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Dynamic Modeling of a Microbial Fuel Cell Considering Anodic Electron Flow and Electrical Charge Storage

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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 impedance 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.

Keywords: Microbial fuel cell, modeling, equivalent circuit, anodic current, capacitive storage

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].

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. 2 I and II show 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.

$$i_o(t) = i_{Ret} + i_{Cdl}(t) \quad (1)$$

where i_{Ret} 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. 2 I-(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. 2 I-(d)) and this models the output current overshoot. It can be seen the capacitor voltage increases up to V_{int} in Fig. 2 I-(e) with a time rate determined by its capacitance and output current:

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

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. 2 II-(a), where output current is zero and capacitor current becomes negative. This models the time delay of increasing output terminal voltage (Fig. 2 II-(b)) with decreased capacitor voltage (Fig. 2 II-(e)), which is given as follows.

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

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

I-(a)

I- (b)

I- (c)

I- (d)

I- (e)

II-(a)

II-(b)

II-(c)

II-(d)

II-(e)

Fig. 2. Internal and external voltage and current of Randles Circuit. I: Output terminal closed at t_0 . II: Output terminal open at t_0 . (a) Equivalent circuit. (b) Output voltage. (c) Output current. (d) Capacitor current. (e) Capacitor voltage.

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. 2 I, 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 from a drained 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.

Fig. 3. Schematic showing cell arrangement at the anode and the cytochrome and nanowire networking allowing for electron flow through the resulting biofilm. Arrows point in the direction of electron flow toward anode. Zone 1 electron storage includes the anode and the cytochromes and nanowires directly attached to the anode. Zone 2 electron storage includes electrons associated with the cell-to-cell protein and nanowire networks. Zone 3 electron storage includes intracellular electron generation and transport.

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 preferential flow, with electrons depleted from Zone 1, followed by Zone 2, and then Zone 3 electrons, the draining of each responding to a series of redox reactions from anode to cell. The resulting total MFC capacitance is the additive capacity of the anode surface area (Zone 1), the electron shuttling capacity of the biofilm network (Zone 2), and the source cells (Zone 3).

In this paper, a dynamic model using a novel electrical equivalent circuit of an MFC system is developed considering the anodic electron flow and electric charge storage in an MFC reactor. The proposed model can also explain the terminal voltage and current characteristics. Two straightforward test methods, short- and open-circuit test, are used to describe the charging and discharging behaviors as well as to determine the equivalent circuit parameters. The proposed parallel double-layer capacitance model provides a simple way to characterize the intrinsic electron and power flow, and the terminal electrical behavior of a typical MFC.

2. Materials and Methods

2.1. Equivalent circuit

In this work, a simple R-C-R network is used to model the electricity generation, anodic electron flow, and electric charge storage of an MFC system, where R_{s1} , R_{s2} , and C_{eq} represents input series resistance, output series resistances, and equivalent double-layer capacitance in parallel with the internal voltage. The series resistances R_{s1} and R_{s2} represents the rate-limiter for metabolic electron production and current flow, respectively, that can be affected by the biofilm characteristics, such as thickness, surface area, and cell concentration; each of which can

Fig. 4. Proposed MFC equivalent circuit, where R_{s1} , R_{s2} , and C_{eq} represents input series resistance, output series resistances, and equivalent double-layer capacitance. The internal voltage V_{int} denotes the thermodynamic voltage that determines the open-circuit voltage.

influence the degree of cell-to-cell networking present within the biofilm. The input resistance R_{s1} dominantly affects the faradaic electron transport and the output resistance R_{s2} determines the draining rate of electrons in the biofilm which is modeled with the double-layer capacitance.

The internal voltage V_{int} denotes the thermodynamic voltage that determines OCV. The OCV is dependent on the rate of electron production by the MFC bacteria. Rate of electron production, in turn, is influenced by bacterial growth parameters, such as nutrient availability. The current generated by electrons transported by the bacteria is defined as i_b , and i_c denotes the non-Faradaic current flowing in and out of the internal double-layer capacitance. The charging direction of i_c is defined as positive. The proposed equivalent circuit can be seen in Fig. 4.

