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Evaluation and enhanced operational performance of microbial fuel cells under alternating anodic open circuit and closed circuit modes with different substrates

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ABSTRACT

The present study evaluates the performance of air-cathode microbial fuel cells (MFCs) under alternating open circuit/closed circuit (OC/CC) modes and its effect on independent-electrode and full-cell potentials, power output (at different external resistances) and the polarization behaviour of the electrodes. Three different types of feeds were evaluated using this approach: (1) phosphorus buffer solution (PBS) with acetate as carbon source, (2) glucose-rich synthetic wastewater, and (3) sewage from wastewater treatment plant enriched with fermented molasses. When MFCs were suddenly switched to CC from OC and then again back to OC from CC, the behaviour of the anodes vs reference electrode (Ag/AgCl, 3 M KCl) was monitored. When electric circuit of the MFCs was switched from open to closed circuit, for all cases: (a) the anode potential-shift (vs Ag/AgCl) reallocated in the positive direction in about 200–400 mV, (b) the air-cathode potential-shift (vs Ag/AgCl) reallocated in the negative direction in about 10–25 mV, and (c) the cell-potential difference started at around 0 mV and progressively increased as the MFC reached stability. This behaviour was consistently reproduced during different OC/CC cycles. The systems studied delivered good performance with both controlled media and industrial wastewater. Additionally, this study provides insightful characterization of the independent-electrode behaviours.

1. Introduction

In recent years microbial fuel cell (MFC) research has scaled several new heights. There has been a remarkable improvement in power density and cell structure [1–12]. For several years, researchers used synthetic wastewater and/or real wastewater as substrate and were able to degrade up to 98% of chemical oxygen demand (COD) [12,13,3,14–22]. There are many studies about cell design and electrode types; for further improvement of the MFC, new and more efficient materials have been reported [11,23–28]. Still, the exact mechanisms through which the bacteria transfer electrons to solid electrodes are not yet fully elucidated. It is well accepted that there exists one or a combination of two types (direct or mediated electron transfer) but which one is the most probable mode is still debatable [7,29–31].

In recent years advanced electrochemical techniques have been employed for the study of MFC, such as impedance spectroscopy [32–35] and cyclic voltammetry [36–38]. These techniques were found to be good for understanding the phenomena occurring during the formation of electrochemically active biofilms (EABs), cell attachment to the anode surface, diffusion coefficients and changed on the internal resistance of MFC. MFCs often operate with a constant external resistance, but practical implementation of MFCs for the aforementioned applications would require them to be robust enough to operate not only under different controllable electrical loads but also under intermittent OC and CC modes of operation.

Thus, the present study deals with understanding the individual electrode potential with respect to the reference electrode when MFCs are running in optimum condition, and there is a sudden shift from CC to OC and vice versa. In such conditions, it was evaluated how anode and cathode behave, with respect to the change in potential and overall MFC performance. With this background, the first two studies were performed with the defined media, whereas

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the last one was carried out with the real complex wastewater, to understand the practical implications of OC and CC modes of operation.

2. Materials and methods

2.1. MFC configuration and operation

Four similar air cathode MFCs were constructed from plexiglass with a total working volume of 25 mL each. The ion permeable membrane used was a Zirfon® separator [39]. Prior to use, the Zirfon® separator was pre-treated and characterized according to Pant et al. [40]. In the air cathode MFC the one side of zirfon® separator was exposed to the anodic chamber that contains substrate and microbes and other side to the VITO cathode. The outer side of VITO cathode was exposed to the air and inner side towards to the Zirfon® separator. The protons were transferred from anodic chamber to VITO cathode through the hydrophilic Zirfon® separator. Zirfon® used in these four MFCs had cross section area of 10 cm^2. All electrodes had an active projected surface area of 10 cm^2. All MFC reactors were operated 26–28 °C. Activated carbon cloth (Ballard, USA) was used as the anode. Gas diffusion cathodes (VITO CORE™) were constructed at VITO (Belgium), as described earlier [12,39,40].

2.2. Inoculation

The cells were inoculated from a previously running MFC, that has been in operation for than 30 months with acetate (10 mM) and phosphate buffer solution (PBS). PBS was composed of (mM): NH_4Cl (3.7), NaCl (6.8), $MgCl_2{\cdot}6H_2O$ (1.0), KH_2PO_4 (3.7) and yeast extract (10 mgL^{-1}). The inoculum enrichment was done as described earlier [12,39]. The microbial diversity of these inocula has been evaluated to be stable over 30 months, with a high predominance of *Geobacter sulfurreducens*. The final medium was flushed with N_2/CO_2 (80:20) for 30 min prior to use the pH was adjusted to 7.0.

