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The effect of catalysts MnO_2, activated carbon and fly ash on the performance of single-chamber Microbial Fuel Cells

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Abstract Microbial fuel cells (MFC) are bioelectrochemical systems that convert the chemical energy contained in waste to electricity, using bacteria as catalysts. In order to boost the power output of MFCs, various approaches are feasible. This study examines the effect of using MnO_2, activated carbon and fly ash as catalysts on the performance of three identical single-chamber MFCs. Ceramic (mullite) tubes run through the chamber providing structural support to the catalyst. Graphite granules were used as the anode electrode for all units. The cells operated in batch mode using glucose (1.5 g COD/L) as substrate. High COD removal efficiencies (>75%) were achieved for all units. The best performance in terms of power output was achieved when using MnO_2 catalyst (P_{max}=2.32 W/m^3).

Keywords: Microbial Fuel Cell, Wastewater treatment, Electricity, Ceramic, Catalyst

1. Introduction

Microbial Fuel Cell (MFC) technology is a promising approach to wastewater treatment because of its unique feature of treating waste with simultaneous electricity generation [Logan 2009]. The wastewater is oxidized in the anode, by electrochemically active bacteria, releasing electrons to the electrode and protons to the solution. The electron flow is directed through the anode electrode, via an external resistance to the cathode [Logan 2008]. The protons are transferred to the cathode through separators such as membranes [Rabaey et al. 2005]. In the cathode compartment, an electron acceptor is reduced on the surface of the cathodic electrode [Bennetto 1990]. The high cost of proton exchange membranes suggests seeking more cost-efficient materials to be used as alternative separators [Daud et al. 2015] Ceramic materials have also shown comparable results with ion-exchange membranes at significantly lower cost [Winfield et al. 2016]. Such ceramic materials examples are mullite and terracotta, both have been used as separators in MFCs, with mullite being more powerful [Tremouli et al. 2018]. Moreover, common electrodes used for the anode are cheap carbon-based materials such as graphite paper, graphite granules and graphite felt [Yaqoob et al. 2020]. Some reactions require the presence of a catalyst; for example, the reduction of O_2 at the cathode is enhanced by a platinum coating on the electrode. However, usage of platinum in MFC has been reduced, due to the high cost of the material [Santoro et al. 2018]. This work examines different materials as cathode catalysts in order to maximize oxygen reduction occurring in single-chamber MFCs, while at the same time the effect of using mullite as a cathode electrode on the cell's performance is also examined. Specifically, MnO_2, fly ash and activated carbon have been selected as catalysts and mullite as the structural material of the cathodes. MnO_2 is a common catalyst used to accelerate the oxygen reduction rate, while fly ash and activated carbon are potential cheap

alternatives, the performance of which is assessed in comparison with MnO_2.

2. Materials and Methods

Three identical single-chamber MFCs have been constructed for this work [Tremouli et al. 2021]. The cells were made of Plexiglas and four ceramic tubes run through the anode chamber of each unit. The anodic setup was similar for all the cells. Graphite granules (250 g) were placed inside the anodic compartment to support the bacterial growth and a graphite rod was embedded in the anode for the electron collection. The mullite tubes were internally coated with the oxygen reduction catalyst. Three different catalysts were tested, one for each cell MnO_2, activated carbon (AC) and fly ash (FA). The oxygen reduction catalytic paste was prepared by mixing graphite paint (12 g), xylene (3 ml), ethanol (3 ml) and 3 g of catalyst for each electrode. Stainless steel mesh was placed on the catalyst paste for better electron collection. The anodic and cathodic electrodes were connected by an external resistance set at 100 Ω, except stated otherwise.

The cells were operated in batch mode and fed with synthetic wastewater (150 cm^3) containing phosphate buffer (3.67 g/L NaH_2PO_4 and 3.45 g/L Na_2HPO_4), potassium chloride (0.16 g/L KCl), sodium bicarbonate (5 g/L $NaHCO_3$), trace elements (1% v/v, described elsewhere [Skiadas & Lyberatos 1998]) and glucose (1.5 g COD/L) as the electron donor. The average measured pH and conductivity of the feed were 7.2 ± 0.13 and 11.5 ± 0.4 mS/cm. During the first three batch cycles, the MFCs were inoculated with anaerobic sludge (10 % v/v) obtained from the Likovrisi sewage treatment plant, Athens, Greece. The bacteria were performed during the first batch cycles, similar to [Tremouli et al. 2019].

