Chapter 10 Performance of a microbial fuel cell using MnO_2 as cathode catalyst

Capítulo 10 Desempeño de una celda de combustible microbiana empleando MnO_2 como catalizador catódico

CALZADO-ARAGÓN, Jenny†, FUENTES-ALBARRÁN, María del Carmen* and ALARCÓN-HERNÁNDEZ Fidel Benjamín

Universidad Autónoma del Estado de Morelos, Escuela de Estudios Superiores de Xalostoc. Av. Nicolás Bravo s/n, Parque Industrial Cuautla, C.P. 62717 Xalostoc, Ayala, Morelos, México.

ID 1st Author: *Jenny, Calzado-Aragón* / **ORC ID**: 0009-0002-6334-8576, **CVU CONAHCYT ID**: 1322232

ID 1st Co-author: *María del Carmen, Fuentes-Albarrán* / **ORC ID**: 0000-0003-1308-1332, **CVU CONAHCYT ID**: 171814

ID 2nd Co-author: *Fidel Benjamín, Alarcón-Hernández* / **ORC ID**: 0000-0002-2465-0898, **CVU CONAHCYT ID**: 131028

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J. Calzado, M. Fuentes and F. Alarcón

*carmen.fuentes@uaem.mx

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Abstract

Microbial fuel cells are electrochemical devices that use microorganisms as catalysts to produce electricity. Oxygen is the most used electron acceptor in the cathodic reaction of these systems, due to its abundance in the environment and high redox potential; however, the slow kinetics in oxygen reduction constitutes a limitation. Platinum (Pt) is the most widely used catalyst to accelerate the oxygen reduction reaction, but its high cost makes its use on a large scale impossible. In this study, the performance of manganese dioxide (MnO_2) as a cathodic catalyst in an H-type microbial fuel cell was examined. The MnO_2 layer on the carbon fiber surface was deposited by simply immersing the carbon in an aqueous $KMnO_4$ solution. The microbial fuel cell was characterized by polarization and power curves. A maximum power peak of 6.09 mW/m^2 was obtained with a current density of 22 mA/m^2, showing that MnO_2 can be a low-cost alternative to be used as catalytic material in the cathode of these devices.

Microbial fuel cell, Cathode Catalyst, Manganese Dioxide

Resumen

Las celdas de combustible microbianas son dispositivos electroquímicos que utilizan microorganismos como catalizadores para la producción de electricidad. El oxígeno es el aceptor de electrones más comúnmente utilizado en la reacción catódica de estos sistemas, debido a su abundancia en el ambiente y alto potencial redox, sin embargo, la lenta cinética en la reducción de oxígeno constituye una limitante. El platino (Pt) es el catalizador más ampliamente utilizado para acelerar la reacción de reducción del oxígeno, pero su alto costo imposibilita su uso a gran escala. En este estudio se examinó el desempeño de dióxido de manganeso (MnO_2) como catalizador catódico en una celda de combustible microbiana tipo H. La capa de MnO_2 sobre la superficie de fibra de carbón se depositó por simple inmersión del carbón en una solución acuosa de $KMnO_4$. La celda de combustible microbiana se caracterizó mediante curvas de polarización y potencia. Se obtuvo un máximo pico de potencia de 6.09 mW/m^2 con una densidad de corriente de 22 mA/m^2, mostrando que el MnO_2 puede ser una alternativa de bajo costo para utilizarse como material catalítico en el cátodo de estos dispositivos.

Celda de combustible microbiana, Catalizador Catódico, Dióxido de Manganeso

1. Introduction

The increase in industrial activity worldwide has led to an increase in the rate of carbon dioxide emissions. The global economy depends on fossil fuels, however, it has been projected that oil and gas reserves will be depleted by 2042 and coal by 2112 (Liew *et al*., 2014). In this context, renewable energies have gained great interest in different areas of research, such as solar, geothermal, wind, and biomass power generation. Microbial fuel cells (MFCs) are a technology that converts the energy contained in organic materials such as biomass and wastewater into electricity using microorganisms as catalysts (Qiu *et al*., 2021, Prasad and Tripathi, 2022). In addition to power generation, this technology finds application for bioremediation, toxic metal recovery, wastewater treatment, seawater desalination processes, etc. (Chaturvedi and Kundu, 2021).

