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# On the dynamic response of the anode in microbial fuel cells

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ABSTRACT

A study of the dynamic response of a microbial fuel cell (MFC) using membrane electrode assemblies (MEAs) designed for air breathing cathode operation is reported. The MFC used four MEAs simultaneously and has a low internal resistance. An increased concentration of glucose produced a non-linear increase in the maximum current reached. The time to reach the maximum current increased with increasing glucose concentrations of 1–7 mM; varying from approximately 2.4 to 4.2 h. The rate at which the current density increased with time was the same for all glucose concentrations up to current densities close to the maximum values. The peak power density varied approximately linearly with glucose concentrations from 2 to 77 mW/m$^2$ (1–7 mM) with a 1 kΩ resistance. The cell response appeared to be linked to a slow process of fuel transport to the bacteria and their metabolic processes. The dynamic response of the anode was analysed in terms of a substrate mass transport model. The application of different current ranges did not significantly change the dynamic response of either the anode community or the MFC polarization characteristics. Thus, it is likely that the bacterial communities that form under MFC operation contain sufficiently "dominant" electro-active species that are capable of producing high power for MFCs.



## 1. Introduction

Microbial fuel cells (MFCs) are a biological system in which biodegradable organic matter is converted into electricity using bacteria as biocatalyst. In MFCs bacteria do not transfer their electrons directly to their characteristic terminal electron acceptor, but rather to a solid electrode [1]. The interest in MFC is increasing because they offer the possibility of directly harvesting electricity from organic waste and biomass [2]. The potential advantages of biological systems over the conventional chemical systems include the ability to operate under neutral conditions and break-down of a wide range of organic material as fuel [3].

A variety of options exists for the design of MFC and these are described in a number of recent reviews dedicated to the understanding of the microbiology of MFC processes [2,4–6]. In an integrated fermentation MFC, fermentation of organic substrates takes place directly in the anodic compartment of a fuel cell, supplying the anode with the fermentation products generated *in situ*. A mediated MFC, involves electron transfer mediators that can shuttle electrons between the microbial biocatalytic system and the electrode [7]. Due to the fact that $O_2$, as a natural electron acceptor, is usually a more efficient oxidant than the anode, compartment of MFCs can be operated under anaerobic conditions. The biomass in such MFCs is a combination of planktonic and biofilm cells attached. The third approach for MFC is when direct electron transfer occurs at the anode and a number of bacteria have been identified with such properties [5].

The extractable power of a fuel cell is affected by a number of factors such as: (i) difference in potentials of the oxidiser and fuel compounds, (ii) irreversible losses due to kinetic limitations of the electron transfer processes at the electrode interfaces and (iii) ohmic resistances. Several studies of MFCs have reported the dynamic behaviour in terms of variations in cell potential or current under conditions of biofilm growth or when caused by changes in operating conditions or parameters. What is frequently seen is the relatively slow response of the MFC in comparison to other fuel cell systems. Several studies of MFCs have been reported the dynamic response of MFCs with regard to their use as a BOD sensors. These include MFCs with chemically mediated electron transfer [8,9] and mediator-less MFCs [10–14]. One important aspect of the dynamic behaviour of MFCs has been frequently determined through the response time and the sensitivity after a step-change of the fuel concentration. The interaction of the MFC volume and flow rate has been shown to change significantly the response.

One parameter commonly used to quantify the performance of MFCs is the Coulombic efficiency, i.e., the electron recovery as electricity from the removed substrate. However, the "inefficiencies" of the process have never been fully identified. One study [14] has shown that when substrate is loaded as pulses, carbon is

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**Nomenclature**

| | |
|---|---|
| $a$ | interfacial area of the biofilm per unit volume ($m^{-1}$) |
| $a_e$ | interfacial electrode area per unit volume of biofilm ($m^{-1}$) |
| $b$ | tafel slope (mV decade$^{-1}$) |
| $C_{B,S}$ and $C_{a,S}$ | concentrations in the bulk and microbial cells respectively (mol m$^{-3}$) |
| $C_{a,S,0}$ | initial glucose substrate concentration is given by (mol m$^{-3}$) |
| $E$ | reversible potentials (V) |
| $E_{anode}$ | anode potential (V) |
| $I$ | current (A) |
| $F$ | Faradays constant (C mol$^{-1}$) |
| $k_{f1}$ | electrochemical rate constant defined in Eq. (8) ($m^{-1}$) |
| $k_{LV}$ | volumetric mass transfer coefficient ($=k_L aV$) ($m^3\ s^{-1}$) |
| $k_L$ | overall mass transport coefficient (m s$^{-1}$) |
| $i_{0,ref}$ | exchange current density (A m$^{-2}$) |
| $n$ | number of electrons |
| $N_{B,S}$ | moles of substrate |
| $R$ | sum of the total resistance of the MFC and external resistance ($\Omega$) |
| $R_{int}$ | sum of electronic, ionic and contact resistance ($\Omega$) |
| $R_{ext}$ | external resistance ($\Omega$) |
| $V$ | biofilm volume ($m^3$) |
| $V_C$ | cathode potential (V) |
| $V_{cell}$ | microbial fuel cell voltage (V) |
| $\Delta V$ | difference between cell voltage and standard potential ($=V_C - E_A$) (V) |
| $\eta$ | polarization potentials (V) |
| $\eta_{A,0}$ | initial anode overpotential (V) |

*Subscripts*

| | |
|---|---|
| A | anode |
| C | cathode |

stored inside the cells during initial high substrate conditions and consumed during starvation, with up to 57% of the current being generated after depletion of the external carbon source.

