

Analytic and Numerical Modeling of Glucose-fueled Enzymatic Biofuel Cell Performance

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ABSTRACT

Analytic and numerical calculation methods for glucose-fueled enzymatic biofuel cell performance are presented. The output voltage as a function of output current density is formulated by considering the steady-state flux balance, mass transport, enzyme reactions, and electrochemical kinetics. Resulting transcendental equation is numerically solved to determine output voltage at a given current density. The equation is approximated to give an explicit solution, leading to analytic formulae of the cell output performance. Comparison with an experimental data shows excellent agreement. Our method provides a handy but powerful tool for cell design optimization and performance prediction.

Keywords: Biofuel cell, Enzyme electrode, Modeling and simulation, Glucose.

1 INTRODUCTION

Fuel cells have been drawing increasing attention due to their high efficiency and absence of harmful gas emission [1]. Hydrogen is the most widely used fuel, but its energy per volume is not so high, and its safe storage can also be a major issue [1]. In recent years, biofuel cells (BFC) emerged as an alternative, which exploit biochemical reactions in oxidizing organic fuels such as alcohols or glucose [2, 3].

In fuel cell research and development, modeling and computer simulations are frequently used in design optimization and performance prediction [4-6]. Although a

number of simulation studies have been reported for such conventional fuel cells, there are not many articles addressing BFC [2, 7]. Especially, to our best knowledge, there is no report on a fully analytic formula for cell output performance in spite of its handiness and usefulness.

In this paper, we report on a fully analytic formula for enzymatic BFC performance (output voltage and power vs. current), along with a numerical simulation method. Both analytic and numerical results show excellent agreement with an experimental data taken from a glucose-fueled enzymatic BFC. With our analytic formula, impact of each parameter on the output characteristic is clearly exposed, and one can easily predict cell performance without any knowledge or skills on numerical simulation techniques.

2 MODEL DESCRIPTION

Fig. 1 illustrates our glucose-fueled enzymatic BFC, which consists of phosphate buffer solution containing glucose, porous anode electrode supporting glucose dehydrogenase (GDH) and electron mediators, proton permeable membrane, wet porous cathode electrode supporting laccase and mediators, and atmosphere. As shown in Fig. 2, glucose (S_a) is oxidized by catalytic reaction due to GDH (E_a) at anode, producing protons (H^+) and electrons. While electrons are passed to anode electrode via electron mediators ($M_a^{(O)}$ and $M_a^{(R)}$), H^+ diffuses through the membrane, and then consumed in the other catalytic reaction by laccase (E_c) with oxygen (S_c) to produce water (P_c). In this reaction, electrons are passed from the cathode with the help of mediators ($M_c^{(O)}$, $M_c^{(R)}$). The anode and cathode chemical reactions are as follows:

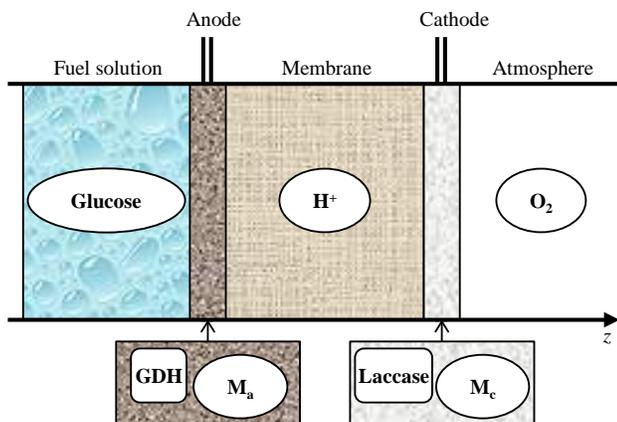


Figure 1: Schematic illustration of the glucose-fueled enzymatic biofuel cell.

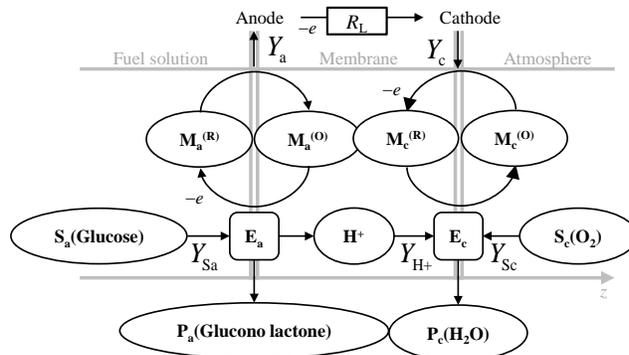
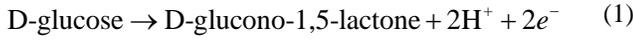


Figure 2: System diagram of reactions and mass transport, where Y_x denotes flux of species x .



