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Analytical expression of transient current-potential for redox enzymatic homogenous system

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ABSTRACT

Mathematical modeling pertaining to the catalytic response of a redox enzymatic system is discussed. The model proposed herein describes the relationship between the electrochemical responses and the kinetic characteristics of the enzymatic reaction. The analytical expressions corresponding to the concentration of co-substrate for steady and non-steady state conditions have been obtained using a new approach to homotopy perturbation method (HPM). Analytical expressions of the plateau current are also presented for steady and non-steady state conditions. Upon comparison, we found that the analytical results of this work are in excellent agreement with the existing limiting case results. Further, the sensitivity of the parameter in transient current potential was also analyzed due to its importance in predicting the relationship between the input value of the parameter and the model results.

1. Introduction

Fuel cell technology is progressing at a very rapid pace. However, there are some challenges to be addressed in order envisage its application in improving hydrogen production, storage, cost reduction and manufacturing [1]. Fuel cells are devices that convert chemical energy into electrical energy. Biofuel cells are considered as the subset of fuel cells that employ biocatalyst and characterized by the type of biocatalysts they employ. Enzymes or whole cells can be used as biocatalyst in biofuel cells [2,3]. Microbial fuel cell utilizes living cells to catalyze the oxidation of the fuel, whereas enzymatic biofuel cells require enzymes for this purpose [2]. These biocatalysts (enzymes, microbes) are economical and their extended usage is expected to lower production cost, due to the limited availability of other transition metal catalysts. In addition, biocatalysts allow the utilization of more complex fuels as compared to the typical fuels, hydrogen and methanol for conventional fuel cells [4,5].

Bhattacharyya and Rengaswemy [6] discussed the modeling of a solid oxide fuel cell using both lumped and distributed modeling approaches. Pradhan et al. [7] studied the impact of electrical effects on the performance of solid oxide fuel cell. Yan et al. [8] proposed a novel dynamical model for microbial fuel cell based on biochemical reactions. Ivanov et al. [4] discussed the existing problems such as low cell voltage, low current density and stability associated with the enzymatic fuel cells. Vizhemehr et al. [9] investigated the generation of electricity in a dual chamber microbial fuel cell. In another work, Limoges and co-workers [10] analyzed the electrochemical responses related to the rate constants, the amount of enzyme on the electrode, concentration and mass transport parameters using the steady state expressions for current and plateau current. Though there are several models and expressions available in the literature that corresponds to various phenomena and processes at biofuel cells, to the best of our knowledge, there is no rigorous analytical expression available till date for the non-steady state current and plateau current.

As a result, in this work we focus on obtaining an expression for steady and non-steady state current, plateau current and the concentration of co-substrate. Further, the expression helps us to analyze the electrochemical response related to the parameters in the biofuel cell for all values of time. In addition, we have also conducted a parameter sensitivity analysis to quantify the effect of the unknown parameter. The importance of this analysis is that it can predict the parameters that should be optimized or determined more accurately through further experimental or simulation studies. The parameter sensitivities are useful to identify where future computational and experimental efforts should be focused. As a result, it will restrict the need for unwanted calculations or measuring physical parameters that do not have a significant effect on the

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Nomenclature

D_P, D_S	diffusion coefficient of co-substrate, substrate
Q, S	concentration of co-substrate, substrate
x	distance from the electrode surface assumed to be planar
C_S^0	bulk concentration of substrate
C_E^0	total concentration of enzyme
$k_1, k_{2,2}$ and k_2	reaction rate constants
t	time
$q=\frac{[Q]}{C_P^0}$	dimensionless concentration of co-substrate
$z=x\sqrt{\frac{k_2C_E^0}{D_P}}$	dimensionless distance
$\tau=k_2C_E^0t$	dimensionless time
$\sigma=k_2C_P^0\left(\frac{1}{k_{2,2}}+\frac{1}{k_{1,2}}+\frac{1}{k_1C_S^0}\right)$	competition parameter
$\xi=-\frac{F}{RT}(E-E_{PQ}^0)$	potential

product quality. We also provide a tabular compilation of plateau current over the entire potential and competition parameter in redox enzymatic homogenous systems.

2. Mathematical formulation

Fig. 1 represents the reaction scheme for the Michaelis–Menten mechanism for co-substrate and substrate. Building upon earlier work for these mechanisms, Limoges and co-worker [10] presented a concise discussion and derivation of the one dimensional mass transport equation for a redox enzymatic homogenous system which is summarized briefly for completeness. When the enzyme being solubilized in the solution, the electrochemical signal that produced during the reaction is governed by the following set of nonlinear partial differential equations [10].

