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Dynamic modeling of a microbial fuel cell considering anodic electron flow and electrical charge storage

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HIGHLIGHTS

- Conventional equivalent circuits have been derived from electrical terminal quantities.
- Anodic electron flow and electric charge storage were not well modeled electrically.
- Novel equivalent-circuit-based model and straightforward test methods are developed.

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ABSTRACT

To describe the anodic electron flow and electric charge storage behavior of an MFC system from an electrical perspective, a dynamic model based on a novel electrical equivalent circuit is developed. Conventional equivalent circuits typically have series impedances to model the system from the standpoint of terminal quantities: output voltage and current. However, the conventional approaches do not properly explain internal anodic electron flow and double-layer charge storage characteristics of MFCs. The proposed model uses an equivalent capacitance in parallel and series resistances to accurately model and characterize the anodic electron flow, electrical charge storage, and the dynamic characteristics of both output voltage and current. Two straightforward test methods are proposed to determine the equivalent circuit parameters. Experimental results showed the validity of proposed MFC model.

1. Introduction

Microbial Fuel Cells (MFCs) have been extensively investigated during the last decade as a novel renewable and sustainable energy source. They use electrochemically active bacteria (EAB) to generate electricity from bio-degradable substrates. When EAB oxidize an electron donor, electron flow through an external circuit from anode to cathode can occur. A growing list of bacteria, including *Geobacter*, *Shewanella*, and *Pseudomonas* spp., are known for their ability to generate electricity [1–3] from oxidizable organic electron donors such as glucose, acetate, fatty acids, and wastewater organic carbon [4–7]. Since the inception of MFC-generated electric power a few decades ago, the power production of MFCs has been improved by orders of magnitude with power densities as high as 19 W/m^2 being reported [8]. However, challenges such as low voltage and power levels, and difficulties in scaling-up still need to be addressed [9,10].

The electrical equivalent circuit approach has been used to explain the external electrical output characteristics, the internal biological and electrochemical behaviors of the MFC system, as well as those of battery and hydrogen-based fuel cell systems [11–13]. Typical electrical equivalent circuit models for MFCs are comprised with series impedances as shown in Fig. 1: (a) shows the simplest equivalent circuit that does not take any dynamic characteristic into consideration and (b) shows a Randles circuit where R_s, R_{ct}, C_{dl}, and Z_w denotes the ohmic resistance, charge transfer resistance, double-layer capacitance, and Warburg diffusion element, respectively [14]. This impedance imitates the dynamic behavior of the MFC in terms of output voltage and current. Generally, techniques such as cyclic voltammetry, current interruption, polarization test, and electrochemical impedance spectroscopy (EIS) have been used to find the equivalent circuit parameters and study transport and reaction kinetics [14–18].

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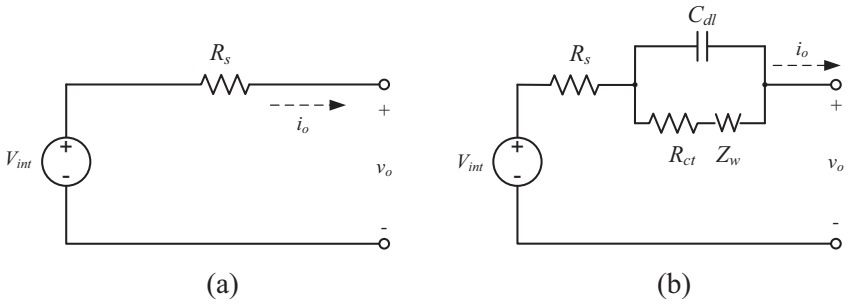

Fig. 1. Typical MFC equivalent circuits. (a) Simplest equivalent circuit without any dynamic characteristic. (b) Randles equivalent circuit with Warburg diffusion element.

As shown, conventional equivalent circuits for electrochemical systems, such as MFCs, typically have impedances in series [12,14,19–21]. While series resistance can explain the voltage drop with load current that can be seen in polarization tests, the double-layer capacitance models the dynamic behavior of output voltage and current, e.g., current overshoot and voltage time delay, caused by the intrinsic capacitance effect in conjunction with the resistances [22]. Typically the EIS test that applies voltages in various frequencies to the reactor is used to find the parameters of equivalent circuits; it captures the changes in impedance magnitude and angle, which can be given by the ratio of voltage and current phasor, then analyzes it to find the circuit parameters. It is well known that constant phase elements (CPEs) can be used to make the equivalent circuit fit the output of the fuel cell system better than capacitors [23]; CPEs have slightly different impedance angles than that of capacitive reactance which is 90°. However, the capacitances in the equivalent circuits do not appear in the polarization tests that measure steady-state responses only.

