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MODELING OF POLARIZATION LOSSES OF A MICROBIAL FUEL CELL

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ABSTRACT

Microbial fuel cells (MFCs) are promising for simultaneous treatment of wastewater and energy production. In this study, a mathematical model for microbial fuel cells with air cathodes was developed and demonstrated by integrating biochemical reactions, Butler–Volmer expressions and mass/charge balances. The model developed is focused on describing and understanding the steady-state polarization curves of the microbial fuel cells with various levels and methods of anode-biofilm growth with air cathodes. This polarization model combines enzyme kinetics and electrochemical kinetics, and is able to describe measured polarization curves for microbial fuel cells with different anode-biofilm growth. The MFC model developed has been verified with the experimental data collected. The simulation results provide insights into the limiting physical, chemical and electrochemical phenomena and their effects on cell performance. For example, the current MFC data demonstrated performance primarily limited by cathode electrochemical kinetics.

INTRODUCTION

Microbial fuel cell technology is a rapidly evolving field in recent years due to its potential applications in wastewater treatment, bioremediation, and electric energy production [1-4]. In microbial fuel cells (MFCs), anode-respiring bacteria (ARB) are used as catalysts to oxidize organic substrates (fuel) to produce electrical current [5, 6]. Electrons produced by the bacteria from the substrates are transferred to the anode and flow to the cathode via an external circuit containing a resistor or a load [5]. In this process, to generate an electrical current,

anode-respiring bacteria must 1) generate electrons via biochemical oxidation of the electron donor (organic substrate) and transfer the electrons to certain redox components, and 2) transfer electrons to a solid anode through extracellular electron transfer (EET) [6, 7]. Intracellular biochemical reactions are involved in the first step, and the conversion of the organic material into carbon dioxide, protons and electrons occurs inside the ARB and the conversion rate is determined by enzyme kinetics. Heterogeneous electron transfer, occurs at the interface between the ARB and the electrode surface are involved in the second step and described by electron transfer kinetics. In the second step, there are three major mechanisms proposed to transfer electrons to the anode, including direct contact, diffusion of soluble electron shuttles and electron transport through a solid conductive biofilm matrix [6, 8]. In each mechanism, various kinetic processes are proposed to describe the electron transfer process. To describe the intracellular potential losses, the Monod model and Nernst-Monod model are used. The Nernst-Monod model is a modified version of the Monod model by considering the anode as the final electron acceptor [8]. To describe the extracellular potential losses, a Bulter-Volmer Model is typically used [6]. In this study, to model the polarization curves of an MFC with an air cathode, we utilize the Butler-Volmer-Monod model to describe the anode kinetics combining the enzyme kinetics and the electrochemical kinetics [8]. The Butler-Volmer-Monod model was developed based upon a simple representation of the underlying biochemical conversions and electron transfer reactions. The Butler-Volmer-Monod model was demonstrated to describe the experimental data significantly better than the Nernst-Monod model [8].

In this study, a mathematical model for microbial fuel cells with air cathode was developed based upon the Butler-Volmer-Monod model. The model developed is focused on describing and understanding the steady-state polarization curves of the microbial fuel cells with various bio-film thickness. This polarization model developed combines enzyme kinetics and electrochemical kinetics, and is able to describe the measured polarization curves for microbial fuel cells. The MFC model developed has been verified with the experiment data. The simulation results provide insights into the limiting physical, chemical and electrochemical phenomena and their effects on cell performance.

EXPERIMENTAL SETUP

MFCs with dual-chambers were made using two 100ml custom borosilicate glass bottles clamped together and separated by a proton permeable Nafion-117 membrane, as shown in Figure 1. MFCs anodes were fabricated using flat titanium squares (0.5cm by 0.5cm), sputtered with 250nm of gold. Insulated stainless steel wire was attached to the backs of the anodes via conductive silver epoxy (MG chemicals), and the entire electrode was covered in silicone (DAP Adhesive Sealent). A defined area on the front of the electrode was left exposed to allow for bacterial adhesion and growth. Cathodes were fabricated by weaving titanium wire through untreated carbon cloth measuring 5cm in height and 2.5cm in length. Electrodes were pre-conditioned in successive rinses of acetone, ethanol, and water prior to use to remove organic contaminants. Microfit connectors (Digi-Key) were used to attach the electrodes to titanium wire that had been threaded through butyl rubber stoppers in each MFC chamber. Electrodes were spaced no more than 2cm apart. Connections were tested with a handheld multimeter, and any electrode with a resistance greater than 1.5ohms was discarded. Prior to use, the entire MFC was autoclaved at 120°C for 20 minutes.