Recently a method [15] to determine the charge transfer resistance and double-layer capacitance of microbial fuel cells (MFCs) was developed. A dynamic model with two parameters, the charge transfer resistance and double-layer capacitance of electrodes, was used to fit the transient cell voltage response to the current step change during the continuous operation of a flat-plate type MFC fed with acetate. There have been some recent publications on the modeling of MFCs [16,17]. A computational model for microbial fuel cells (MFCs) based on redox mediators with several populations of suspended and attached biofilm microorganisms, and multiple dissolved chemical species has been developed [16]. The evolution in time of important MFC parameters (current, charge, voltage and power production, consumption of substrates, suspended and attached biomass growth) were simulated under several operational conditions by the model. The model however requires a large number of parameters to implement which are not available for the current work and often are difficult to determine. Simpler models based on practical but reasonable assumptions regarding operation can still help to understand and simulate behaviour.

In this paper we report a study of the dynamic response of an MFC using membrane electrode assemblies (MEAs) designed for air breathing cathode operation. The cell is designed to use four MEAs simultaneously and has a low internal resistance. The dynamic response of the anode is analysed in terms of a basic combined substrate mass transport model.

## 2. Materials and methods

### 2.1. Reactor configuration

The MFC was of rectangular construction (internal dimensions 3.2 cm (l) × 3.2 cm (w) × 4.2cm (h); reactor volume ~42 ml) and made from acrylic (Fig. 1). Four MEAs were fitted to each side wall of the MFC and were operated under air-breathing conditions. Four MEAs would also help to provide more statistically significant data by averaging out variations in MFC potential responses. Previous work has shown that MFCs set up with identical materials and under identical operation can produce significant variations in performance [18]. In this work potentials typically varied by ±10% around the average values quoted.

Each MEA had an active area of 6 cm$^2$, giving a total of 24 cm$^2$ for the cell. The cathodes on all the sides of the cell were exposed to ambient air and fuel solution was added between the MEAs. The MFC was assembled by connecting the anodes and cathodes in parallel. Silicone rubber was used as the gasket at the perimeter of the MEA and acrylic cell which was held together with several threaded tie-bolts with nuts.

### 2.2. MEA preparation

The cathode was made from a commercial 60 wt.% Pt/C (E-Tek) with Pt loading of 0.3 mg/cm$^2$, coated onto a gas diffusion backing layer. The backing layer consisted of carbon paper (Toray, E-Tek) to which a gas diffusion layer was applied. The gas diffusion layer consisted of ultrasonically mixed carbon black (Ketjen black 300), acetone and 10% PTFE suspension. Catalyst layers were then applied to the substrata (diffusion backing layer) by spraying an ultrasonically mixed ink containing the electrocatalyst, nafion solution (Aldrich) and acetone. The membrane electrolyte used in this work was pre-treated perfluorinated membrane (Golden Energy Ltd., China). This membrane material is similar to nafion (DuPont) but of lower cost. The anode was non wet proof carbon paper (Toray, E-Tek) MEAs were prepared by hot pressing for 3 min at 100 °C and 50 kg/cm$^2$ pressure. Titanium mesh was attached to the top of all electrodes of the MEA to act as electrode connections.

### 2.3. Feed

The feed used in the MFC was minimal salts medium with glucose as the electron donor. The feed solution was prepared by dissolving the required concentration of glucose (mM) and inorganic salts [$NH_4$–N ($NH_4Cl$) – 40 mg/L; Mg ($MgCl_2$) – 10 mg/L; Cu ($CuSO_4$) – 0.1 mg/L; Ca ($CaCl_2$) – 5 mg/L; Mn ($MnSO_4$) – 0.1 g/L and Zn ($ZnCl_2$) – 0.1 g/L] in 900 mL of distilled water (pH 7.0). The medium was autoclaved (121 °C, 10 min) prior to addition of 50 mL of potassium phosphate buffer (0.5 M, pH 7.0). Before starting the experiments nitrogen gas was sparged vigorously for 20 min at a rate of 40 mL/min to establish anaerobic conditions.

### 2.4. Inoculum

Reactors were seeded with 5% anaerobic sludge collected from an anaerobic digester at Hexham municipal sewage treatment plant, Northumberland, UK. A proportion of the anaerobic digested sludge (100 ml) was sieved (2 mm mesh) and washed twice successively with 100 ml of degassed (with nitrogen gas) sterile potassium phosphate buffer (25 mM, pH 7.0) in order to remove any organic matter adhered to the microbial cells and surroundings. This was subsequently centrifuged (5000 *g*, 5 min and 22 °C) into a pellet and re-suspended in 50 ml of sterile degassed potassium phosphate buffer. This mixer was used as inoculum (suspended solids composition of 42.87 g SS/L and 38.83 mg VSS/L).

### 2.5. Reactor operation

For initial biofilm formation on the anode and start-up of the reactor 2 mM glucose based feed was used as a fuel source. The reactor was operated under batch mode conditions connected to a 1 kΩ external load unless otherwise stated. Fresh fuel was added every time the voltage fell to a low value, followed by purging with oxygen-free nitrogen gas in order to maintain anaerobic conditions in the reactor. The reactor was polarized and voltage measurements were collected as a function of time and under different operating conditions of external resistance and glucose concentration.

### 2.6. Electrochemical measurements

The change in fuel cell voltage under different external loads was recorded using a data acquisition system (ADC 16, Pico Technology Ltd., UK) connected to a personal computer via a RS 232 Pico high resolution analog cable. For determination of the power output, variable resistances (10, 25, 50 100, 200, 400, 600, 800, 1000, 5000 and 10 kΩ) were applied as an external load. The resistance between the electrodes was reduced stepwise and the value of potential taken when the value had stabilised. The voltage stabilisation time varied from load to load. With a large resistance it was