To explain the operation of an MFC with the proposed equivalent circuit, two test methods are also developed: short-circuit and open-circuit test. The tests will run the MFC in two extreme operating conditions in terms of terminal quantities: maximum output current with zero voltage and maximum output voltage with zero current. These short- and open-circuit approach is widely used to characterize various electric devices, such as transformers and synchronous

machines. The implementation of the tests is quite straightforward and instrumentation will measure just output current and voltage for short- and open-circuit test, respectively.

Before running the short-circuit test, the MFC under test needs to be left open-circuited until the output voltage is stabilized at OCV, which indicates that the internal capacitance is completely charged. Note that the conventional model's capacitance is completely discharged in this condition, which is not correct. If the capacitor voltage is in steady-state, i.e., $dv_{Ceq}/dt = 0$, that means the charging current becomes zero as shown in (4),

$$i_c(t) = C_{eq} \frac{dv_{Ceq}(t)}{dt} \quad (4)$$

where, v_{Ceq} denotes the voltage across the equivalent capacitance. This matches with the MFC's bioelectrochemical behavior that the electron transport of EAB stops when there is no current path and the MFC's electric charge storage is full. Then the output terminals are short-circuited as in Fig. 5 I-(a) to provide the minimum resistance output path, i.e., $v_o = 0$. The output current i_o will have a sharp peak and exponential decay before it stabilizes at a certain level as shown in Fig. 5 I-(b), which can be modeled with two current components from charge storage i_c and bacterial charge transport i_b .

The out-rush current with high peak i_c is from the MFC's internal electric charge storage and it will exponentially decrease to zero where the charge storage is completely depleted. The peak of the current overshoot is determined by the internal voltage and output series resistance R_{s2} as can be given as follows.

$$i_c(t) = -\frac{V_{int}}{R_{s2}} e^{-t/\tau_o} \quad (5)$$

where τ_o denotes the output time constant $R_{s2}C_{eq}$. Even though the electrons are discharging from biofilm in the given condition, this is modeled as capacitor charging current in the conventional

Fig. 5. I: Short-circuit test - Output terminal closed at t_0 . II: Open-circuit test - Output terminal open at t_0 . (a) Equivalent circuit. (b) Output voltage. (c) Capacitor current. (d) Capacitor voltage.

model. In the short-circuit operation, the input series resistance R_{s1} does not affect the dynamics of i_c because the stored electrons in the MFC reactor are discharged through R_{s2} . After the stored charges are all discharged, i.e., $i_c = 0$, the output current will only contain i_b , which is given as follows.

$$i_b(t) = \frac{V_{int}}{R_{s1} + R_{s2}} \quad (6)$$

This is the current generated by bacteria at the anode electrode with the maximum rate in the given condition because the output terminals are short-circuited to provide current path with minimum external resistance. This Faradaic current is modeled as DC, because the dynamics of internal voltage is quite slower than that of the charge storage current. Furthermore, the production of bacterial electrons and the subsequent transport of electrons to the anode is species specific and difficult to predict in MFCs with mixed bacterial species, such as that seen with sludge wastewater inocula.

Once the output current is stabilized down to a steady-state value i_b in (6), the MFC output terminals are opened for open-circuit test. Because the electrons stored in the charge storage has been completely discharged during the short-circuit test and the output terminals are open, the charges transported by bacteria can only flow through the internal double-layer capacitor. This operation is modeled with capacitor discharge in the conventional model, which contradicts with the actual power flow. The terminal voltage is identical with the voltage across the internal double-layer capacitor because there is no output current and it increases in an exponential fashion up to its internal thermodynamic voltage V_{int} .

$$v_o(t) = v_{Ceq}(t) = V_{int} \left(1 - e^{-t/\tau_i}\right) \quad (7)$$

where, τ_i denotes the input time constant $R_{s1}C_{eq}$. Similarly with the short-circuit test, the output series resistance does not affect this rising dynamics of terminal voltage. Furthermore, the output voltage will rise from V_{oI} , which is the capacitor voltage defined by the voltage across the series resistance R_{s2} during the short-circuit test. This phenomenon is well known from the current

interruption test method [15]. The MFC output voltage waveform of the open-circuit test is shown in Fig. 5 II.

