



# A comprehensive impedance journey to continuous microbial fuel cells



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## ARTICLE INFO

### Article history:

Received 1 November 2014

Received in revised form 7 April 2015

Accepted 9 April 2015

Available online 17 April 2015

### Keywords:

Air-cathode MFC

External resistance

Hydraulic retention time

Electrochemical impedance spectroscopy

Power density

## ABSTRACT

The aim of the present work was to characterize the impedance response of an air-cathode MFC operating in a continuous mode and to determine intrinsic properties that define its performance which are crucial to be controlled for scalability purposes. The limiting step on electricity generation is the anodic electrochemically-active biofilm, independently of the external resistance,  $R_{ext}$ , utilized. However, for  $R_{ext}$  below 3 k $\Omega$  the internal impedance of the bioanode remained invariable, in good correspondence to the power density profile. The hydraulic retention time (HRT) had an effect on the impedance of both the bioanode and the air-cathode and especially on the overall MFC. The lowest HRT at which the MFC was operable was 3 h. Yet, the variation on the HRT did not have a significant impact on power generation. A two constant phase element-model was associated with the EIS response of both bioanode and air-cathode, respectively. Consistency was found between the CPE behaviour and the normal power-law distribution of local resistivity with a uniform dielectric constant, which represented consistent values with the electrical double layer, the Nernst diffusion layer and presumably the biofilm thickness. These results have future implications on MFC monitoring and control, as well as in providing critical parameters for scale-up.

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## 1. Introduction

Microbial fuel cells (MFCs) operating in a continuous mode have been found to be more suitable than batch or fed-batch ones for both increased COD removal and power generation [1]. However, when a MFC operates in a continuous mode, power and substrate degradation will inevitably decay if the rate of the electrolyte flow exceeds those of substrate consumption and microbial growth [2]. Given the typical anaerobic conditions of MFC-bioanodes, both factors are typically slow. Substrate and biomass dilution can be avoided by maintaining an appropriate retention time, which in turn will ensure high volumetric conversion rates of COD at high conversion efficiency, as well as maximized power generation. The hydraulic retention time (HRT) refers to the average lapse that a soluble compound (e.g. the substrate) remains in the microbial fuel cell. It is usually expressed in hours (h) and it is estimated by the ratio between the electrolyte volume (V) and the electrolyte flow rate (Q) [3]. Although the use of the HRT is one of the most important parameters that affect the design (dimensioning) and operation of numerous types of bioreactors and wastewater treatment units only a limited number of works have addressed its effects on the performance of continuous MFCs.

The HRT affects the contact between the substrate and the microbes in MFCs; in general, the higher the HRT in the anode chamber the more efficient the treatment (e.g. coulombic efficiency) and the higher the power production [4]. The HRTs reported for continuous mode MFCs vary in the order of 2–48 h [1,5,6], which are in general higher than those adopted for well-established wastewater treatment systems (3–12 h) [7]. This implies that in order for MFCs to be competitive with existing processes, the configuration or operation of MFCs should be modified to process higher organic loading rates at a lower HRT [2]. Yet, several authors have demonstrated saturation-type relationships arising at low HRTs [8,9], so a good balance must be established.

The effect of HRT on the electrical properties of a MFC can be assessed with electrochemical impedance spectroscopy (EIS). Based on EIS characterization, Feng et al. assessed the internal resistances ( $R_{int}$ ) of a MFC as a function of the HRT, finding that indeed at higher HRTs power density was increased.  $R_{int}$  is composed by several types of resistances, namely the polarization resistance ( $R_p$ ), the charge transfer resistance ( $R_{ct}$ ) and the ohmic resistance ( $R_{ohm}$ ). Depending on the rate-limiting steps, some MFCs also include a diffusion resistance ( $R_{dif}$ ) [10]. All these resistances can be extracted with relative ease from EIS data [11]. A way to reduce  $R_{dif}$  is to decrease the HRT which creates more uniform COD concentrations across the MFC [5] and moderates the effective thickness of the hydrodynamic diffusion layer. The cathode is typically the rate-limiting component of MFCs [12–14].

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Air-cathodes are preferred not only because they require less space compared to other cathode configurations, but also because they contribute less to the overall MFC resistance [1,11]. At the air-cathode of MFCs, limitations of proton or oxygen transfer onto the catalytic layer most likely account for  $R_{ct}$ , yet it is  $R_{ohm}$  and not  $R_{ct}$  which has been found as the limiting step of the cathodic reaction [10]. However, Wen et al. noted that the polarization resistance of a bioanode can be higher than that of the (bio)cathode, e.g. for a sequential anode–cathode MFC, indicating that the performance of the anode affected much more the MFC operation than the cathode [15]. The limiting contributions of the anode and cathode to the total  $R_{int}$  will ultimately depend on the reactor design, type of organic matter to be treated, type of electrodes and the strength of the wastewater.

A second parameter of high importance on MFC design and operation, that is often obviated, is the magnitude of the external resistance ( $R_{ext}$ ) interconnecting anode and cathode. As in any electric power source, maximum power is drawn when the external resistance ( $R_{ext}$ ) equals the internal resistance of the power source; when this is disregarded energy losses will be found. A  $R_{ext}$  significantly lower than the MFC  $R_{int}$  value leads to a low power output, hence an optimal  $R_{ext}$  value ( $R_{ext} \sim R_{int}$ ) should be maintained.  $R_{ext}$  regulates the electron flux through the MFC circuit [16]. Increased external resistance also impacts on biomass growth, changes in the bacterial community structure (e.g. reduced microbial community composition) and lowering of the current generated, especially during the initial phases of biofilm development [17]. On the long term, the power output at a given steady state strongly depends on the selected  $R_{ext}$ . Low  $R_{ext}$  promotes growth and metabolic activity of the electrochemically-active microorganisms since electron transport to the cathode is facilitated [16].

