side. When the cathodic biocatalyst was the chalcogenide, the cathode had a loading of $1.0 \text{ mg/cm}^2 \text{ Ru}_x\text{Mo}_y\text{Se}_z$ 20 wt% dispersed in Vulcan carbon XC-72 as it was mentioned above. The catalytic ink was prepared by mixing $11.1 \text{ } \mu\text{L/cm}^2$ Nafion® 5 wt% and $333.3 \text{ } \mu\text{L/cm}^2$ of ethanol and the resulting suspension was sprayed onto the PEM of a home fabricated electronic semiautomatic device. Afterwards, the PEM was pressed the by hot pressing (4.4 kg/cm^2) at 120°C for 3 min to improve adherence of catalyst to the membrane [7,8].

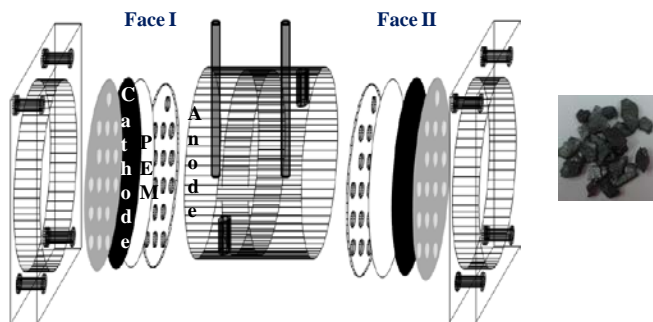


Figure 1. Schematic diagram a microbial fuel cell *MFC-C* (material electrode granular graphite).

2.2. Catalyst synthesis

The $\text{Ru}_x\text{Mo}_y\text{Se}_z$ catalyst was synthesized by decarbonylation of transition-metal carbonyl compounds in organic solvent, under refluxing [9-11]. The $\text{Ru}_x\text{Mo}_y\text{Se}_z$ catalyst was synthesized by reacting 0.07 mM $\text{Ru}_3(\text{CO})_{12}$ (Aldrich) with 0.20 mM $\text{Mo}(\text{CO})_6$ (Strem) and 0.20 mM of elemental selenium (Strem) in a chemical reactor containing 150 mL of 1,6-hexanediol for 3 hours at 230 °C. The un-reacted precursors and the organic reaction medium were eliminated by several washes using organic solvents, and dried overnight at room temperature [7,8].

The catalyst was composed of uniform agglomerates of nanocrystalline particles with an estimated composition of $\text{Ru}_6\text{Mo}_1\text{Se}_3$, embedded in an amorphous phase. Tafel slopes for the ORR remained invariant with temperature at $-0.116 \text{ V dec}^{-1}$ with an increase of the charge transfer coefficient in $d\alpha/dT = 1.6 \times 10^{-3}$, ascribed to an entropy turnover contribution to the electrocatalytic reaction. The apparent activation energy was $45.6 \pm 0.5 \text{ kJ mol}^{-1}$. The catalyst generated less than 2.5% hydrogen peroxide during oxygen reduction [7,8].

2.3. Municipal Leachates

The cells were loaded with 12 ml of municipal leachates. The characterization of the leachate is given in Table 1. The high COD and BOD_5/COD ratio indicated that the leachate is young and highly biodegradable. The cells were also loaded with 90 mL of mixed liquor from Mn(IV)-reducing bacteria, mesophilic.

Table1. Characterization of municipal leachate

Parameters	Value
pH	8.26
COD (g/L)	12.3
BOD (g/L)	6.3
Conductivity (mS/cm)	36.7
SO_4^{2-} (mg/L)	281.1

2.4 Inoculum: sample collection and enrichment

Sample from soil was collected in the CINVESTAV-IPN to a depth 2 m that was transferred to anaerobic bottle. The soil sample was moved to the laboratory without oxygen contact, and 5g of soil sample was suspended in 50 mL of anaerobic saline solution. 5 mL of sample was transferred to 50 mL metal-reduction medium with acetate and Mn (VI). Duplicate enrichments were incubated at 30 °C for 15 d in the dark condition. The enrichment procedure was repeated 3 times.

2.5 Electrochemical and analytical methods

Potential sweep experiments were carried out from open-circuit cell voltage (E_{OCP}), to the final potential of 0.02 V at a scan rate of 1mV/s, performed in a potentiostat/galvanostat Voltalab model PGZ402 [12,13]. Values of R_{int} were estimated from the slopes of corresponding regression lines selected in the linear range of the polarization curves. The current (I_{MFC}), power (P_{MFC}) and volumetric power (P_V) were calculated as previously described [14]. The power density was normalized to the projected cathode surface area (surface power density P_{S-max}). The COD and VSS of the liquors of sulphate-reducing seed bioreactor and cells were determined according to the Standard Methods [15]. Manganese (Mn II) contents were determined by a modification of the method of Brewer and Spencer [16] and the presence of Mn (IV) was assessed with a benzidine acetate reagent [17].

3. Results and discussion

The first set of experiments consisted of the application of $Ru_xMo_ySe_z$ as a cathodic catalyst for ORR in the *MFC-G*. Each face (I and II) of the *MFC-G* was characterized by separate (I and II), in series, and parallel electric arrangements (Figure 2).

Parallel connection of faces increased P_{V-max} up to 1239 mW/m³ value, compared with 575 and 818 mW/m³ for face I and face II by separate (*MFC-G*). Parallel connection significantly decreased the R_{int} of the cell and almost doubled volumetric power, respectively. The P_{V-max} for the *MFC-G* when faces were connected in series and parallel were higher than that reported by Ortega-Martinez *et al.* [18], when characterizing a novel, multi-face parallelepiped *MFC* (Pt for ORR). This cell was fitted with a ‘sandwich’ cathode-membrane-anode assemblage in five of their faces. When the 5 faces of the *MFC-P* were connected in series and parallel, the P_{V-max} achieved values of 62 and 570 mW/m³, respectively.

