Application of $Ru_xmo_ySe_z$ for Oxygen Reduction Reaction in Cathode and Two Anodic Material on the Performance of Two Single Chamber Microbial Fuel Cells

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Abstract

The objectives of our work were to evaluate *(i)* the application of calcogenide catalyst of the type $Ru_xMo_ySe_z$ for oxygen reduction reaction (ORR) in the cathode, and *(ii)* the effect of the type of the two anodic materials on the performance of two microbial fuel cells (MFCs). A new design of a single chamber MFC-A was built with a plexiglass cylinder, the two extreme circular faces were fitted with PEM-cathode assemblage, *i.e.*, left and right faces. The anode consisted of 65 triangular pieces of graphite filling the anodic chamber. The single chamber MFC-B had a 'sandwich' arrangement anode-PEM-cathode. The cathodes were made of flexible carbon-cloth containing 1mg/cm^2 $Ru_xMo_ySe_z$ catalyst. The cell was loaded with a sulfate-reducing inoculum and a mixed organic substrate. The MFC was characterized by linear sweep potential method. First, each face (left and right) of the MFCs was characterized by separate. The $P_{V\text{-}max}$ values for MFC-A were 1 200 and 1 125 mW/m^3 and those of MFC-B were 43 mW/m^3 for both separate faces. The values of R_{int} obtained were 146 and 167 Ω for MFC-A and MFC-B were 1 612 and 1 397 Ω, respectively. The MFC-A showed higher values of $P_{V\text{-}max}$ by a factor of 22.6 and 18.7. The R_{int} decreased by a factor of 11 and 8 for MFC-A. Parallel connection significantly decreased the internal resistance of the cell and almost doubled volumetric power for both cells. Power derived by cell A with cathode calcogenide catalyst was slightly inferior to that of a similar cell with Pt although the cost of the first catalyst is significantly lower than that of Pt, 90% lower. Finally, application of graphite anode made of small triangular pieces significantly improved the performance of a MFC-A that used $Ru_xMo_ySe_z$ as a cathodic catalyst for ORR.

1. Introduction

Microbial fuel cells (MFC) constitute a promising technology for sustainable production of alternative energy and waste treatment [1]. Platinum has been commonly used as a catalyst of oxygen reduction reaction (ORR) in MFCs. Yet the high cost of an MFC is mainly due to the high price of Pt. This, in turn, deters 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]. One of the actual challenges in microbial fuel cells research consists of the application of new electrochemically active catalytic materials ($Ru_xMo_ySe_z$) [3,4], such as alternate electrocatalysts to replace the extensive use of the more expensive platinum. On the other hand anode materials have been, watch

later in microbial fuel cells in attempts to increase the power output per unit volume of reactor. Several types of materials and shapes have been used, such as carbon paper, graphite plate, carbon cloth, carbon mesh, granular graphite, granular activated carbon, carbon felt, reticulated vitrified carbon, carbon brush, stainless steel mesh [5,6].
The objectives of our work were to evaluate *(i)* the application of calcogenide catalyst of the type $Ru_xMo_ySe_z$ for oxygen reduction reaction (ORR) in the cathode, and *(ii)* the effect of the type of the two anodic materials on the performance of two microbial fuel cells (MFCs).

2. Experimental section

2.1. Microbial fuel cell architecture

A new design of a single chamber MFC-A was based on extended electrode surface (larger ξ, ratio of electrode surface to cell volume) and the arrangement of the anode-PEM-cathode. The cell was built with a plexiglass cylinder, the two extreme circular faces were fitted with PEM-cathod assemblage, i.e., left and right faces. The anode consisted of 65 triangular pieces of graphite (1.4 x 1.8 x 0.5 cm, side x height x thickness) filling the anodic chamber. The single chamber MFC-B had an assemblage or 'sandwich' arrangement of the anode-PEM-cathode [7] The cathodes were made of flexible carbon-cloth containing 1mg/cm^2 $Ru_xMo_ySe_z$ catalyst [3].
On the other hand, the design of a single chamber MFC-C was similar to the MFC-A except that the cathode was made with Toray flexible carbon-cloth that contained 0.5mg/cm^2 platinum catalyst (Pt 10 wt%/C-ETEK), instead of the calcogenide. All the cathodes in both cells MFC-A and MFC-B were in direct contact with atmospheric air on the perforated metallic plate side.

