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# The internal resistance of a microbial fuel cell and its dependence on cell design and operating conditions

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ABSTRACT

The internal resistance $R_{int}$ of a mediator-less microbial fuel cell (MFC) has been determined as a function of cell voltage using electrochemical impedance spectroscopy (EIS) for a MFC with and without *Shewanella oneidensis* MR-1. The same tests were performed for a MFC containing small stainless steel (SS) balls in the anode compartment with a graphite feeder electrode as in a packed bed cell. It has been found that $R_{int}$ decreased with decreasing cell voltage as the increasing current flow decreases the polarization resistance of the anode and the cathode. The ohmic components of $R_{int}$ played a very minor role. In the presence of MR-1 $R_{int}$ was lower by a factor of about 100 than $R_{int}$ of the MFC with buffer and lactate as anolyte. $R_{int}$ was also significantly lower for the anode containing SS balls with buffer and lactate as anolyte. For the MFC containing SS balls in the anode compartment no significant further decrease of $R_{int}$ could be obtained when MR-1 was added to the anolyte since in this case the polarization resistance of the anode was lower than that of the cathode. Similar trends were observed in the cell voltage ($V$)–current ($I$) curves that were obtained using potentiodynamic sweeps and the power ($P$)–$V$ curves that were calculated from the $V$–$I$ curves.

## 1. Introduction

Microbial fuel cells (MFC) are novel electrochemical devices in which microorganisms catalyze the oxidation of various organic and inorganic substances to produce electric current. Bacteria present in the anode compartment oxidize the fuel and transfer electrons to the anode. These electrons pass through an external circuit and reach the cathode where they combine with the protons which pass through the ion-exchange membrane that separates the anode and the cathode compartments and reduce oxygen at the cathode to water. There are a variety of factors that can affect the overall performance of a MFC [1,2]. While the internal resistance $R_{int}$ has been recognized as an important parameter determining the performance of a microbial fuel cell [3–6], very little information can be found concerning $R_{int}$ of MFCs. There seems to be a difference in the definition of $R_{int}$ for MFCs. Logan et al. [7] state that $R_{int}$ contains contributions from the polarization behavior of the anode and cathode in addition to contributions from ohmic components. Aelterman et al. [8] seem to define $R_{int}$ as a parameter that contains only the ohmic components as indicated by the statement that $R_{int}$ values were determined according to the current interrupt method. This method can be used to measure the ohmic component of $R_{int}$, but not the contributions from the polarization behavior of the anode and the cathode.

In the present study electrochemical impedance spectroscopy (EIS) has been used to characterize the properties of the anode and cathode at their corresponding open-circuit potentials (OCPs) and also to determine $R_{int}$ of the MFC at various operating cell voltages. The characterization of the electrochemical properties of the anode and cathode is facilitated by the placement of reference electrodes in the anode and the cathode compartments [9,10].

EIS is one of the most extensively used steady state techniques to characterize electrochemical systems [11–14]. In EIS, an ac signal is applied in a wide frequency range (usually 100 kHz–1 mHz) at a fixed operating potential to characterize the properties of the system. Since only a small signal is applied for the recording of an impedance spectrum, EIS is essentially a non-destructive technique. The electrochemical properties such as the polarization resistance and the capacitance of the anode and the cathode of the system being studied can be determined by fitting the measured impedance data to appropriate equivalent circuits (ECs). The application of EIS in the evaluation of the properties of a MFC has been discussed in detail elsewhere [10].

The definition of $R_{int}$ used in this study was:

$$R_{int} = R_p^a + R_p^c + R_\Omega = R_p^{cell}, \tag{1a}$$

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where $R_p^a$ and $R_p^c$ are the polarization resistances of the anode and cathode, respectively and $R_\Omega$ contains the ohmic contributions of the electrodes, the anolyte and catholyte and the membrane. $R_p^{cell}$ is the dc limit of the impedance of the MFC, i.e. the impedance for $f \to 0$, where $f$ is the frequency of the applied ac signal.

Since for the MFC under investigation $R_p^a + R_p^c \gg R_\Omega$, Eq. (1a) becomes:

$$R_{int} = R_p^a + R_p^c. \tag{1b}$$

Since the $R_p$ values depend on the current flow in the MFC, it becomes apparent that $R_{int}$ should depend on the cell voltage V and this dependence was evaluated in the present investigation.

## 2. Experimental approach

To measure the dependence of the internal resistance of a MFC on its cell voltage for different operating conditions, experiments were performed using two different anolytes and two types of electrode configuration in the anode compartment. The construction of the MFCs and the various experiments that were performed in each case are explained below.

### 2.1. Cell construction

#### 2.1.1. MFC with porous graphite felt as the anode

A dual compartment MFC was used. Bare graphite felt (GF-S6-06, Electrolytica) was used as the anode and the cathode. The cathode was electroplated with platinum at a loading of 0.15 mg/cm$^2$ [15]. A proton-exchange membrane (Nafion® 424, DuPont) was used to separate the anode and cathode compartments. Each electrode had an apparent surface area of 20 cm$^2$ and was connected to a Pt-wire lead by a conductive carbon epoxy (EPOX-4, Electrolytica).