The series of reactions generate the electron flow from anode to cathode through electric load (R_L), and thus electric power is drawn from the BFC.

3 FORMULATIONS

As conventional fuel-cell modeling methods, we consider the steady-state flux balance to formulate the cell output voltage as a function of current density [1]. The mass transport, enzyme reactions, and electrochemical kinetics are described by Fick's law, Michaelis-Menten (M.M.) equation [8], and Butler-Volmer equation, respectively. After a lengthy calculation, a transcendental equation describing the relationship between output current density J [A/m²] and overpotential at anode η_a [V] or cathode η_c [V] is finally obtained as

$$J = F \left| Y_x^0 \left(\frac{C_{\text{Mx(O)}}}{C_{\text{Mx(O)}}^0} e^{-\alpha_{\text{Mx}} n_{\text{Mx}} F \eta_x / RT} - \frac{C_{\text{Mx(R)}}}{C_{\text{Mx(R)}}^0} e^{(1-\alpha_{\text{Mx}}) n_{\text{Mx}} F \eta_x / RT} \right) \right|, \quad (3)$$

where subscript 'x' is to be literally replaced by 'a' for anode and 'c' for cathode, F [C/mol] denotes Faraday's constant, Y_x^0 [mol/s.m²] the coefficient of electrode reaction flux, $C_{\text{Mx(O,R)}}$ [mol/L] the concentrations of the oxidized or reduced forms of the electron mediators, α_{Mx} the charge transfer coefficients of electrode reaction, n_{Mx} the number of electrons per electrode reaction, R [J/mol.K] the gas constant, and T [K] the absolute temperature. The included quantities are given by the following equations:

$$C_{\text{Ma(O)}} = K_{\text{EaMa}} \left[\frac{\beta_a l_a k_{\text{Ea}} C_{\text{Ea}}}{J/F + \beta_a l_a v_{\text{Ea}}^0} - \frac{K_{\text{EaSa}}}{C_{\text{Sa}}(z_a)} - 1 \right]^{-1}, \quad (4)$$

$$C_{\text{Mc(R)}} = K_{\text{EcMc}} \left[\frac{\beta_c l_c k_{\text{Ec}} C_{\text{Ec}}}{J/F + \beta_c l_c v_{\text{Ec}}^0} - \frac{K_{\text{EcSc}}}{C_{\text{Sc}}(z_c)} - \frac{K_{\text{EcH}^+}}{C_{\text{H}^+}(z_c)} - 1 \right]^{-1}, \quad (5)$$

$$C_{\text{Sa}}(z_a) = C_{\text{Sa}}(-\infty) - \frac{d_a J}{\beta_a D_{\text{Sa}} F}, \quad (6)$$

$$C_{\text{Sc}}(z_c) = C_{\text{Sc}}(\infty) - \frac{d_c J}{\beta_c D_{\text{Sc}} F}, \quad (7)$$

$$C_{\text{H}^+}(z_c) = C_{\text{H}^+}(z_a) - \frac{d_m J}{D_{\text{H}^+} F}, \quad (8)$$

$$C_{\text{Ma(R)}} = C_{\text{Ma(R)}}^0 + C_{\text{Ma(O)}}^0 - C_{\text{Ma(O)}}, \quad (9)$$

$$C_{\text{Mc(O)}} = C_{\text{Mc(O)}}^0 + C_{\text{Mc(R)}}^0 - C_{\text{Mc(R)}}, \quad (10)$$

$$v_{\text{Ea}}^0 = \frac{k_{\text{Ea}} C_{\text{Ea}}}{1 + K_{\text{EaSa}}/C_{\text{Sa}}(-\infty) + K_{\text{EaMa}}/C_{\text{Ma(O)}}^0}, \quad (11)$$

$$v_{\text{Ec}}^0 = \frac{k_{\text{Ec}} C_{\text{Ec}}}{1 + K_{\text{EcMc}}/C_{\text{Mc(R)}}^0 + K_{\text{EcSc}}/C_{\text{Sc}}(\infty) + K_{\text{EcH}^+}/C_{\text{H}^+}(z_a)}, \quad (12)$$

$$Y_x^0 = n_{\text{Mx}} k_{\text{Mx}} \left(C_{\text{Mx(R)}}^0 \right)^{\alpha_{\text{Mx}}} \left(C_{\text{Mx(O)}}^0 \right)^{1-\alpha_{\text{Mx}}}, \quad (13)$$