2.3. Substrate for MFC

MFC-1 was fed with acetate (10 mM) and PBS. MFC-2 was feed with glucose rich synthetic wastewater (glucose 2 g L^{-1}, yeast extract 0.34 g L^{-1}, ammonium chloride 0.84 g L^{-1}, potassium di hydrogen phosphate 0.136 g L^{-1}, di potassium hydrogen phosphate 0.234 g L^{-1}, magnesium chloride hexa hydrate 0.084 g L^{-1}, ferric chloride 0.05 g L^{-1}, sodium thioglycolate 0.1 g L^{-1}). MFC-3 and MFC-4 were fed with half strength and high strength industrial wastewater as described earlier [12]. The full strength industrial wastewater had COD of 9968 ± 32 mg/L, pH 7.34 ± 0.12, NH_4^+–N 520.12 ± 12 mg/L and conductivity of 4.02 ± 0.08 mS/cm. The half strength wastewater had a COD of 4984 ± 32 mg/L, pH 7.14 ± 0.12, NH_4^+–N 354 ± 12 mg/L, and conductivity of 3.16 ± 0.08 mS/cm. All experiments were first performed with a defined medium in MFC-1 and afterwards repeated in MFC-2, MFC-3 and MFC-4 with other substrates for more reliability of the system.

2.4. Analytical measurement and calculation

Power generation of the MFCs at different external loads ($R_{external}$) was determined using polarization measurements. Polarization curves were obtained by changing the external resistance from 1 Ω to 11,000 Ω, using a decade resistance box (Escorp product). The corresponding voltage (V) generated was measured by using a high impedance multimeter [Fluke 189 true RMS]. Data were recorded after readings stabilized for at least 10 min. Current density generated was calculated according to $I = V/(A^*R)$, and power density was calculated according to $P = V^2/(A^*R)$ (A = electrode surface area; R = external resistance). Parameters like pH, electrical conductivity (EC), dissolved oxygen (DO), open circuit voltage (OCV), internal resistance and COD were monitored on a regular basis, which allow mapping the changes during the bioelectrochemical process at the electrode. pH and DO were measured using a multimeter (wtw 340i). The EC was measured using a conductivity metre (Knick SE204). The resistance between the electrodes was measured using a milliohm resistance metre (HIOKI 3560 AC mO HiTester). COD of the acetate solution in MFC was measured using a COD testing kit (DR LANGE). Acetate in the MFC solution was measured using ion chromatograph (IC) analysis and bicarbonate was measured by a total inorganic carbon analyzer (TIC).

3. Results and discussion

The four MFC were operated for a long stabilization period (14–16 days) for the initial setup of the cell potential. In the initial start-up period all the MFCs were operated in the CC mode. The external resistance values were derived for the polarization curves for the obtaining the maximum power density. In the initial stage (MFC-1 and MFC-2) the substrate fed was synthetic wastewater (acetate and glucose rich). In the later stage the complex high strength wastewater was used in MFC-3 and MFC-4. These different wastewaters were studied to see the behaviour of MFCs with defined substrate and complex wastewater feed. The MFC-3 was fed with COD of 9800 mg/L, while the MFC-4 was fed with COD of 4900 mg/L. Here the all the results favour that CC to OC and OC to CC were having the similar trends with both synthetic wastewater and complex wastewater, however the difference was observed in the cell potential shift.

When the cell potential stabilized at the desired conditions, then the MFCs were suddenly shifted from CC to OC. The drop in potential was compared with the different substrates in a similar air-cathode MFC setup. The external resistance value was determined through the external resistance for the maximum power production as it also changed with the change in substrate. After the cell potential stabilized again in OC mode, MFCs were connected with external load and their operation in CC mode was later on resumed. The time required for the potential to be stabilized again was monitored.

3.1. OC/CC performance with acetate rich medium in air cathode MFC

The acetate-fed air-cathode MFC was operated for 162 days. In the initial days the cell potential developed gradually and it became stable after the formation of the electrochemically active (EA) biofilm on the anode surface. During the first 14 days MFC-1 was operated in semi open/closed circuit for initial acclimatization and development. In this period, every day a polarization curve was prepared by changing the external resistance. After the first 14 days of such OC/CC, the MFC-1 was continuously operated in closed circuit (1480 Ω external resistance) for the remaining duration of the experiment. These experiments were performed to investigate the behaviour of the anode potential vs reference electrode (Ag/AgCl), after steady state of EA-biofilm formation on anode surface. When MFCs were suddenly switched to close from open circuit and then again back to open from closed circuit, then the behaviour of anode vs reference electrode (Ag/AgCl–3 M KCL) was monitored and the cell potential was compared with the standard redox potential.

Fig. 1A shows the CC to OC behaviour for the anode electrode with respect to reference electrode and in this case, a sudden drop in cell potential was observed when external resistance was removed from the circuit. The anode electrode cell potential with respect to the reference electrode reached stable relaxation within the next 10 min to −360 ± 12 mV range (Fig. 1A). Fig. 1B shows the OC to CC