A conventional microbial fuel cell (MFC) consists of two compartments separated by a proton exchange membrane. The anode is commonly maintained under anaerobic conditions, while the cathode may be suspended in aerobic solutions or exposed to air. In the anode compartment, microorganisms degrade organic matter, generating electrons and protons during their metabolism, with the anode becoming the electron acceptor. Electrons flow from the anode to the cathode through an external electrical circuit that commonly includes a resistor, while protons migrate to the cathode through the membrane that separates the two compartments. Finally, at the cathode, a final electron acceptor is reduced (Logan *et al*., 2006, Bazina *et al.*, 2023).

At the cathode of a MFC, oxygen is commonly used as the final electron acceptor due to its abundant availability in the environment and its high redox potential, however, the slow kinetics in the oxygen reduction reaction (ORR) is a limitation (Rizmani-Yazdi, *et al*., 2008). Pt has been widely used due to its favorable electrocatalytic performance relative to cathodic ORR in a MFC, but its high cost prohibits its use for commercial applications.

Different materials have been proposed as efficient catalysts for ORR, which include, carbon-based electrocatalysts, including heteroatoms (N, S, P, F, etc.) doped carbon catalysts (metal-free electrocatalysts), as well as transition metal-based electrocatalysts (Peera *et al*., 2021).

In particular, manganese dioxide materials with different crystal structures have been widely used as cathode catalysts in microbial fuel cells, due to their low cost, good catalytic activity and because they are environmentally friendly. MnOx possess great structural diversity, combined with their physical and chemical properties, in addition to their wide applications in catalysis (Deng *et al*., 2022), batteries (Zhuo *et al*., 2020) and supercapacitors (AlAnazi *et al*., 2023). Several researches have focused on the employment of MnO_2 as a cathode catalyst in MFCs employing different methods such as hydrothermal and electrodeposition to improve the performance of a MFC in electricity production (Phonsa *et al*, 2018, Majidi *et al*., 2019, Chen *et al*., 2022).

In this work, the performance of an H-type microbial fuel cell using MnO_2 as a cathodic catalyst was investigated for electricity production. The work was developed in three stages, in the first one, the synthesis and spontaneous deposition of MnO_2 on a carbon fiber electrode was performed, then the H-type MFC was assembled by monitoring the acclimation time of the cell, finally the fuel cell was characterized by polarization and power curves to examine its performance.