$$D_P\frac{\partial^2[Q]}{\partial x^2}-\frac{C_E^0}{\frac{1}{k_1[S]}+\frac{1}{k_{1,2}}+\frac{1}{k_{2,2}}+\frac{1}{k_2[Q]}}=\frac{\partial[Q]}{\partial t} \qquad (1)$$

$$D_S\frac{\partial^2[S]}{\partial x^2}-\frac{C_E^0}{\frac{1}{k_1[S]}+\frac{1}{k_{1,2}}+\frac{1}{k_{2,2}}+\frac{1}{k_2[Q]}}=\frac{\partial[S]}{\partial t} \qquad (2)$$

where D_P, D_S are the diffusion coefficient of co-substrate and substrate, respectively; Q, S is the concentration of co-substrate and substrate, respectively; x is the distance from the electrode surface (electrode assumed to be planar); C_S^0 is the bulk concentration of substrate; C_E^0 is the total concentration of enzyme; k_1, $k_{2,2}$ and k_2 are the reaction rate constants; t is the time. Furthermore, Eqs. (1) and (2) was obtained under steady state conditions of the various forms of the enzyme. The corresponding reaction diffusion equation is given in [10]. However, the diffusion profiles in biofilm will be much more complex and unlikely to follow this model. The initial and boundary conditions for Eq. (1) is given as

$$t=0,\quad \text{and}\quad x=\infty,\quad x\geq 0,\quad [Q]=0,\quad [S]=C_S^0 \qquad (3)$$

$$x=0,\ t\geq 0:\quad [Q]=\frac{C_P^0}{1+\exp\left[\frac{F}{RT}(E-E_{PQ}^0)\right]},\quad \frac{\partial[S]}{\partial x}=0 \qquad (4)$$

$$x=\infty,\quad \partial[Q]/\partial x=0 \qquad (5)$$

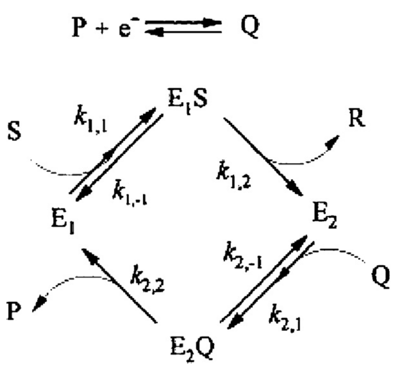

Fig. 1. Reaction scheme for substrate and co-substrate.

The current flowing through the electrode is proportional to the co-substrate

$$i=FSD_P\left(\frac{\partial[Q]}{\partial x}\right)_{x=0} \qquad (6)$$

where E is the electrode potential; E_{PQ}^0 is the standard potential of the P/Q couple; F is the Faraday constant; S is the surface area of the electrode. Let us consider the reaction diffusion equation for co-substrate under the control of the catalytic response by the enzymatic reaction in non-steady as follows [10]:

$$D_P\frac{\partial^2[Q]}{\partial x^2}-\frac{C_E^0}{\frac{1}{k_{1,2}}+\frac{1}{k_1C_S^0}+\frac{1}{k_{2,2}}+\frac{1}{k_2[Q]}}=\frac{\partial[Q]}{\partial t} \qquad (7)$$

2.1. Dimensionless form

Eq. (7) takes the dimensionless form upon the introduction of the following set of non-dimensional variables:

$$z=x\sqrt{\frac{k_2C_E^0}{D_P}},\quad q=\frac{[Q]}{C_P^0},\quad \xi=-\frac{F}{RT}(E-E_{PQ}^0),$$
$$\sigma=k_2C_P^0\left(\frac{1}{k_{2,2}}+\frac{1}{k_{1,2}}+\frac{1}{k_1C_S^0}\right),\quad \tau=k_2C_E^0t \qquad (8)$$

Using the above dimensionless variables, Eq. (7) assumes the following normalized form:

$$\frac{\partial^2q(z,\tau)}{\partial z^2}-\frac{q(z,\tau)}{1+\sigma q(z,\tau)}=\frac{\partial q(z,\tau)}{\partial\tau} \qquad (9)$$

The corresponding initial and boundary conditions are

$$\tau=0,\quad q=0 \qquad (10)$$

$$z=0,\quad q=\frac{1}{1+\exp(-\xi)} \qquad (11)$$

$$z=\infty,\quad q=0\quad \text{and}\quad \frac{\partial q}{\partial z}=0 \qquad (12)$$

The dimensionless current is given as [10]

$$\varphi^C=-\left(\frac{\partial q}{\partial z}\right)_{z=0}=\frac{i}{FSC_P^0\sqrt{D_Pk_2C_E^0}} \qquad (13)$$

The current reaches the plateau current, when $\xi\to\infty(E\ll E_{PQ}^0)$:

$$\varphi_{pl}^C=\frac{i_{pl}}{FSC_P^0\sqrt{D_Pk_2C_E^0}} \qquad (14)$$

3. A novel approach to homotopy perturbation method (HPM)

The homotopy perturbation was first proposed by He [11]. This method is used to find an approximate analytical solution for linear and nonlinear problems. The homotopy perturbation method is a combination of the perturbation method and homotopy in topology. The benefit of this technique is that it does not require a