where K_{EaMa} , K_{EcMc} , K_{EaSa} , K_{EcSc} , K_{EcH^+} [mol/L] are the M.M. constants, β_x the number of electrons produced or consumed per enzyme reaction, l_x [m] the porous electrode thicknesses, k_{Ex} [s⁻¹] the linear constants of enzymatic reactions, $C_{\text{Sa}}(-\infty)$ [mol/L] the glucose concentrations in the fuel solution, $C_{\text{Sc}}(\infty)$ [mol/L] the dissolved O₂ concentrations in the cathode solution, $C_{\text{H}^+}(z_a)$ [mol/L] the proton concentration at anode, D_{Sa} , D_{Sc} and D_{H^+} [m²/s] are diffusion constants of glucose, oxygen, and H⁺, respectively, d_x [m] the diffusion thicknesses, d_m [m] the membrane thickness, $C_{\text{Mx(O,R)}}^0$ [mol/L] the initial concentrations of the oxidized or reduced forms of the electron mediators, and k_{Mx} [s⁻¹] the charge transfer rates of electrode reactions.

Eq. (3) is solved for the overpotentials η_a or η_c for a given current density J , and they are used to calculate the cell output voltage V [V] as a function of J using the following equation:

$$V(J) = E_{\text{c,eq}} - E_{\text{a,eq}} - \eta_a(J) + \eta_c(J) - \eta_{\text{Ohm}}(J). \quad (14)$$

Here, $E_{x,\text{eq}}$ [V] are the open circuit potentials given by

$$E_{x,\text{eq}} = E_{x,0} + \frac{RT}{n_{\text{Mx}} F} \ln \left(\frac{C_{\text{Mx(O)}}^0}{C_{\text{Mx(R)}}^0} \right), \quad (15)$$

where $E_{x,0}$ [V] are the standard potentials. In Eq. (14), η_{Ohm} [V] denotes resistive overpotential given by

$$\eta_{\text{Ohm}}(J) = A_m R_m J, \quad (16)$$

where A_m [m²] and R_m [Ω] are the membrane area and resistance, respectively.

In general, the transcendental equation Eq. (3) must be solved numerically to obtain the overpotentials η_a or η_c for a given current density J , so that some mathematical software is required. However, by taking only a dominant exponential term in Eq. (3) (Tafel approximation [9]), explicit and analytic formulae for the overpotentials can be obtained as

$$\eta_a(J) = \frac{RT}{(1-\alpha_{\text{Ma}}) n_{\text{Ma}} F} \ln \left[\frac{J}{F Y_a^0} \frac{C_{\text{Ma(R)}}^0}{C_{\text{Ma(R)}}(J)} \right], \quad (17)$$

$$\eta_c(J) = -\frac{RT}{\alpha_{\text{Mc}} n_{\text{Mc}} F} \ln \left[\frac{J}{F Y_c^0} \frac{C_{\text{Mc(O)}}^0}{C_{\text{Mc(O)}}(J)} \right]. \quad (18)$$

These formulae are used in Eq. (14) to give explicit analytic expression of $V(J)$, which is useful in quick hand calculation without any mathematical softwares required.

Table 1: Parameters used in our calculation.

