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Staged Microbial Fuel Cells with Periodic Connection of External Resistance

Dídac Recio-Garrido[1,2], Boris Tartakovsky[2]
Michel Perrier[1]

[1]*Department of Chemical Engineering, École Polytechnique de Montréal, C.P.6079 Succ., Centre-Ville Montréal, QC, Canada H3C 3A7 (Tel: +1-514-340-4711 ext. 4130; e-mail: Michel.Perrier@polymtl.ca).*
[2]*National Research Council of Canada,6100 Royalmount Ave., Montréal, QC, Canada H4P 2R2 (Tel: +1-514-496-2664; e-mail: Boris.Tartakovsky@cnrc-ntc.gc.ca)*

Abstract: Reactor staging is widely used in wastewater treatment where treatment norms are achieved by connecting two or more reactors in series. The first reactor operates at high carbon source loads and the last reactor performs the final polishing. Microbial Fuel Cells (MFCs) are bioelectrochemical devices designed for direct electricity production from organic matter. Periodic connection of the MFC external electrical resistance was demonstrated to increase performance. An engineering tool to understand this periodic mode of operation is developed. Effluent quality control can be ensured by developing control strategies able to reject variability in the influent concentration while tracking a desired set-point.

Keywords: Microbial fuel cell; dynamic modelling; reactors in series; intermittent operation; effluent quality control; PID.

1. INTRODUCTION

Microbial Fuel Cells (MFCs) are bioelectrochemical devices designed for direct electricity production from organic matter. Similar to conventional fuel cells, they consist of two electrodes connected by an external electrical circuit. The MFC anodic compartment benefits from the biocatalytic activity of exoelectricigenic bacteria, which externally release electrons from the oxidation of organic matter. The released electrons flow through the external electrical circuit while protons migrate to the cathode to reduce oxygen and form water (Logan 2008).

Microbial fuel cells are able to treat low strength wastewater. Their ability for energy recovery provides an opportunity to develop a novel wastewater treatment technology (Du et al. 2007). In such context, reactor staging is widely used where treatment norms are achieved by connecting two or more reactors in series with the first reactor operating at high carbon source loads and the last reactor performing the final polishing. Staging increases treatment performance (Pinto et al. 2010a) as it resembles a plug flow reactor. An increase in the reactor volume results in a decrease of the power density due to an increase of the internal resistance with the volume of the reactor (Clauwaert et al. 2008). Thus, stacking smaller MFCs in series and parallel is a way to increase voltage and current densities.

As any other electrical voltage source, the electrical power produced by the MFCs suffers dramatic losses when the external resistance does not match the value of the internal resistance of the reactor. For this reason, research has been devoted to tracking internal resistance in MFCs by adjusting the external resistance (Woodward et al. 2010). However, the external resistance cannot be changed in practical applications. Recent works have demonstrated that intermittent connection counteracts considerable losses in power output as compared to MFC operation with fixed external resistance (Grondin et al. 2012), particularly when operating at values of the external resistance which were below the internal resistance. While previous works study the effect of time connection and switching frequency experimentally (Gardel et al. 2012, Grondin et al. 2012, Coronado et al. 2013a), there is still a lack of an engineering tool useful to further extend the understanding of the periodic operation effect on MFC performance. Very few studies have considered the effect of the connection time and switching frequency in the MFC performance and microbial structure. In this way, MFC dynamic modelling could shed some light in the subject and be used for developing MFC-based treatment systems with high volumetric power output.

The significant charge storage capacity of electrochemically active biofilms (Schrott et al. 2011) results in a complex non-linear behavior during intermittent connection of the external resistance in MFCs. This results in a combination of fast, i.e. time constants in the order of milliseconds, charge/discharge dynamics with much slower dynamics of microbial biofilm growth and decay, i.e. time constants in the order of hours to days. Such behavior has not been described by previous MFC models (Recio-Garrido et al. 2016a). Taking that into account, this study presents a combined bioelectrochemical-electrical (CBE) model of an MFC obtained by combining fundamental equations based on mass and electron balances with equations describing an equivalent electrical circuit. Accordingly, the presented CBE model describes both fast (milliseconds) and slow (hours and days) MFC dynamics and is used to describe the behavior of two staged MFCs operated under periodic connection of the external resistance. Steady-state values are used to study the effect of connection time ratio and switching frequency on MFC performance.

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2. MATERIALS AND METHODS

2.1 MFC Design and Operation

Experiments were conducted in two membraneless air-cathode MFCs with an anodic compartment volume of 50 mL. The two MFCs were connected in series, i.e. the effluent of the first reactor was the influent of the second reactor. MFC design and operating conditions are provided elsewhere (Coronado et al. 2013a).

Throughout the tests, the two MFCs were operated using intermittent connection or pulse-width modulated connection of the external resistor (R-PWM mode). Each MFC was electrically independent. Such operation involved connecting the external resistor (R_{ext}) to MFC terminals with a low resistance (<0.4 Ω) electronic switch (ADG801, Analog Devices Inc.). The switch was computer-controlled using a Labjack U3-LV data acquisition board (LabJack Corp., Lakewood, CO, USA). The data acquisition board was used to record MFC voltage at a maximum rate of 22,500 scans s^{-1}. More details are provided in Coronado et al. (2013a).