2.2. Model Extract and Biocatalyst

The cells were loaded with 7 ml from a model extract similar to the produced metabolites profile found in the biological hydrogen production from the organic fraction of the municipal solid wastes [8], [9], [10]. The model extract was concocted with a mixture of the following substances (in g/L): acetic acid (1.4), propionic acid (0.3) and butyric acid (0.2) as well as acetone (0.04) and ethanol (0.08) and mineral salts such as $NaHCO_3$ and Na_2CO_3 (3 each) and K_2HPO_4 and NH_4Cl (0.6 each). Organic matter concentration of model extract was ca. 35 g COD/L. The cells were loaded with 143 mL 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 120 mL/d with an influent whose composition was (in g/L): sucrose (5.0), acetic acid (1.5), $NaHCO_3$ (3.0), K_2HPO_4 (0.6), Na_2CO_3 (3.0), NH_4Cl (0.6), plus sodium sulphate (13.0).

2.3. Electrochemical technical and analytical methods

Potential sweep experiments were carried out at a scan rate of 0.1mV/s from open-circuit cell voltage (E_{OCP}), to the potential final 0.02mV, the potential sweep were performed in a potentiostat/galvanostat Voltalab model PGZ402 [15, 16].

The current (I_{MFC}), power (P_{MFC}), power density (P_{An}), volumetric power (P_V) and coulombic efficiency (η_{Coul}) were calculated as previously described [7].

The COD and VSS of the liquors of sulphate-reducing seed bioreactor and cells were determined according to the Standard Methods [11]. In addition, the individual concentrations of volatile organic acids and solvents in the model extract were analyzed by gas chromatography in a chromatograph Perkin Elmer Autosystem equipped with a flame ionization detector as described elsewhere [12].

3. Results and discussion

First, each face (I and II) of the MFC-A and MFC-B was characterized by separate (Figure 1a,b). Values of $E_{MFC, OCP}$ obtained were 0.591 and 0.593 V for the left and right face (MFC-A), and 0.332 and 0.311 V for the left and right face the cell B, respectively (Table 1). The $P_{V\text{-}max}$ values for MFC-A were 1 200 and 1 125 mW/m^3, the corresponding values in MFC-B were 53 and 60 mW/m^3 for both separate faces, that is, much lower (Table 1). The polarization curves were very close to straight lines; the values of R_{int} were estimated from the slopes of corresponding regression lines as 146 and 167 Ω for MFC-A and MFC-B were 1 612 and 1 397 Ω, respectively.

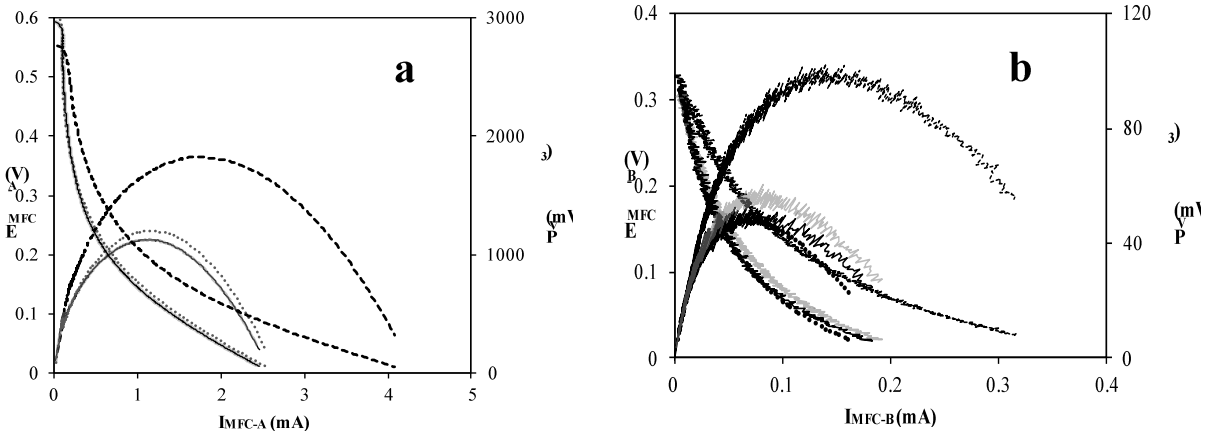

Figure 1. Curves of polarization: (a) MFC-A and (b) MFC-B
(-, face I; -, face II; .., series and --, parallel) and volumetric power (-, face I; -, face II; .., series and --, parallel) of microbial fuel cells using a sulphate-reducing and $Ru_xMo_ySe_z$

