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Analytical expression of transient and steady-state catalytic current of mediated bioelectrocatalysis

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ABSTRACT

Mediated bioelectrocatalysis is very useful to build bioreactors, biofuel cells and it can also be employed for measuring enzyme kinetics and protein redox potentials. Mathematical modeling of a mediated bioelectrocatalysis has been discussed. An analytical expression of the concentration of mediated bioelectrocatalysis for the steady- and non-steady-state conditions have been derived using Danckwerts' expression and new approach to homotopy perturbation method. Here the concentration of substrate is sufficiently higher than the Michaelis constant and the redox reaction of a mediator is obeying the Nernst equation at an electrode surface. The analytical expressions of steady- and non-steady-state catalytic current are also reported. Our analytical results are compared with previous limiting case results and satisfactory agreement is noted.

1. Introduction

Recently there has been significant interest in mediated electrocatalytic processes including those based on enzyme reaction. In an enzymatic oxidation (or reduction) reaction electrons can be regenerated by electrochemical reactions of the compounds at an electrode surface. This type of coupling of the enzymatic reactions with the electrochemical reactions is called bioelectrocatalysis [1,2]. There are several reviews of biofuel cells that uses biocatalysts have been reported in the literature [3,4]. Mediated bioelectrocatalysis is very useful to build bioreactors, biofuel cells and it can also be employed for measuring enzyme kinetics [5]. As a basis for the analytical application of the peroxidase-modified amperometric electrodes, the heterogeneous electron transfer properties of peroxidases were discussed by Ruzgas et al. [6]. The steady-state limiting current of mediated bioelectrocatalysis as a function of the bulk mediator concentration was derived. Ohgaru et al. [7] described several applications of these equations for the enzyme kinetic analysis.

Barton [8] presented a numerical simulation of an enzyme-catalyzed oxygen cathode. The electrochemical performance of a redox polymer mediated glucose anode catalyzed by glucose oxidase and supported on a multiscale carbon material is reported [9]. Barton and his co-workers have analyzed about bioelectrocatalytic electrodes based on experimental data [10–16]. Hettige et al. [17] presented a quantitative study of multiple enzyme systems immobilized on porous electrodes. Hudak et al. [18] demonstrated a biocatalytic fuel cell cathode operating with gas-phase air or oxygen. Kar et al. [19] reported a simulation of multi-step enzyme catalysis and cofactor-mediated electron transfer in a bio-anode of a methanol biofuel cell. Wen et al. [20] discussed the carbon nanotube-modified biocatalytic microelectrodes with multiscale porosity. To model the mediated enzyme electrodes, reaction–diffusion equations in electrodes have been solved by approximate analytical treatments under suitable limiting cases [5,21,22], and by numerical methods [8,21–23].

Matsumoto et al. [24] investigated the properties of the current-potential for the steady-state condition. Also Matsumoto et al. [24] discussed the significance and the advantage of the enzyme kinetic analysis based on mediated bioelectrocatalysis. To the best of our knowledge, there is no rigorous analytical expression of the transient current for mediated bioelectrocatalysis has been reported [24]. This system is pretty readily analyzed numerically and so an approximate analytical solution derived in this paper is compared against the limiting case and numerical solution. This approach has been used very successfully by Bartlett and Pratt [22]. In this work, we study the non-steady and steady-state catalytic current performance of mediated bioelectrocatalysis. The analytical expressions for the concentration of the mediator and the catalytic current are derived using Danckwerts' expression and new approach to homotopy perturbation method.

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Nomenclature

[E]	Bulk concentration of the enzyme (mol/cm^3)
[S]	Concentration of the substrate (mol/cm^3)
[M_{ox}]	Concentration of the oxidized mediator (mol/cm^3)
[M]*	Bulk concentration of the oxidized mediator (mol/cm^3)
K_S	Michaelis constant for the substrate (mol/cm^3)
K_M	Michaelis constant for the mediator (mol/cm^3)
D_M	Diffusion coefficient of the mediator (cm^2/s)
k_{cat}	Catalytic constant (s^{-1})
x	Distance from the electrode surface (cm)
I	Current (μA)
A	Surface area of the electrode (cm^2)
E	Electrode potential (v)
$E_M^{0'}$	Formal potential of the mediator (v)
n_S	Number of electrons of substrate
n_M	Number of electrons of mediator
F	Faraday constant (C mol^{-1})
R	Gas constant (J k^{-1} mol^{-1})
T	Absolute temperature (k)
u	Dimensionless concentration of the oxidized mediator (none)
τ	Dimensionless time (none)
α'	Dimensionless parameter, $\left(1+a\frac{[M]^*}{K_M}\right)^{-1}$ (none)
η_M	Dimensionless parameter, $\exp\left\{n_M F(E-E_M^{0'})/(RT)\right\}$ (none)
a	Dimensionless parameter, $\eta_M/(1+\eta_M)$ (none)
k=	$(n_S/n_M)k_{cat}[E]/[D_M(a+K_M)]$ (cm^{-2})
α=	$(n_S/n_M)k_{cat}[E]/K_M$ (s^{-1})
φ=	$(n_S/n_M)k_{cat}[E]/[K_M+a\ \ [M]^*]$ (s^{-1})
ϕ=	$\frac{(n_S/n_M)k_{cat}[E][S]^*}{a[M]^*[S]^*+aK_S\ \ [M]^*+K_M[S]^*}$ (s^{-1})
β=	$\rho^2 D_M+\varphi$ (s^{-1})
ρ=	$\frac{(2n+1)\pi}{2l}$ (cm^{-1})
γ=	$\rho^2 D_M+\phi$ (s^{-1})