MFCs store electric charges similar to capacitors, as well as generate instantaneous power [9,10,22]. The double-layer capacitor in equivalent circuits can be used to model this intrinsic capacitance effect. Fig. 2I and II shows how the conventional Randles circuit models the operation of an MFC with double-layer capacitor. The output current i_o is given as the sum of the currents through double-layer capacitor and resistor in the RC network.

$$i_o(t) = i_{Rct} + i_{Cdl}(t) \tag{1}$$

where i_{Rct} and i_{Cdl} is the current in the resistor and capacitor branch, respectively. Assuming an initial steady-state condition at open-circuit voltage, the output current sharply increases as the series capacitor in the equivalent circuit is charged when the switch is closed at t_0 in Fig. 2I-(c). This is because the capacitor voltage is zero when the output voltage has been at open circuit voltage (OCV) for a while before the switch is closed. The capacitor draws a large current when the terminals are closed (Fig. 2I-(d)) and this models the output current overshoot. It can be seen that the capacitor voltage increases up to V_{int} in Fig. 2I-(e) with a time rate determined by its capacitance and output current:

$$v_{Cdl}(t) = \frac{1}{C_{dl}} \int i_{Cdl}\, dt \tag{2}$$

where v_{Cdl} is the voltage across the double-layer capacitor.

On the other hand, when the output terminals are open, the double-layer capacitor discharges through the parallel resistor when the load decreases, as shown in Fig. 2II-(a), where output current is zero and capacitor current becomes negative. This models the time delay of increasing output terminal voltage (Fig. 2II-(b)) with decreased capacitor voltage (Fig. 2II-(e)), which is given as follows.

$$v_o(t) = V_{\text{int}} - v_{Cdl}(t) \tag{3}$$

The output voltage reaches OCV, once the capacitor is completely discharged.

This conventional series impedance model works well for the output voltage and current as it is derived from them; however, it does not properly describe the charge storage characteristics of MFCs in terms of internal power flow by anodic electrons. As a capacitive energy storage, an MFC should discharge energy for high load current and store the charges when the load current is less than the anodic current. But, as can be seen in Figs. 2I, II (d)-(e), the double-layer capacitor in series represents the internal power flow in the opposite direction, which makes it inadequate to model the anodic electron flow and electric charge storage behaviors of MFCs.

The role of electrode biofilms in optimal MFC operation is being elucidated. Widely accepted, however, is the ability of the anode biofilm to generate, accumulate and release charges [24–29]. Viewing the biofilm in this manner equates it to a rechargeable battery; there is a voltage source capable of replenishing electrons to a capacitor. The source of electrons in the MFC is bacterial respiration associated with the oxidation of an electron donor, such as acetate, freeing electrons to move through electron transport systems associated with the cell through to extracellular electron carriers with increasingly positive redox potentials, through to the anode, which itself can hold charge and acts as the terminal electron acceptor. In such a system, as electron flow is retarded, such as that seen in MFCs with high Faradaic impedance, the internal voltage can increase to the point that electrons can back-up in the biofilm causing a shutdown of respiration, the charging source, in order to avoid oxidative damage to the cell [29,30]. When electron flow is free, as seen under closed circuit conditions, electrons quickly discharge, draining the biofilm. While the biofilm can be recharged during respiration, charging is dependent on the rate-limiting metabolic production of electrons by bacterial cells.

A currently supported model for MFC capacitance lies with the network of cytochrome proteins, electron carriers, which define a series of redox reactions, within the anode biofilm. Anode charge and composition influence the bacterial community composition of the resulting biofilm [30,31]. Bacterial community composition, in turn, directly contributes to the resulting electrogenic protein network connecting cells to each other and to the anode [25,31–33]. Studies performed on the electron-transfer dynamics of these biofilm networks [34] have identified multiple sources of electron storage at the anode, as shown in Fig. 3, including charge stored by cytochromes, e.g., c-type and multiheme, directly interacting with the anode and the anode itself (Zone 1); charge stored by cytochrome and nanowire networks indirectly associated with the anode (Zone 2); and charge stored within intracellular cytochromes associated with individual cellular respiration (Zone 3). Each source of charge acts as a capacitor, allowing for sequential draining of stored electrons under discharging conditions. Similar to the discharge from capacitors in series, following a pattern of