#### 2.1.2. MFC with packed bed of stainless steel balls as the anode

In this type of cell construction, stainless steel balls (Micro Surface Engr. Inc.) of 2 mm diameter were used as a packed bed anode in the anode compartment. The total surface area of the SS balls was about 130 cm$^2$. The graphite electrode acted as the feeder electrode. Apart from this packed bed construction, all other components were the same as for the MFC described above.

The assembled MFCs were autoclaved at 121 °C for 15 min prior to the addition of any liquid media. Sterile Ag/AgCl reference electrodes were inserted into both the anode and the cathode compartments after autoclaving. Anaerobic conditions were maintained in the anode compartment of the MFC by continuously passing filtered nitrogen gas through the compartment at a rate of 20 mL/min. Aerobic conditions were maintained in the cathode compartment by continuously passing air at a rate of 40 mL/min.

Electrochemical experiments were performed with two different anolytes:

- A1, buffer and lactate
- A2, buffer, lactate and MR-1.

The buffer solution contained 50 mM PIPES ($C_8H_{18}N_2O_6S_2$) and 7.5 mM NaOH (pH 7.0). The same buffer solution was used in the anode and the cathode compartments. Lactate served as the sole electron donor. The same cell was used for the two sets of experiments with different anolytes.

### 2.2. Bacterial growth conditions

*Shewanella oneidensis* MR-1 was grown in a PIPES-buffered minimal media (pH 7.0) containing 18 mM lactate as the sole electron donor, 50 mM PIPES, 7.5 mM NaOH, 28 mM $NH_4Cl$, 1.3 mM KCl, 4.3 mM $NaH_2PO_4 \cdot H_2O$ and 10 mL/L each of vitamin, amino acid and trace mineral stock solutions. Batch cultures were grown at 30 °C and agitated at a rate of 140 rpm until the late stationary phase was achieved [15]. The cells were then harvested and injected into the MFC such that an optical density ($OD_{600}$) of 0.4 was achieved in the anode compartment (the buffer served as the diluting medium).

### 2.3. Electrochemical techniques

The experimental test sequence for both anolytes and the two different cell configurations was begun by measuring the impedance spectra of the anode and the cathode at their corresponding OCPs. A potential sweep was then performed for the cell to determine the *V–I* curve followed by EIS measurements at various applied cell voltages.

A Gamry PCI4/300 potentiostat was used for all electrochemical measurements. Gamry EIS300 software was used for recording of impedance spectra, while DC105 software was used for recording the potential sweep curves.

#### 2.3.1. Electrochemical impedance spectroscopy

EIS measurements were performed for the anode and the cathode at their OCP and for the MFC at four applied cell voltages: $V_o$, $V_{max}$, $V_1$ and $V_{sc}$ in a frequency range of 100 kHz–1 mHz [10]. When the impedance spectra of the anode were recorded, the cathode served as the counter electrode and vice versa. When recording the impedance spectra of the cell, the anode served as the working elec-

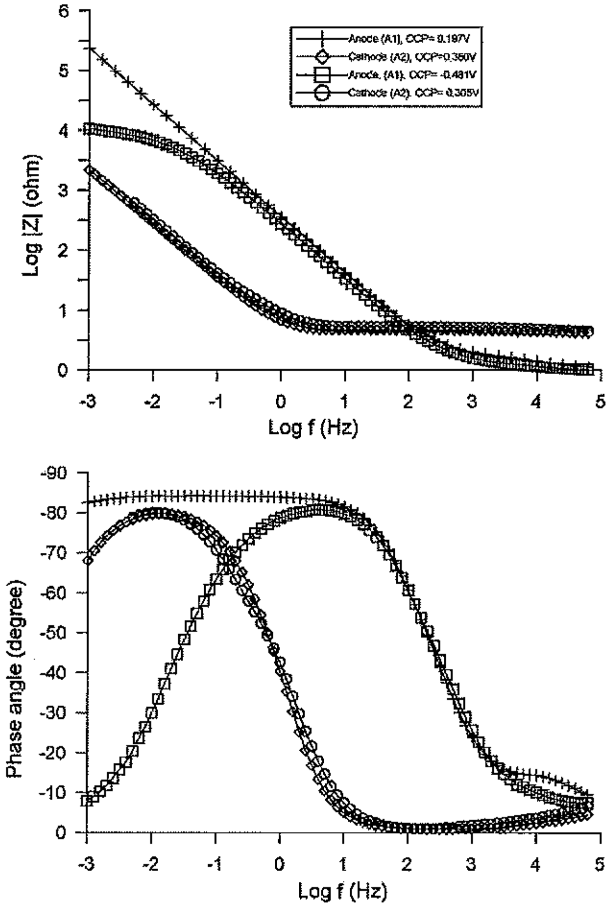

**Fig. 1.** Impedance spectra for the anode and the cathode for two different anolytes.