2. Description of the mathematical model

We assume a redox enzyme reaction for the oxidation of a substrate (S) with an electron acceptor (M_{ox}) to yield its product (P) and the reduced form of mediator (M_{red}). The bioelectrolytic reaction can be written as follows:

$$S+(n_S/n_M)M_{ox}\xrightarrow{v_S,v_M}P+(n_S/n_M)\ \ M_{red} \tag{1}$$

where n_S and n_M are the number of electrons of S and M respectively and v_S and v_M (=$(n_S/n_M)v_S$) are the enzymatic reaction rates of the oxidation of S and the reduction of M_{ox} respectively. In mediated bioelectrocatalysis for the substrate oxidation, M_{red} is oxidized at an electrode surface to generate M_{ox}, and the redox couple M_{ox} | M_{red} functions as an electron transfer mediator from the enzyme to the electrode.

$$M_{red}\underset{\leftarrow k}{\overset{\vec{k}}{\rightleftharpoons}}M_{ox}+n_M\ \ e^- \tag{2}$$

where $\vec{k}$ and $\leftarrow k$ are the electron-transfer rate constants. The mass balance equation for this reaction is given below [24,25]:

$$\frac{\partial[M_{ox}(x,t)]}{\partial t}=D_M\frac{\partial^2[M_{ox}(x,t)]}{\partial x^2}-v_M \tag{3}$$

where

$$v_M=\frac{(n_S/n_M)k_{cat}[E]}{1+K_S/[S]+K_M/[M_{ox}]} \tag{4}$$

where M_{ox} and D_M are the concentration and diffusion coefficient of the oxidized mediator respectively. k_{cat} is the catalytic constant and [E] is the concentration of the enzyme in solution. K_S and K_M are the Michaelis constants for the substrate and mediator respectively. x and t are the distance from the electrode surface and time respectively. When the electrode reaction of the M_{ox} | M_{red} couple obeys the Nernst equation, the initial and boundary condition at the surface is given by [24,25]:

$$M_{ox}(x,0)=0;\quad [M_{ox}(x)]_{x=0}=\frac{\eta_M[M]^*}{1+\eta_M};\quad \eta_M=\left(\frac{[M_{ox}(x)]}{M_{red}(x)}\right)_{x=0}$$
$$=\exp\left[\frac{n_M F(E-E_M^{0'})}{RT}\right] \tag{5}$$
$$[M_{ox}(x)+M_{red}(x)]_{x=0}=[M]^*$$

where $E_M^{0'}$ is the formal potential of the M_{ox} | M_{red} couple and E is the electrode potential. F and A are the Faraday constant and electrode surface area. R and T are the gas constant and absolute temperature respectively. When no enzyme reaction occurs in the bulk phase, the boundary condition is given by:

$$[M_{ox}(\infty,t)]=0 \tag{6}$$

The current (I) is given by:

$$\frac{I}{n_M FA}=-D_M\left.\frac{d[M_{ox}(x)]}{dx}\right|_{x=0} \tag{7}$$

3. Analytical expressions of the concentration and current

3.1. Case (i): Homogeneous system in the presence of excess amounts of substrate when the mediator is in the reduced form in the bulk phase

We now consider the case where the mediator-enzyme reaction is rate-determining. The mediated bioelectrocatalytic current reaches a steady-state when the bulk concentration of the substrate ([S]*) is sufficiently higher than the Michaelis constant for the substrate (K_S) [24]. In this case ($[S]^*/K_S >> 1$), the enzyme/substrate reaction kinetics are saturated (rate is independent of substrate concentration) and the steady-state kinetics of the redox enzyme reaction (Eq. (4)) is expressed by the Michaelis–Menten equation (Eq. (8)).

Fig. 1 (a) shows the typical electron flow in mediated bioelectrocatalysis. Ikeda and Kano [1] obtained the current (experimental and theoretical) in enzyme mediated bioelectrocatalysis process when the substrate concentration is larger than the Michaelis-Menten constant for the substrate. When the enzyme in the bulk phase is completely reduced with [S](i.e.$K_S/[S]^* \le 1$), v_M in the equation (4) is reduced to [24,26]:

$$v_M=\frac{(n_S/n_M)k_{cat}[E]}{1+K_M/[M_{ox}]} \tag{8}$$

The mass balance equation for this reaction is as follows:

$$\frac{\partial[M_{ox}(x,t)]}{\partial t}=D_M\frac{\partial^2[M_{ox}(x,t)]}{\partial x^2}-\frac{(n_S/n_M)k_{cat}[E]}{1+K_M/[M_{ox}]} \tag{9}$$

No enzyme reaction occurs in the bulk phase, since only the reduced form of M is in the bulk phase. When all M_{ox} is in the reduced form in the bulk phase, the initial and boundary conditions can be written as follows:

$$M_{ox}(X,0)=0;\quad [M_{ox}(x=0)]=\frac{\eta_M[M]^*}{1+\eta_M}=a[M]^*;\ [M_{ox}(\infty,t)]=0 \tag{10}$$