Figure 1: Two-chamber MFC tested in this study.

MFCs were inoculated with G. sulfurreducens in carbonate buffer media composed of: 0.25g/L NH4Cl, 0.6g/L NaH2PO4, 0.1g/L KCl, 2.5g/L NaHCO3, 1.64g/L CH3COONa, and 10ml/L

of trace vitamin and mineral solution based on Wolfe's formulation (ATCC.org). The cathode was filled with 100ml of Phosphate buffer containing: 0.31g/L NH4Cl, 10.76g/L NaH$_2$PO$_4$, 17.32g/L Na$_2$HPO$_4$, and 0.117g/L KCl. All media was autoclaved at 120°C for 20 minutes prior to use. The anode buffer was continuously stirred, and the anode attached to the cathode via a 560ohm resistor. 40mM fumarate was added to the growth media as an electron acceptor to promote growth and decrease MFC startup time. Anode media was exchanged for fumarate-free solution after 2 days once the anolyte became turbid. After planktonic bacteria were removed, anodic media was exchanged every 3-4 days for 90ml of fresh media, with each exchange constituting one batch cycle. For oxygen reducing cathodes, air was bubbled through a 0.2micron sterile filter into the cathode chamber.

Electrochemical performance were measured using a Gamry Instruments potentiostat. The measurements were made after the MFC was disconnected and allowed to sit at open circuit voltage (OCV) for at least 60 minutes, or until the cell voltage stabilized. Linear sweep voltammetry (LSV) method was used with the anode as the working electrode and the cathode as the counter and reference electrode.

MODEL DEVELOPMENT

The MFC model developed in this study is a steady-state electric model that simulates relations between the cell voltage and cell current that account for anode losses, cathode losses, and ohmic losses. The fuel cell voltage is expressed as Equation (1), where E^0 is the open circuit voltage, η_{anode} is the anode overpotential, $\eta_{cathode}$ is the cathode overpotential and η_{ohmic} is the ohmic overpotential.

$$E = E^0 - \eta_{\_anode} - \eta_{\_cathode} - \eta_{\_ohmic} \qquad (1)$$

In this study, anode overpotential is described by the Bulter-Volmer-Monod model [9]. The Bulter-Volmer-Monod model accounts for both enzyme kinetics and the Bulter-Volmer electron transfer kinetics. The Butler-Volmer-Monod model was developed based upon the underlying biochemical conversions and electron transfer reactions. It is demonstrated that the Butler-Volmer-Monod model was able to describe the experimental data significantly better than the Nernst-Monod model [8]. At steady state, the model can be described by the relationship between current density and anode overpotential as Equation (2),

$$i = i_{lim} \frac{1 - e^{-\frac{F}{RT}\eta_{\_anode}}}{K_1 \cdot e^{-(1-\alpha)\frac{F}{RT}\eta_{\_anode}} + K_2 \cdot e^{-\frac{F}{RT}\eta_{\_anode}} + \left(\frac{K_M}{S} + 1\right)} \qquad (2)$$

where F is the Faraday's constant, R the gas constant, T the operating temperature, $\eta_{\_anode}$ the anode overpotential, i the current density, i_{lim} the limiting current density, α the charge transfer coefficient of the anodic reaction, K_M the Michaelis-

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Menten constant describing the effect of substrate on the biochemical conversion, S the substrate concentration [9]. Under the conditions of steady state and no product inhibition, K_1 can be interpreted as the ratio on how fast the biochemical reaction compared to the electrochemical reaction, while K_2 describes the ratio of the forward reaction from intermediates to product over the backward reaction of the intermediates to the substrate [9]. The limiting current is defined as Equation (3), where n is the moles of electrons involved in the reaction, F the Faraday's constant, k the forward rate constant of the enzyme reaction, and X_T the total amount of the redox component in the bio-film, where the biochemical oxidation occurs.