2.2 Numerical Methods and Calculations

Matlab R2014a (Mathworks, Natick, MA, USA) was used for all calculations. Parameter estimation was performed using the *fmincon* subroutine of the Matlab Optimization Toolbox™ and the model equations were solved using a variable order integration method for stiff differential equations (*ode15s*). Additional information can be found elsewhere (Recio-Garrido et al. 2016b, Pinto et al. 2010b). On-line estimations of the equivalent circuit model parameters were carried out using the algorithm described by Coronado et al. (2013b).

3. RESULTS AND DISCUSSION

3.1 Model Formulation and Structure

The CBE model structure (Fig. 1) was obtained by combining equations describing microbial, carbon source and electron balances of the bioelectrochemical model developed by Pinto et al. (2010b) with equations describing the equivalent electrical circuit (EEC) of a MFC presented by Coronado et al. (2013a). The EEC model only accounts for the internal capacitance and resistance of the anode thus lacking biomass and carbon source material balances. CBE model assumptions are inherited from Pinto et al (2010).

Similar to the EEC model, internal resistance R_1 represents the electrolyte ohmic resistance, while a resistor/capacitor circuit is included to describe the internal capacitance C and the activation losses R_2. Accordingly, MFC internal resistance R_{int} is defined as

$$R_{int} = R_1 + R_2. \quad (1)$$

MFC mass balances are given by the following equations:

$$\frac{dS}{dt} = -q_e X_e - q_m X_m + D(S_{in} - S), \quad (2)$$

$$\frac{dX_e}{dt} = \left(\mu_e - K_{d,e} - \alpha_e D\right)X_e, \quad (3)$$

$$\frac{dX_m}{dt} = \left(\mu_m - K_{d,m} - \alpha_m D\right)X_m, \quad (4)$$

$$\frac{dM_{ox}}{dt} = -Y q_e + \gamma \frac{I_{cell}}{mFVX_e}, \quad (5)$$

Where S is the substrate (acetate) concentration consumed by the electricigenic bacteria X_e, capable of producing electricity by means of an intracellular mediator M_{ox}, or by the methanogenic archaea X_m that produce methane. S_{in} is the input substrate concentration, $D = Fin/V$ is the dilution rate with the input flow rate F_{in} and the volume of the anodic compartment V. K_d is the microbial decay rate, Y is the yield of oxidized mediator, γ is the mediator molar mass, m is the number or electrons transferred, F is the Faraday constant and I_{cell} is the current produced by the MFC. The corresponding microbial growth rates μ and substrate consumption rates q are defined using multiplicative Monod kinetics as follows:

$$\mu_e = \mu_{max,e}\left(\frac{S}{K_{s,e}+S}\right)\left(\frac{M_{ox}}{K_M+M_{ox}}\right), \quad (6)$$

$$q_e = q_{max,e}\left(\frac{S}{K_{s,e}+S}\right)\left(\frac{M_{ox}}{K_M+M_{ox}}\right), \quad (7)$$

$$\mu_m = \mu_{max,m}\left(\frac{S}{K_{s,m}+S}\right), \quad (8)$$

$$q_m = q_{max,m}\left(\frac{S}{K_{s,m}+S}\right), \quad (9)$$

with K_S and K_M the Monod half rates for the substrate and oxidized mediator terms, respectively.

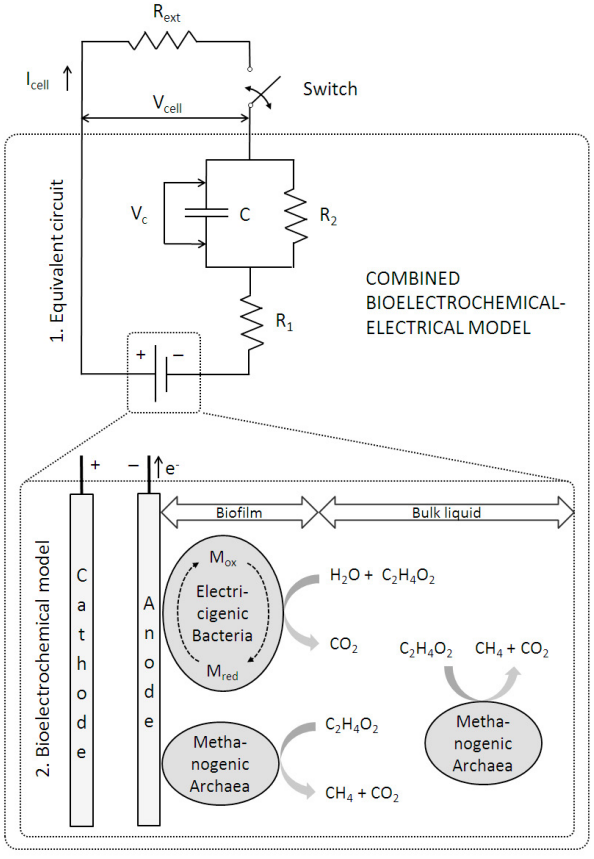

Fig. 1. Schematic diagram of the CBE model for MFCs presented in Recio-Garrido et al. (2016b).