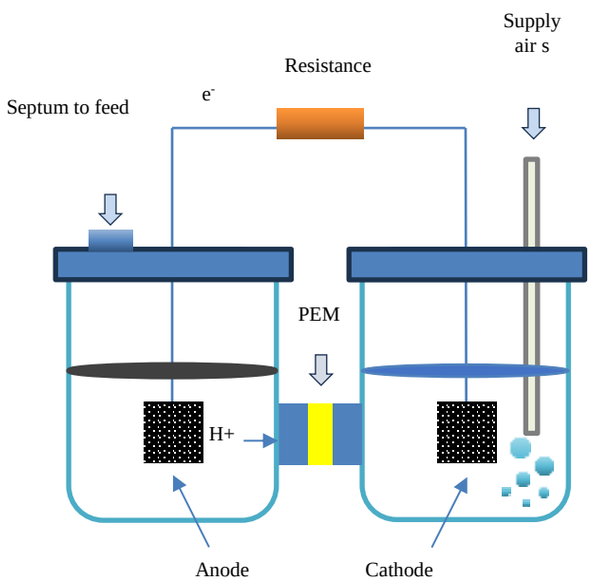
2. Experimental methodology

2.1. Microbial Fuel Cell Configuration

The microbial fuel cell (MFC) had an H-type configuration. The system consisted of two cylindrical glass compartments, with a diameter of 6 cm and a height of 8 cm, with a volume of 226.20 cm^3 each (Figure 2.1). A Nafion® 117 proton exchange membrane was used to separate the MFC compartments, and rim chamber gaskets were used between the compartments to prevent leakage. Air was constantly bubbled into the MFC catholyte using a fish tank pump. In the anolyte, a consortium from domestic wastewater and acetate (0.003 mol L^{-1}) was used as carbon source, in addition to a buffer solution (NH4Cl, 0.31 g L^{-1}; KCl, 0.31 g L^{-1}; NaH2PO4-2H2O, 3.32 g L^{-1}; Na2HPO4-2H2O, 10.32 g L^{-1}), this compartment was maintained under anaerobic conditions.

Carbon fiber (Fibre Glast Developments Corporation) was used for the electrodes, both electrodes had an area of 0.0018 m^2. The following sections describe the treatment given to the anode and the MnO_2 deposit on the MFC cathode. The cell was kept in operation for a period of 26 days at room temperature. Carbon fiber was used for the external connection.

Figure 2.1 Schematic of microbial fuel cell



Source of Consultation: Own Elaboration

2.2. Treatment of the anode

The anode was immersed in acetone for 10 minutes at 29°C, then washed with ethanol under the same conditions and left to dry at room temperature. Next, the electrode was immersed in a 50% v/v nitric acid solution and kept in agitation for 4 hours at 80°C, and then washed several times with distilled water. The electrode was then dried in the culture oven for 1.5 hours at 120°C. The purpose of the anode treatment was to favor the adhesion of the bacteria, as well as to decrease the internal resistance, in addition to promoting the electronic transfer between the microorganisms and the anode (Cai, *et al*., 2013).

2.3. Preparation of MnO_2 and deposition on the cathode

The cathode was placed in a 50 mL solution of 0.1 mol L^{-1} potassium permanganate ($KMnO_4$) for approximately 8 hours. By this procedure, the MnO_2 is spontaneously deposited on the carbon fiber electrode by simply immersing the carbon in the solution (Ma *et al*., 2007). Once the indicated time had elapsed, the electrode was removed from the solution and allowed to stand for 30 minutes to allow the excess to drain. It was then placed in a culture oven at 90°C for 2 hours to dry completely. After the procedure was completed, the catalyzed cathode could be used for the following applications.

2.4. Data acquisition and characterization of the MFC

The H-type MFC was kept in operation for a period of 26 days. The acclimatization stage of the cell consisted of the colonization of the anode by the microorganisms. During this period, the open circuit voltage of the MFC was recorded using a multimeter (Steren Professional Deluxe Multimeter with PC interface, Model: MUL-600). When the cell reached a stable voltage, the cell was characterized by means of polarization and power curves, using an external resistor (R_{ext}), varying it in a range from 2 to 10 kΩ and recording the corresponding voltage obtained in the cell (E_{MFC}). For each pair of values (Ω-V) obtained experimentally, the current was calculated according to ohm's law:

$$I = \frac{E_{MFC}}{R_{ext}} \quad (1)$$

The polarization curve was obtained by plotting cell voltage vs. current. The power density curve was obtained from the polarization curve, plotting the power density vs. current density, considering that the cell power (P_{MFC}) is defined as:

$$P_{MFC} = \frac{E^2{}_{MFC}}{R_{ext}} \quad (2)$$

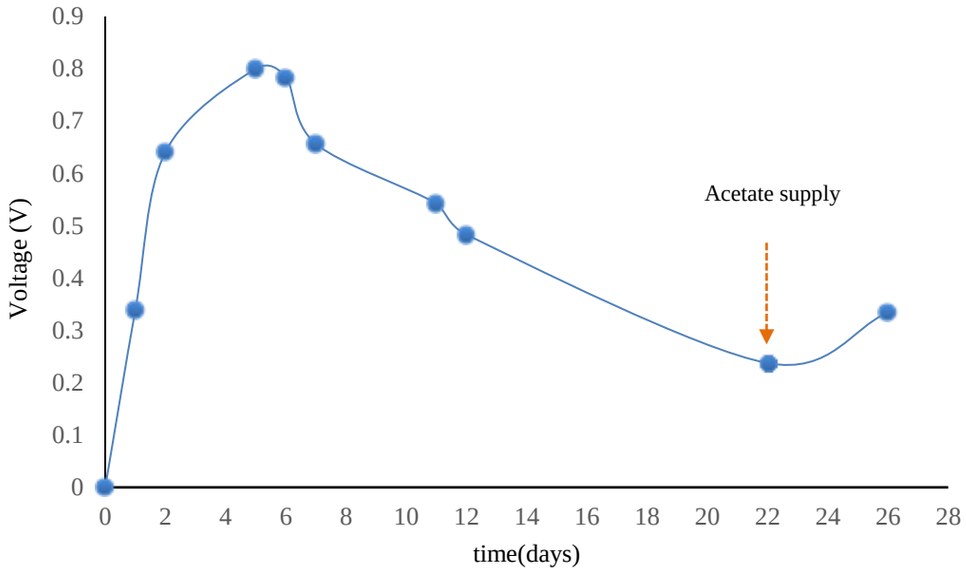
The power density obtained in this study was normalized to the area of the anode (mWm^{-2}).

3. Results

3.1. Acclimatization stage

Graph 3.1 shows the cell voltage as a function of operating time. During the first 5 days of operation, an exponential increase in voltage was observed, reaching a maximum of 0.8 V. Subsequently, the voltage began to decrease gradually, registering 0.24 V after 22 days of operation, which could be due to the depletion of organic matter by the microorganisms contained in the anode. In order to provide the carbon source to the MFC, acetate was supplied (as shown in the graph), increasing the voltage to 0.33 V. The system was monitored for a period of 26 days.