$$i_{lim} = n \cdot F \cdot k \cdot X_T \qquad (3)$$

In this study, MFCs with air cathode were tested and simulated using the model developed. For MFC with air cathode, it was found that dissolved oxygen exhibits Monod-type behavior and the cathode overpotential can be expressed as Equation (4):

$$i = n \cdot F \cdot k^0 \cdot \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \cdot exp\left[(\beta - 1)\frac{F}{RT} \cdot \eta_{\_cathode}\right] \quad (4)$$

where k^0 is the rate constant of the cathode reaction under standard conditions, β the charge transfer coefficient of the cathodic reaction, $\eta_{\_cathode}$ the cathode overpotential, C_{O_2} the concentration of dissolved oxygen in the cathode compartment, K_{O_2} the half velocity rate constant for dissolved oxygen.

The ohmic overpotential is calculated using Equation (5):

$$\eta_{\_ohmic} = i\left(\frac{d^m}{k^m} + \frac{d_{cell}}{k^{aq}}\right) \qquad (5)$$

where d^m and d_{cell} are the thickness of the membrane and the distance between the electrodes, respectively; k_m and k^{aq} are the conductivities of the membrane and the solution, respectively.

RESUTLS AND DISSCUSIONS

Model Verification

The polarization model was verified against the experimental data acquired from MFCs with air cathode at 110 and 160.5 hours of anode bio-film growth. The comparison between the measured and simulated current density and cell voltage, presented in Figure 2, shows that the model results agree well with the experiment data. It's noted that the model can well describe the polarization curves for the various bio-film growth levels. The MFC model physical parameters and constants used in the simulation are listed in Table 1, and the tuned MFC parameters are listed in Table 2. It is noted that the limiting current density is among the adjustable parameters listed in Table 2. In the verification process, parameters (such as charge transfer coefficients and reaction rates) related to the

activation polarization region of the i-V curve were first evaluated and adjusted to obtain better fittings. After that the value of the limiting current density for both conditions were iterated until the simulation result fits best to the experiment data. The resulting limiting current densities determined from the verification process were 2.5 and 4 A·m^{-2} for the 110 hour and 160.5 hours growth, respectively. The limiting current densities determined by the verification process agreed well with the limiting current densities observed from the experiments.
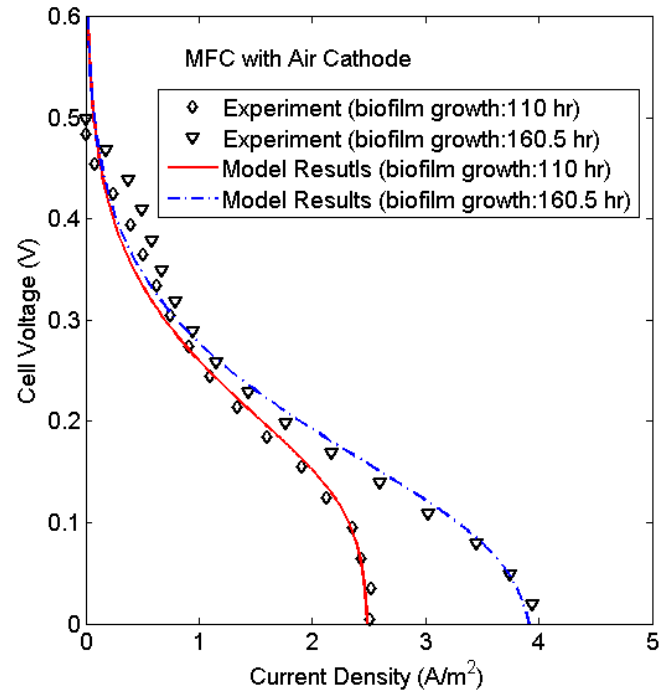
Figure 2: Comparison between simulation results and experimental data for an MFC with anode bio-film growth for 110 hours and 160.5 hours.