2.2. Parameter identification

Using the aforementioned short- and open-circuit tests, the parameters of the proposed MFC equivalent circuit can be identified. The step-up voltage V_{ol} in the open-circuit test shown in Fig. 5 II-(b) can be measured and it is given as follows, because until right before the circuit is open, the capacitor voltage is same as the voltage across R_{s2} .

$$V_{ol} = V_{int} \frac{R_{s2}}{R_{s1} + R_{s2}} = R_{s2} i_b \quad (8)$$

Hence, using the open-circuit voltage V_{oc} as V_{int} and steady-state output current i_b (6) measured from short-circuit test, the resistances R_{s1} and R_{s2} can readily be derived as

$$R_{s2} = \frac{V_{ol}}{V_{oc}} (R_{s1} + R_{s2}) \quad (9)$$

$$R_{s1} = \frac{V_{oc}}{i_b} - R_{s2} \quad (10)$$

The expression of the output voltage of the open-circuit test can be found using curve fitting techniques and can be modeled typically with multiple dynamics in the biofilm as described in Fig. 3; however, a single equivalent capacitance C_{eq} is estimated by using the integrated current in this paper for a simplified representation of the MFC's electric charge storage capacity. This is similar to the Coulomb Counting method for battery analysis [35]. The output current in the short-circuit test can be integrated to determine the equivalent capacitance as follows.

$$C_{eq} = \frac{1}{V_{oc}} \int i_b(t) dt \quad (11)$$

2.3. MFC reactor and experimental setup

For this work, a single-chamber air-cathode MFC reactor was developed in a 450mL food container (HPL807, Lock & Lock) using a 2"-diameter carbon brush anode (#313239, Mill-Rose Company, OH) and 1.5"×1" 5-layer membrane electrode assembly (HA5-MEA, FuelCellsEtc, TX). The MEA has 410 micron gas diffusion layer in both side of the 2-mil proton exchange membrane (Nafion 212), as well as catalyst layers (60 wt% Pt on Vulcan, 0.5 mg/cm²). The polycarbonate brackets and rubber gaskets (2"×1.5") were fabricated by in-house machine shop. The brackets hold the cathode MEA between the rubber gaskets with 0.5" 4-40 aluminum screws. A piece of 1-mm titanium wire (45485-BY, Alfa Aesar, MA) is also used in the cathode electrode.

The reactor was inoculated using the sludge from a local water treatment facility. The 50 mM phosphate buffer solution contained 2 g/L CH₃COONa, 0.31 g/L NH₄Cl, 0.13 g/L KCl, 3.321 g/L NaH₂PO₄·2H₂O, and 10.317 g/L Na₂HPO₄·12H₂O. The reactor was operated in fed-batch mode at room temperature and refilled with new medium until the output voltage became stable.

The terminal voltage and current of MFC was measured with a digital oscilloscope (TDS2014C, Tektronix, OR), and a current probe (TCP312A, Tektronix, OR) with amplifier (TCPA300, Tektronix, OR). Short- and long-term voltage waveforms were recorded using the digital oscilloscope and data logger (DI-710-UL, Dataq Instruments, OH) with 25Hz and 0.2Hz sampling rates, respectively. The reactor terminals were manually short-circuited and opened for each test run. The experimental setup can be seen in Fig. 6.

Fig. 6. Experimental setup

3. Results and Discussion

A series of short- and open-circuit tests were performed after the reactor reached a steady-state voltage with 1 k Ω resistive load. Ten test sets were carried out approximately every week and a 500 Ω load resistor was connected between the tests. The reactor was left open-circuited overnight before each short-circuit test and open-circuit test followed right after about 70 sec of short-circuit test. The short-circuit current and open-circuit voltage waveforms can be seen in Fig. 7. The terminal voltage and current was zero in short- and open-circuit test, respectively. Only three experimental data sets are shown in Fig. 7 to clearly show the maximum, minimum, and median levels. The result from other tests were in between the boundary around average value. Complete experimental data can be found in the online supplemental data. It can be seen that the actual waveforms match well with the theoretical output of the proposed equivalent circuit. The level of peak output current i_{pk} and the Faradaic current i_b varied between 20 and 25 mA, and 1 and 1.5 mA average, respectively, as can be seen in Fig. 7 (a) and (b), indicating that the parameters of equivalent circuit vary as the stored energy was depleted by previous short-circuit test and reactor's operation time accumulates. However, the generation performance of MFC in terms of output voltage and current was maintained around an average

Fig. 7. Short-circuit test results: (a) Initial sharp increase and exponential decay of output current. (b) Bacterial charge transport current i_b . Open-circuit test results: (c) MFC terminal voltages. (d) MFC terminal voltages (zoomed).

level, although fluctuating, without significant degradation during the test period. It should be noted that the short-circuit current of Day 1 test decreased at 68.5 sec; because the test was terminated earlier than others. The medium was not replaced during the whole test period (59 days) because the output voltage of reactor at 500 Ω and OCV were sustained.