The cells were monitored continuously with voltage recording using a Keysight LXI Data Acquisition. Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) were carried out to assess the performance of the cells using Potentiostat – Galvanostat (PGSTAT128N – AUTOLAB) and an Ag/AgCl reference electrode. The model used to fit EIS results was according to previous publications [Tremouli et al. 2021]. The pH and conductivity were measured by digital instruments (WTW INOLAB PH720) and (WTW INOLAB) respectively. Soluble COD was measured according to the standard methods [Standard Methods 2012].

3. Results

Figure 1 presents the current output versus time for the acclimation and operation of the three cells distinguished by color depending on the catalyst used (Green = MnO_2, Red = AC, Blue =FA). The arrows indicate the point when no further sludge is added in the feed.

Following sludge inoculation, the current peaks during each successive cycle continue to increase, due to the adapting bacteria. The acclimation is finished once the maximum current is repeatable. The acclimation period for MnO_2 cell was 700 h, for the FA cell 240 h and for the AC cell 440h, respectively. The FA cell acclimated faster than the other 2 cells, as it presented first repeatable current peaks. Following the acclimation, the maximum current

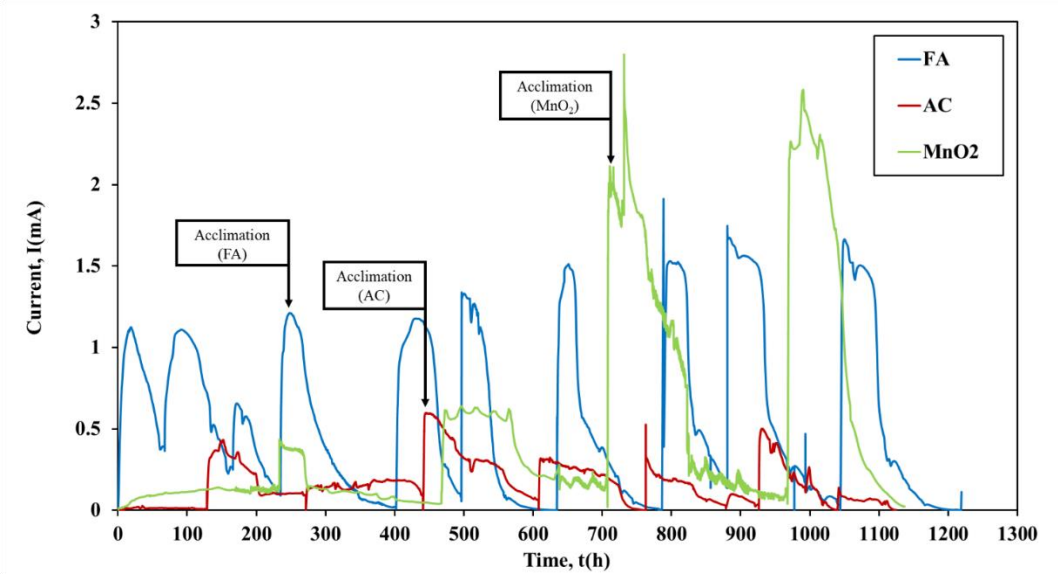

Figure 1: Current output versus time during acclimation and operation of the three cells (Green = MnO_2, Red = AC, Blue = FA). Arrows indicate the points in time where acclimation for each cell was considered complete.

enrichment and adaptation of the electrochemically active

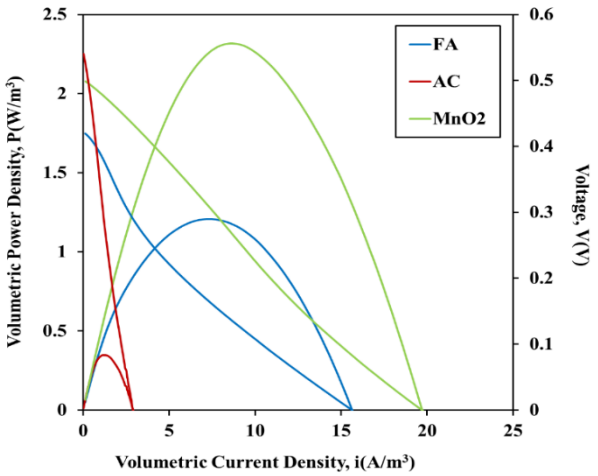

Figure 2: Volumetric power density versus volumetric current density versus voltage as extracted by LSV experiment on all three cells. (Green = MnO_2, Red = AC, Blue = FA)

(I_{max}) for the MnO_2 was recorded at the 4th cycle and was equal to 2.79 mA. The FA cell achieved I_{max} equal to 1.9 mA at the 6th cycle. The AC cell peaked at 0.6 mA, though the maximum current produced in each cycle was unstable, as can be observed in Figure 1. The average COD removal of the MnO_2 and FA cells was 81% and of the AC cell 78%. The Coulombic efficiency (CE) was 12% – 14 % for the MnO_2 cell, while for the FA cell ranged between 6%– 18% and for the AC cell ranged between 2% – 7%. The increase in the maximum current corresponded to the increase in the CE for the MnO_2 and FA cells. The AC cell due to the low current output did not achieve similar CEs, indicating that the organic matter was mainly consumed by antagonistic microorganisms, which did not contribute to the current production.