Table 1. MFC Model Physical Parameters and Constants			
	Description	Value	Unit
F	Faraday's constant	96485.4	C·mol^{-1}
R	Gas constant	8.3144	J·mol^{-1}·K^{-1}
T	Temperature	298	K
d^m	Thickness of membrane	1.778*10^{-4}	m
k^m	Conductivity of membrane	17[10]	S·m^{-1}
k^{aq}	Conductivity of the aqueous solution	2	S·m^{-1}
A_m	Area of Membrane	4.524*10^{-4}	m^2

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	Description	Value	Unit
d_{cell}	Distance between anode and cathode	0.02	m
V_a	Volume of anode compartment	$9*10^{-5}$	m^3
V_c	Volume of anode compartment	$9*10^{-5}$	m^3
E^0	Cell open circuit potential	0.57 [11]	V
C_{O_2}	Initial concentration of oxygen in the cathode	0.3125[10]	$mol \cdot m^{-3}$
C_{Ace}	Initial concentration of acetate in the anode	20	mM

Table 2. MFC model Parameters.

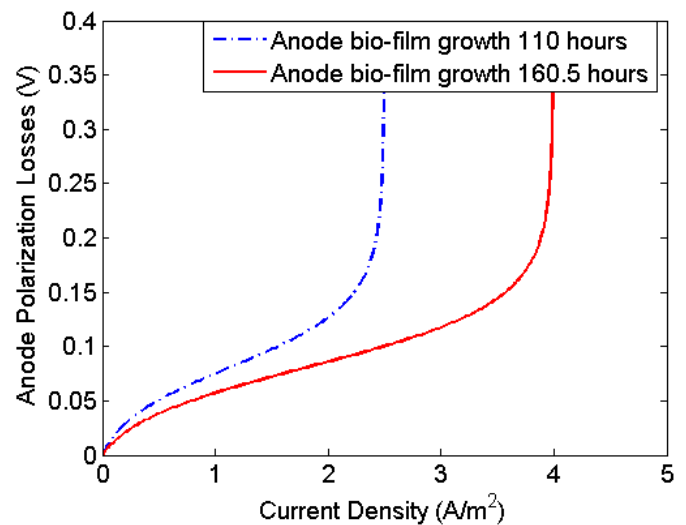|	Description	Value	Unit
α	Charge transfer coefficient of anode	0.5	
K_1	Ratio of biochemical reaction to the electrochemical reaction[9]	0.9	
K_2	Ratio of forward reaction to backward reaction in the enzyme reaction[9]	20.2	
i_{lim}	Limiting current density	2.5 (110 hr) 4 (160 hr)	$A \cdot m^{-2}$
k^0	Rate constant of cathode reaction at standard condition	$2.53*10^{-4}$	$mol \cdot m^{-2} \cdot h^{-1}$
K_{O_2}	Half velocity rate constant for dissolved oxygen	0.004[9]	$mol \cdot m^{-3}$
β	Charge transfer coefficient of Air cathode	0.58	

Loss Contributions

The anode polarization losses simulated using the model are shown in Figure 3. The results of the anode polarization agreed well with the experiment carried out by Torres's group [7]. Anode biofilm with longer growth time will lead to higher limiting current and less polarization losses under same operating current. The model developed in this study is able to simulate the overpotentials from ohmic, cathodic, and anodic losses. The analyses of sources of overpotentials is simulated and presented in Figure 4 and Figure 5. It is noted that the cathode overpotential is dominant in both low and high current density region in MFC with air cathode, for both 110 hours and 160.5 hours of anode-biofilm growth. Compared to the electrode overpotential, the overall ohmic overpotentials are relatively small. The simulation results indicate that ORC MFCs experience significant cathode limitations. Proton transporting out of the biofilm is proved to be one of the main limitations for current generation [12]. This limitation can be mitigated by using a high buffer concentration [12]. In our cell with acetate and high phosphate buffer, the anode were operating close to the best possible conditions with no limitation from substrate diffusion.

Figure 3: Modeling results of anode polarization losses for MFCs at 110 hours and 160.5 hours of anode-biofilm growth.