Graph 3.1 MCC acclimatization stage

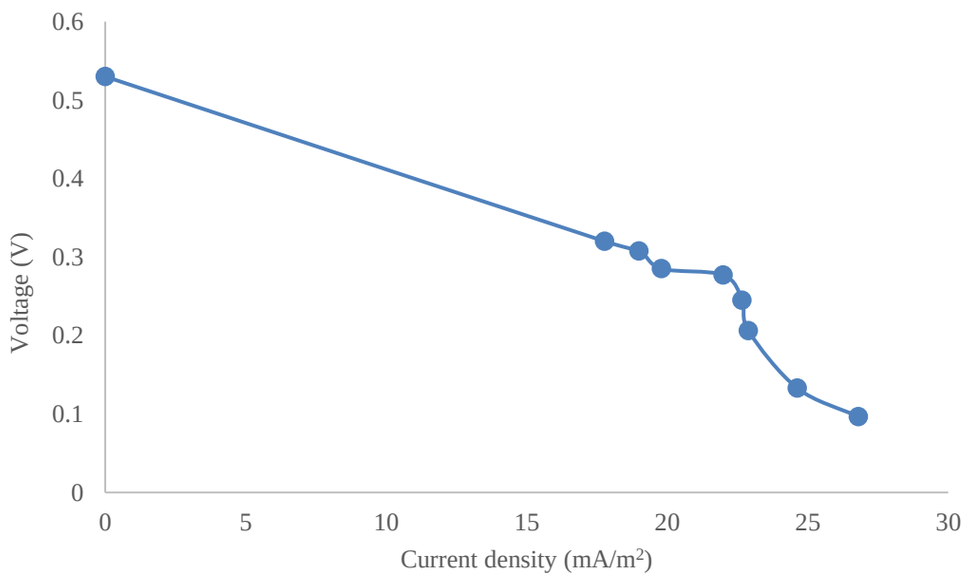


Source of Consultation: Own Elaboration

3.2. Polarization curve and power density

Graph 3.2 shows the polarization curve obtained in the MFC. It can be observed that the cell reached an open circuit voltage of 0.53 V, rapidly decaying to 0.32 V. This rapid loss of voltage at low currents corresponds to the activation losses, i.e., the activation energy that the reactant species of both electrodes must overcome. The anode is influenced by the type of substrate used as well as the microbial culture, while the cathode depends on the reduction kinetics (Rizmani-Yazdi *et al*., 2008). Graph 3.2 also shows a zone of almost linear voltage drop in an interval of 0.3 and 0.25 V, in this region is located the maximum peak power generated by the cell, some of the factors that influence these losses are the cell configuration and the resistivity of the different conductors, so it is important to minimize these potential losses to optimize the performance of a MFC (Clauwaert *et al*., 2008). Finally, the graph shows a rapid potential drop at high current densities.

Graph 3.2. Polarization curve



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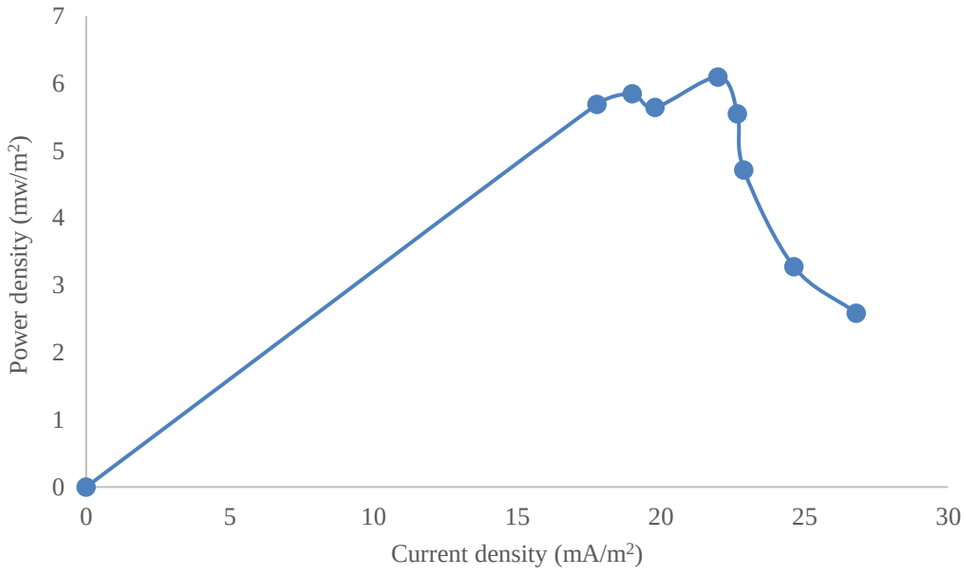
Graph 3.3 shows the power density obtained in the cell as a function of current density. The MFC obtained a maximum peak power of 6.09 mW/m^2 with a current density of 22 mA/m^2. (Fuentes *et al*., 2020) used the same method as this study to obtain MnO_2. The crystalline structure they identified was birnessite-type MnO_2. The method used in this work to deposit the catalyst on the MFC cathode has several advantages over other synthesis methods, and it is certainly attractive from a cost-effectiveness point of view, since unlike other synthesis methods it is simple and allows preparing a low-cost catalyst.

Graph 3.3 Power Density Curve



Source of Consultation: Own Elaboration

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Conclusions

– In this study, birnesite-type MnO_2 was synthesised on a carbon fibre cathode by simply immersing the electrode in an aqueous solution of $KMnO_4$.

– Using this catalytic material in an H-type MFC, a maximum power output of 6.09 mW/m2 with a current density of 22 mA/m^2 was obtained.

– Domestic wastewater is an ecological liability that can be used in a MFC to generate electricity, while at the same time purifying this waste.

– For future work, it is suggested to optimise the cell configuration to reduce ohmic losses, as well as to increase the conductivity of the system to improve the power output.

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