Regardless of the effects on the microbial community structure and diversity, it is consistently observed that the different communities are capable of producing the same level of power production. This means that when bio-anode reactions are rate-limiting the source of inoculum can be overlooked to achieve comparable performances. Because of this view, Lyon et al. established that changing  $R_{ext}$  does not improve MFC performance [17]. Nonetheless, contrary to these findings, other authors have found that the magnitude of the external resistance is key for a sustainable power output [19]. More recently, Eustace et al. have highlighted the importance of the external resistance on the kinetic rates of microbial electrocatalysis [20]. Given these controversies, further elucidation of the effect of the external resistance on MFC performances is necessary. Unlike the case of the HRT, the impedance response associated with this effect is not explained so far. Hitherto, EIS can shed more light on the effect of the applied  $R_{ext}$  on MFC power production and the related rate-limiting processes.

The aim of this work was to evaluate the effect of various ERs with a fixed HRT and, vice versa, various HRTs with a fixed ER, on the impedance response of an air-cathode MFC operating in a continuous mode. Such evaluation would lead to determine intrinsic properties that define the MFC performance, and which are crucial to be controlled for scalability purposes, such as the behaviour of the polarization resistance, charge transfer resistance, and capacitances associated with the double layer and hydrodynamic (Nernst) diffusion layer.

## 2. Materials and methods

### 2.1. Design and operation of single chamber air-cathode MFC

The air-cathode MFC (10 cm × 10 cm × 2.3 cm) was constructed from Plexiglas with a total working volume of 220 mL. The ion permeable separator was Zirfon® (100 cm<sup>2</sup>). Prior to its use, the Zirfon® membrane was pre-treated to improve its wettability, by placing it in 70 °C phosphate buffer (PBS) for 2 h. Sodium acetate (10 mM) was used as a substrate. The composition of the PBS has been detailed elsewhere [21–23]. The electrolyte was fed from an external reservoir bottle which was constantly stirred by magnetic means at 120 rpm. Ag/AgCl,

3 M KCl (+199 mV vs. SHE) was the reference electrode and coiled Pt wire functioned as a counter electrode (CE). Carbon felt (100 cm<sup>2</sup>) was used as anode, while a cold-rolled activated carbon gas diffusion electrode (100 cm<sup>2</sup>), namely VITO CORE™, was used as cathode [23]. To prevent interference of gases (O<sub>2</sub> or H<sub>2</sub>) which can be produced at the CE during the polarization measurements, Zirfon® ion permeable separator was placed between the working electrode and the CE. Air (21% O<sub>2</sub>) was fed to the air compartment at the PTFE side of the gas-diffusion electrode at an overpressure of 5 mbar g by means of a water column (5 cm). All MFC reactors were operated 26–28 °C.

### 2.2. Inoculation

The cells were inoculated from a previously running MFC that was in operation for 30 months with acetate (10 mM) and phosphate buffer solution (PBS) as supporting electrolyte. PBS was composed of (mM): NH<sub>4</sub>Cl (3.7), NaCl (6.8), MgCl<sub>2</sub>·6H<sub>2</sub>O (1.0), KH<sub>2</sub>PO<sub>4</sub> (3.7) and yeast extract (10 mg·L<sup>-1</sup>). The inoculum enrichment was done according to Sevda et al. [20]. The final medium was flushed with N<sub>2</sub>/CO<sub>2</sub> (80:20) for 30 min, prior to use. The pH was adjusted to 7.0.

### 2.3. Analytical measurements and calculations

Power generation of MFCs at different external loads ( $R_{ext}$ ) was determined using the polarization measurements. Polarization curves were obtained by progressive change of the external resistance from 1 Ω to 1.1 × 10<sup>3</sup> 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 multimeter). The data were taken after the readings stabilized for at least 10 min. Power density was calculated according to Eq. (1):

$$P = (V^2/A) \times R_{ext}. \quad (1)$$

Parameters like pH, electrical conductivity (EC), dissolved oxygen (DO), open circuit potential (OCP), internal resistance ( $R_{int}$ ) and COD were monitored on a regular basis. These allow to map 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 meter (Knick SE204). The internal resistance between the electrodes ( $R_{int}$ ) was measured using a milliohm impedance meter (HIKI 3560 AC mO HiTester). The concentration of volatile fatty acids in the MFC was measured using ion chromatography (IC). Bicarbonate was measured by a total inorganic carbon analyser (TIC). COD was measured using a COD testing kit (HACH LANGE).

### 2.4. Electrochemical characterization by electrochemical impedance spectroscopy

Electrochemical measurements were performed using a VersaSTAT 3F potentiostat and frequency response analyser (Princeton Applied Research, USA). EIS analyses were performed only when cell potential reached steady state. EIS was characterized from 10 kHz to 1 mHz at an AC amplitude of 10 mV. Validity of EIS data was verified with Kramers–Kronig transforms. EIS response was evaluated as a function of hydraulic retention time (3, 6, 12, 24 and 48 h) and external resistances (0.1, 1, 2, 3, 6, 10 kΩ and the open circuit condition representing an infinite resistance). Experiments were done in three electrode full cell configurations. The choice for the range of external resistances was based on our knowledge on the polarization behaviour of the MFC and intended to represent situations from an infinite external resistance (i.e. open circuit conditions) to a non-limiting situation as observed from the response of the MFC. The range selected for the hydraulic retention times intended to represent conditions from close to stagnancy (i.e. 48 h) to a situation before washout.

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