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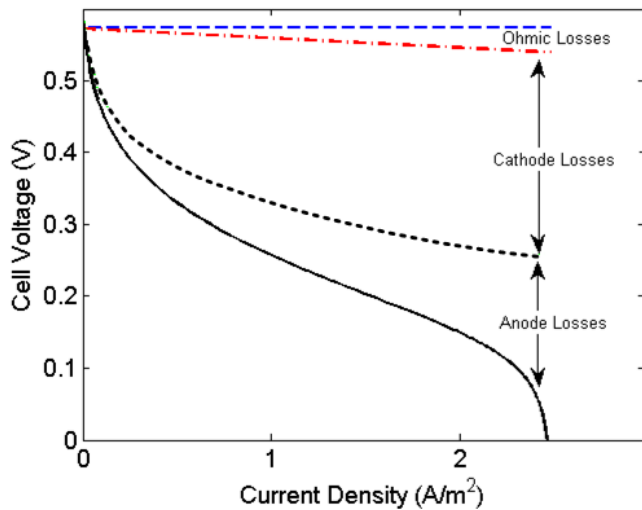
Figure 4: Modeling results for ORC MFCs at 110 hours of anode-biofilm growth.
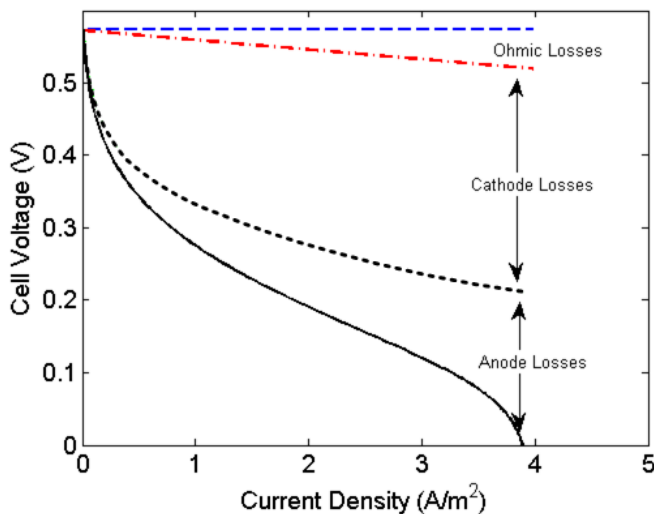
Figure 5: Modeling results for ORC MFCs at 160.5 hours of anode-biofilm growth.

SUMMARY AND CONCLUSIONS

In this study, a mathematical model for microbial fuel cells with air cathode was developed. The model developed is focused on describing and understanding the steady-state polarization curves of the microbial fuel cells. This polarization model developed combines enzyme kinetics and electrochemical kinetics using the Butler-Volmer-Monod relation, and is able to describe the measured polarization curves for microbial fuel cells with various anode-biofilm growth levels as tested in this study.

The polarization model was verified against data from O_2 reducing MFCs at 110 and 160.5 hours of growth, and the model results agree well with the experiment data. This study

provides a basis for describing polarization curves of MFCs. The method can also be applied to an MFC fed with other fuels such as artificial wastewater (a solution of glucose and glutamic acid).

The simulation results provide insights into the limiting physical, chemical and electrochemical phenomena and their effects on cell performance. The model developed in this study integrated the Bulter-Volmer-Monod anode model into a full MFC polarization model therefore the dynamic growth of the bio-film in the anode (equation 3) is incorporated to the limiting current density of the MFC model. This study represents a first step towards a dynamic biofilm growth model which will allow rate limiting processes to be identified as the biofilm grows. The limiting current density depend on the thickness of the biofilm (and morphology, though one could assume that the surface topography remains relatively constant as the biofilm grows), and due to the asymmetric nature of the polarization curve, specifically the sharp dropoff at the limiting current, is directly related to the peak power density as well. Further, the performance of a MFC with various operating and electrode conditions can be simulated and the source of the losses and the rate limiting processes can be identified using the model developed in this study.

Simulation results indicated that the losses of the MFCs with various anode-biofilm growth tested were dominated by the cathode. Cathode overpotential is dominant in both low and high current density region in the current MFCs with air cathode. To increase the power density of the MFCs and to be competitive with other sources of renewable energy, novel cathode structure and reaction catalysts need to be improved.

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