Table 1 presents the average measurements of pH and conductivity at the end of the operation cycles. In comparison with the feed, all cells presented an increase in the pH. This increase is thought to have been caused by two factors. First, the continuous reduction of air's O_2 in the surface of the cathodic electrodes, as this process consumes the $[H^+]$ and secondly, anaerobic microbial reactions happening because of both electrogenic and other bacteria. Conductivity measurements presented an increase in two cells (MnO_2 and AC), while the FA cell presented a small decrease. The increase of the conductivity is presumably caused by the microbial activity; breaking down substances and increasing the dissolved ions in the anode, similar to [Karthikeyan et al. 2016].

Table 1. Average pH and conductivity values of the wastewater of the three cells.

Measurement	MnO_2	FA	AC
pH	7.5±0.9	7.7±0.1	8±0.3
Conductivity (mS/cm)	15.2 ±2.4	10.8±0. 1	13.8 ±1.6

Figure 2 presents the results of Linear Sweep Voltammetry experiments on the three cells. The maximum power was achieved by the MnO_2 cell (2.32 W/m^3) whereas the FA cell (1.21 W/m^3) and the AC cell (0.35 W/m^3) produced lower power output. The OCVs (open circuit voltages) obtained were 0.489 V for the MnO_2 cell, 0.419 V for the

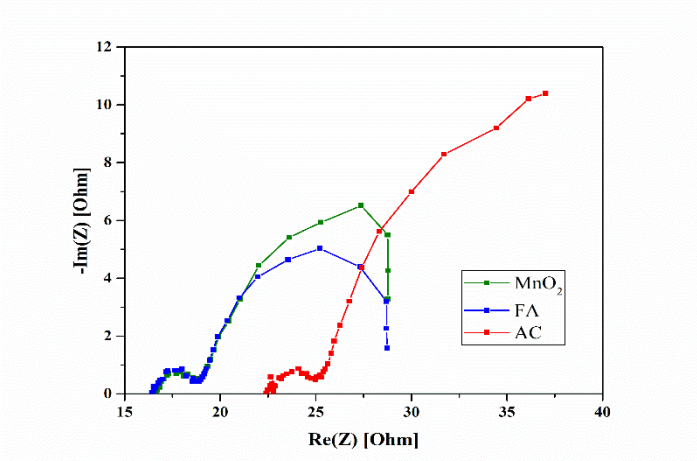

Figure 3: Nyquist plots of the 3 cells.

FA cell and 0.54 V for the AC cell, respectively. The AC cell reached the highest voltage in open-circuit conditions, although it yielded the lowest power production in comparison with the other cells. The MnO_2 cell produced both the highest current and power. The linear polarization curves indicate that ohmic losses dominate in all units. The FA cell achieved the highest CE among the three cells, but its maximum volumetric power density was 1.2 W/m^3.

Table 2. EIS fitted results for all cells from Figure 3

Fitted Parameters	MnO2	FA	AC
R_S (Ω)	16.1	16.5	22.1
R_{BF} (Ω)	2.1	2.7	11.2
C_{BF} (F)	$0.4 \cdot 10^{-3}$	$0.3 \cdot 10^{-3}$	$12.1 \cdot 10^{-6}$
C_{CT} (F)	$7.2 \cdot 10^{-3}$	$7.9 \cdot 10^{-1}$	0.04
R_{CT} (Ω)	9.9	34.6	56.4

The results from EIS also explained the lower maximum power output for all the cells. Although MnO_2 and FA depicted similar results in solution resistance (R_S), FA cell experienced larger values of charge transfer resistance, leading thus to lower power curves, as shown in Figure 2. AC cell depicted lower resistances in biofilm (R_{BF}), and charge transfer (R_{CT}) leading to Warburg resistance thus explaining the low power output.

4. Conclusion

In this work, three MFCs were operated in order to compare MnO_2, AC and FA as oxygen reduction catalysts. Mullite was selected as the material for the cathode and graphite for the anode electrodes. The cell with the MnO_2 achieved a higher power output and COD removal efficiency (2.32 W/m^3) when compared with the FA cell (1.21 W/m^3) and AC cell (0.35 W/m^3). Further study is needed in order to identify the factors contributing to these results as well as to examine the long-term operation stability of these catalysts.

Acknowledgments

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