The MFC-A with graphite anode made of small triangular pieces showed higher values of $P_{V\text{-}max}$ by a factor of 22.6 and 23.4. The proportion of R_{int} decreased by a factor of 11 and 8 for MFC-A. Parallel connection significantly decreased the internal resistance of the cell and almost doubled volumetric power for FMC-A and MFC-B, respectively. Also, it outstandingly increased the volumetric power efficiently. The $P_{V\text{-}max}$ for MFC-A was comparable with the value reported by Zhong et al. [13]. Thus, our work demonstrated that parallel connection was more appropriate regarding electrochemical characteristics of cells than series connection.

Table 1. Effect of the type of anodic material on cell characteristics MFC-A and MFC-B with different connections of their two faces (electrodes).

Type cell	Type connection	$E_{MFC,OCP}$ (V)	$P_{An\text{-}max}$ (mW/m^2)	$P_{V\text{-}max}$ (mW/m^3)	$I_{MFC\text{-}max}$ (mA)	R_{int} (Ω)
MFC-A Graphite triangular pieces	**Separate faces**	0.591	5.2	1200	2.5	146
		0.593	4.9	1125	2.4	167
	Series[a]	0.628	2.5	1124	2.9	162
	Parallel[b]	0.506	4.1	1829	4.1	69
MFC-B Sandwich electrodes with carbon cloth anode	**Separate faces**	0.332	4.2	53	0.2	1 612
		0.311	4.7	60	0.2	1397
	Series[a]	0.313	1.9	48	0.2	1874
	Parallel[b]	0.308	4.1	102	0.3	820

[a] the two facial electrodes were connected in series; [b] the two facial electrodes were connected in parallel; MFC, new design of single chamber cell; $E_{MFC\text{-}OCP}$, open circuit potential; $P_{An\text{-}max}$, maximum power density; $P_{V\text{-}max}$, maximum volumetric power; $I_{MFC\text{-}max}$, maximum current intensity.

Afterwards, first each face of the MFC-C with the application Pt as a cathodic catalyst for oxygen reduction reaction was characterized by separate (left and right). Second, the MFC-C was characterized with the two faces connected in series and parallel (Figure 2).

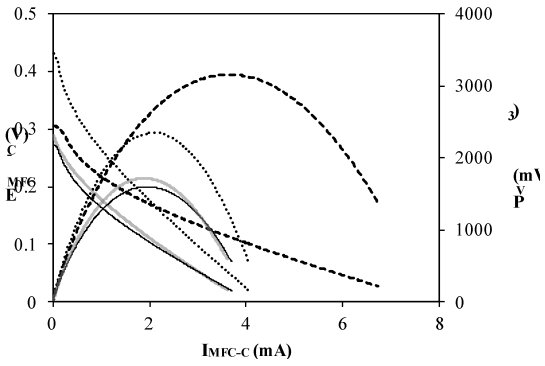

Figure 2. Curves of polarization of MFC-C (-, face I; -, face II; .., series and --, parallel) and volumetric power (-, face I; -, face II; .., series and --, parallel) of microbial fuel cells using a sulphate-reducing and Pt

Values of $E_{MFC,\ OCP}$ obtained from the separate faces were relatively low, 0.276 and 0.325 V for the left and right face, respectively. Series and parallel connection showed potentials 0.432 and 0.309 V, respectively (Table 2). The $P_{V\text{-}max}$ values were 1 600, 1 700, 2 349 and 3 158 mW/m^3 for separate faces, and series and parallel connection, respectively. The corresponding R_{int} were 55, 62, 83 and 33. The $P_{V\text{-}max}$ of separate face electrodes was high and comparable with the value 1010 of mW/m^3 reported by [13]. Parallel connection significantly decreased the internal resistance of the cell (33 Ω) and almost doubled volumetric power (Table 2), likely due to increased current intensity of 4.1 mA. The results for $P_{V\text{-}max}$ for parallel connection can increase the volumetric power significantly. The internal resistance values in this work were in the low side of the range reported in the literature [14].