As the reactor terminals were opened after the short-circuit test, the output voltage increased from zero to open circuit voltage as shown in Fig. 7 (c). The dynamic characteristics of rising voltage was determined by the internal voltage and intrinsic charge storage/release mechanism, and the time constants showed an overall decreasing trend as can be seen in Fig. 7

Fig. 8. Equivalent circuit parameters. (a) Series resistance R_{s1} and R_{s2} . (b) Equivalent capacitance C_{eq} and generated energy. (c) Open circuit voltage and bacterial charge transport current i_b .

(d); however, they also fluctuated between boundary values in other tests, which is shown in the supplemental data.

Parameters for the proposed equivalent circuit were extracted from each data set, which can be seen in Table I. In average, the reactor parameters were $R_{s1} = 557.50\Omega$, $R_{s2} = 28.47\Omega$, and $C_{eq} = 83.16\text{mF}$. The stored energy E_{meas} in the reactor that was measured by the voltage and current during the short-circuit test was 16.52mJ in average, which matched well with the theoretical energy E_{cal} , 16.47mJ, calculated from the equivalent circuit parameters.

Table I. Identified Equivalent Circuit Parameters

	Day 1	Day 9	Day 16	Day 19	Day 23	Day 31	Day 38	Day 45	Day 52	Day 59	Ave.
V_{int} [V]	0.624	0.644	0.601	0.632	0.616	0.632	0.616	0.64	0.644	0.644	0.623
I_b [mA]	1.034	1.049	0.978	0.857	1.694	0.751	1.984	1.012	0.902	1.505	1.177
V_{ol} [mV]	23.39	28.31	47.54	41.08	45.54	20.62	38.15	24.15	17.23	33.23	31.92
R_{s1} [Ω]	580.6	586.9	566.4	689.4	336.8	814.4	291.2	608.8	694.6	405.9	557.5
R_{s2} [Ω]	22.60	26.98	48.62	47.92	26.89	27.46	19.23	23.88	19.09	22.09	28.48
C_{eq} [F]	0.097	0.098	0.064	0.087	0.076	0.085	0.083	0.059	0.091	0.091	0.083
Energy [J]	0.019	0.020	0.012	0.018	0.015	0.017	0.016	0.012	0.019	0.019	0.017

$$\bar{E}_{meas} = \frac{1}{N} \sum_{n=1}^N \int v_{on} \cdot i_{on} dt \quad (12)$$

$$\bar{E}_{cal} = \frac{1}{2} \bar{C}_{eq} \bar{V}_{oc}^2 \quad (13)$$

where, N is the number of test sets and the bar denotes an average value of all test data sets.

As well as the time constant of the open-circuit tests, the series resistances, equivalent capacitance, and generated energy had slightly decreasing trends while they fluctuate around the trend line as shown in Figs. 8 (a) and (b). Decreasing capacitance matched with the decreasing trend of time constant of rising voltage in the open-circuit tests. The open circuit voltage and the bacterial charge transport current i_b in Fig. 8 (c), on the other hand, showed a slightly increasing trend.

The reactor used in this manuscript showed reasonably consistent output during the test period and operated much longer than expected. No additional treatment, adjustment or measurement was made to observe the change of performance during the test period over a single batch cycle. It is not clear at this point how the reactor was able to sustain quite longer than typical small batch reactors. Authors will continue to investigate as a future work.

4. Conclusion

In this paper, a novel equivalent circuit based model for the MFC considering the anodic electron flow and electric charge storage was proposed. The proposed equivalent circuit explains the internal anodic electron flow of an MFC accurately compared to the conventional equivalent circuits with series impedance. Two straightforward test methods, short- and open-circuit test, were also suggested to operate the MFC at the maximum charging and discharging condition of internal capacitance to identify the parameters of proposed equivalent circuit. Experimental result shows the validity of proposed equivalent circuit based modeling.

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