On the one hand, the increment of P_{V-max} for our *MFC-G* could be attributed to the increase of the total electrode surface area by the application of granular graphite, and this, in turn, would have improved the electron transfer microbe-to-anode process [38]. Also, our work demonstrated that parallel connection of cell faces was more appropriate. On the other hand, the increase of power could be ascribed to the use of the enriched inoculum.

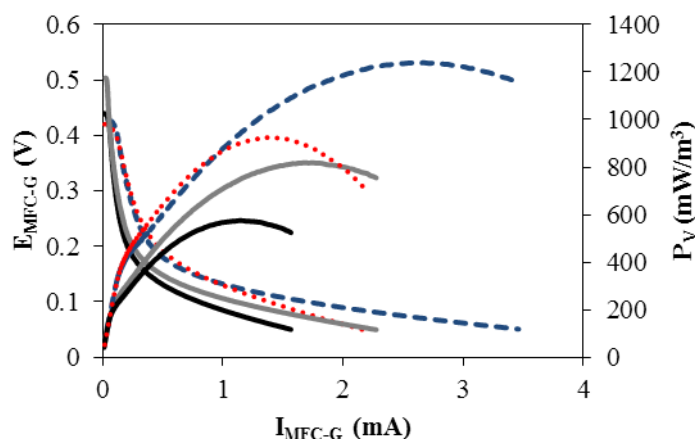


Figure 2. Curves of polarization: *MFC-G* (—, face I; ---, face II; ···, series and ---, parallel) and volumetric power (—, face I; ---, face II; ···, series and ---, parallel) of microbial fuel cell using a inoculum enriched in Mn(IV)-reducing bacteria and $Ru_xMo_ySe_z$ catalyst.

It is known that inocula cultured with metal cations as electron acceptors (such as Fe(III) or Mn(IV) as in our work) very often end enriched in electrochemically active bacteria that facilitate the electron transport between bacteria-substrate to anode [18].

Figure 3 shows the time course of voltage of the *MFC-G* loaded with a inoculum enriched in Mn(IV)-reducing bacteria during 260 h of operation. The *MFC-G* was connected to an $R_{ext} = 1\,800\,\Omega$. The gray area shows that the maximum, open circuit potential (the 24 h and without a resistance in the external circuit) of the cell was 411 V. Two repetitive cycles of electricity generation with 3 500 mg/L municipal leachate were carried out (Period I and Period II in Fig. 3). In Period I, for one cycle a maximum voltage of 0.285 V was obtained that was associated to a volumetric power of 437 mW/m³. A possible factor contributing to relatively low potential and volumetric power in this Period could be lack of acclimation of the inoculum enriched to the new substrate. In effect, inoculum enriched used in our experiments were fed with an acetate solution as carbon source.

In Period II, the cell reached a maximum potential of 0.433 V that was associated to an attractive maximum volumetric power of 1 045 mW/m³. These values were higher than those reported by Vazquez-Larios et al. [19] with a *MFC* equipped with sandwich electrodes AMC and sulfate-reducing inoculum. After day 248 the potential of the cell fell, presumably to substrate depletion. Yet, we did not validate this assumption because the experiment was terminated at day 260.

The noticeably improvement of potential and power in Period II over Period I suggests that either an acclimation from acetate to leachate as carbon source or an in-cell enrichment or both might have occurred [20].

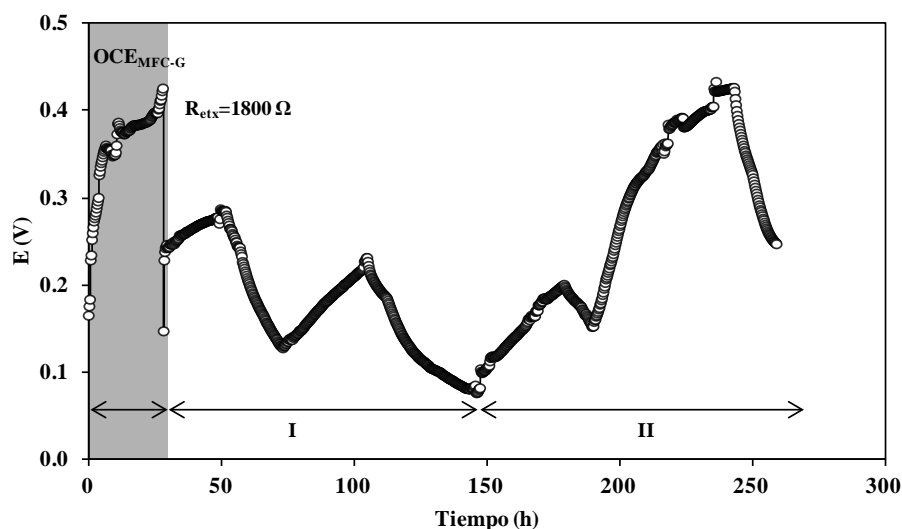


Figure 2. Time course of voltage outputs of MFC-G cell using a inoculum enriched in Mn(IV)-reducing bacteria, fed with a municipal leachates and $Ru_xMo_ySe_z$ catalyst.

4. Conclusion

We conclude that it is feasible to produce electric energy from municipal leachates of Mexico City using a Mn(IV)-enriched inoculum in a cell that uses a calchogenide catalyst as an alternative cathodic catalyst to Pt. During the repetitive batch operation of the *MFC-G* loaded with an actual leachate there was preliminary evidence of either an in-cell enrichment process or acclimation to the change of carbon source.

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