Table 2. Effect the type catalyst for oxygen reduction reaction in the cathode: MFC-A and MFC-C with different connections of their two faces (electrodes).

Type cell	Type connection	$E_{MFC,OCP}$ (V)	$P_{An\text{-}max}$ (mW/m^2)	$P_{V\text{-}max}$ (mW/m^3)	$I_{MFC\text{-}max}$ (mA)	R_{int} (Ω)
MFC-A						
Calcogenide catalyst	**Separate**	0.591	5.2	1200	2.5	146
	faces	0.593	4.9	1125	2.4	167
	Series[a]	0.628	2.5	1124	2.9	162
	Parallel[b]	0.506	4.1	1829	4.1	69
MFC-C	**Separate**	0.276	7.0	1 600	3.7	55
Pt catalyst	**faces**	0.325	7.5	1 700	3.6	62
	Series[a]	0.432	7.9	2 349	4.0	83
	Parallel[b]	0.309	6.9	3 158	7.0	33

[a] the two facial electrodes were connected in series; [b] the two facial electrodes were connected in parallel; MFC, new design of single chamber cell; $E_{MFC\text{-}OCP}$, open circuit potential; $P_{An\text{-}max}$, maximum power density; $P_{V\text{-}max}$, maximum volumetric power; $I_{MFC\text{-}max}$, maximum current intensity.

The relatively low values of $P_{An\text{-}max}$ obtained in this work could be due lack of acclimation of the inoculum to the new subtrate. The microbial consortium in the sulphate-reducing inoculating bioreactor was acclimated to a substrate that consisted of sucrose and acetic acid, as well as sodium sulfate as electron acceptor. After transferring the inoculum to the MFC, the substrate fed was a model extract that neither contained sucrose nor sulphate (the substrate was a mixture of acetic, propionic and butyric acids as well as acetone and ethanol and mineral salts.) That is, the absence of acclimation to the new substrate could have played a negative effect on MFC performance. Furthermore, the inoculum was not previously enriched for electrochemically-active bacteria (also known as anodophilic or exoelectrogenic bacteria). As it is known, most of these microorganisms are dissimilatory metal reducing microorganisms, and their presence and predominance in the consortia anchored in MFCs are associated to high power outputs [17-20].

4. Conclusion

On the one hand, the MFC-A equipped of anodic triangular graphite pieces showed higher values of $P_{V\text{-}max}$ and significant lower internal resistances than the cell B with sandwich electrodes and anodic carbon cloth.

On the other hand, the power derived by cell A with cathode calcogenide catalyst was 42% inferior to that of a similar cell with Pt (cell C) although the cost of the first catalyst is significantly lower (90%) than that of Pt. The lower power harvested using calcogenide catalyst is easily offset by the savings associated to Pt replacement. Since the cost of Pt is US$ 31.4/g, whereas the cost of Ru is US$ 2.63/g, nearly 80-90% savings in the overall cost of cell construction might be achieved by using the calcognide-based catalyst.

Our results have have demonstrated the promising application of graphite anode made of small triangular pieces on performance of a MFC-A that used $Ru_xMo_ySe_z$ as a cathodic catalyst for oxygen reduction reaction.

5. References

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7. Appendix

E_{MFC}	voltage output of the cell
MFC	microbial fuel cell
MFC-A	new design of a single chamber microbial fuel cell with triangular pieces of graphite as anode and calcogenide catalyst in the cathode
MFC-B	two-face single chamber microbial fuel cell with two sandwich electrode with calcogenide catalyst in the cathode
MFC-C	single chamber microbial fuel cell with triangular pieces of graphite as anode and Pt catalyst in the cathode
P_{An-max}	maximum power density
PEM	proton exchange membrane
P_{V-max}	maximum volumetric power
R_{int}	internal resistance
SR-In	sulphate-reducing inoculum