	Description	Value	Unit
$C_{Sa}(-\infty)$	Bulk glucose concentration	1.0	mol/L
$C_{Sc}(\infty)$	Bulk O ₂ concentraion	$2.0 \cdot 10^{-4}$	mol/L
$C_{H^+}(z_a)$	H ⁺ concentration at anode	$4.0 \cdot 10^{-7}$	mol/L
C_{Ea}	GDH concentration in anode	$2.0 \cdot 10^{-5}$	mol/L
C_{Ec}	Laccase concentration in cathode	$1.5 \cdot 10^{-3}$	mol/L
D_{Sa}	Glucose diffusion constant in fuel solution	$1.0 \cdot 10^{-9}$	m ² /s
D_{Sc}	O ₂ diffusion constant in cahode solution	$5.0 \cdot 10^{-9}$	m ² /s
D_{H^+}	H ⁺ diffusion constant in membrane	$1.0 \cdot 10^{-4}$	m ² /s
β_a	Number of electrons per anode enzyme reaction	2	-
β_c	Number of electrons per cathode enzyme reaction	4	-
d_a	Anode diffusion layer thickness	$1.0 \cdot 10^{-4}$	m
d_c	Cathode diffusion layer thickness	$1.0 \cdot 10^{-6}$	m
d_m	Membrane thickness	$21 \cdot 10^{-6}$	m
l_a	Anode electrode thickness	$1.0 \cdot 10^{-3}$	m
l_c	Cathode electrode thickness	$1.0 \cdot 10^{-3}$	m
K_{EaSa}	M.M. constant for GDH and glucose at anode	$1.0 \cdot 10^{-3}$	mol/L
K_{EcSc}	M.M. constant for Laccase and O ₂ at cathode	$1.0 \cdot 10^{-10}$	mol/L
K_{EaMa}	M.M. constant for GDH and mediator at anode	$2.0 \cdot 10^{-4}$	mol/L
K_{EcMc}	M.M. constant for Laccase and mediator at cathode	$2.0 \cdot 10^{-5}$	mol/L
K_{EcH^+}	M.M. constant for Laccase and H ⁺	$5.0 \cdot 10^{-6}$	mol/L
k_{Ea}	GDH linear constant for enzyme reaction	$4.0 \cdot 10^3$	1/s
k_{Ec}	Laccase linear constant for enzyme reaction	$5.0 \cdot 10^2$	1/s
k_{Ma}	Charge transfer rate at anode	$1.0 \cdot 10^{-6}$	m/s
k_{Mc}	Charge transfer rate at cathode	$1.0 \cdot 10^{-4}$	m/s
α_{Ma}	Charge transfer coefficient at anode	0.5	-
α_{Mc}	Charge transfer coefficient at cathode	0.5	-
n_{Ma}	Number of electrons per anode electrode reaction	1	-
n_{Mc}	Number of electrons per cathode electrode reaction	1	-
$C_{Ma(R)}^0$	Open circuit value of $C_{Ma(R)}$	$2.4 \cdot 10^{-2}$	mol/L
$C_{Ma(O)}^0$	Open circuit vale of $C_{Ma(O)}$	$6.0 \cdot 10^{-3}$	mol/L
$C_{Mc(R)}^0$	Open circuit vale of $C_{Mc(R)}$	$1.0 \cdot 10^{-7}$	mol/L
$C_{Mc(O)}^0$	Open circuit vale of $C_{Mc(O)}$	$5.0 \cdot 10^{-2}$	mol/L
$E_{a,0}$	Standard potential vs. Ag/AgCl for anode mediator	-0.16	V
$E_{c,0}$	Standard potential vs. Ag/AgCl for cathode mediator	0.256	V
A_m	Membrane area	$1.0 \cdot 10^{-4}$	m ²
R_m	Membrane resistance	10	Ω

4 COMPARISON WITH EXPERIMENTAL DATA

Fig. 3 shows a comparison among analytic (red solid line), numerical (green solid line), and experimental (green symbols) results of the cell output voltage and power as a function of current density. The parameter values used are shown in Table 1. Some of the parameter values are based on experimental results such as cyclic voltammetry or impedance spectroscopy, while others are calibrated to fit experimental data. As can be seen in the figure, both of our analytic and numerical results show excellent agreement with experimental data. This indicates that our calculation methods are effective in data analysis and performance predictions. Note that there is a slight discrepancy between numerical and analytic results at low output current density. This is due to the fact that the magnitude of the exponential terms in Eq. (3) is comparable at low overpotential (low output current density). In such a range, the approximation used to obtain Eqs. (17) and (18) is no longer valid. Although this inherent error in the analytic formulae cannot be avoided, it has relatively small impact in the output power because of small output current density.

5 CONCLUSION

Analytic and numerical calculation methods for glucose-fuelled enzymatic biofuel cell performance have been presented. Comparison with an experimental data showed excellent agreement. Our method provides a handy but powerful tool for cell design optimization and performance prediction.

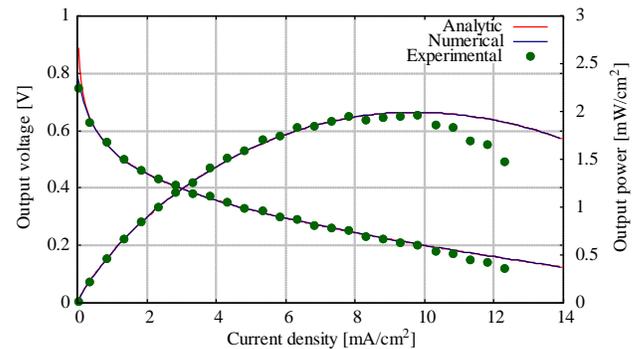


Figure 3: Cell output voltage and power as a function of output current density. Red solid line: analytically calculated with Eqs. (14), (17) and (18), green solid line: numerically calculated with Eqs. (3) and (14), Symbols: experimental data.

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