Electrochimica Acta 230 (2017) 89–97

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Theoretical treatment of diffusion and kinetics of osmium redox polymer mediated glucose oxidase enzyme electrodes: Analytical expression of current density for varying potential

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ARTICLE INFO

Article history:
Received 6 August 2016
Received in revised form 30 December 2016
Accepted 23 January 2017
Available online 24 January 2017

Keywords:
Mathematical modeling
Biofuel
Osmium redox polymer
Non-linear reaction diffusion equation
Glucose oxidase enzyme electrodes

ABSTRACT

We present for the first time a mathematical model of osmium redox polymer mediated glucose oxidase enzyme electrodes. This model is based on a system of three coupled nonlinear reaction-diffusion equations under steady-state conditions for biochemical reactions occurring in the biofuel cells that describes the oxidized mediator, oxygen and substrate (Glucose) concentration within the biofuel cell. Simple analytical expressions for the concentration of oxidized mediator, oxygen and substrate and the corresponding current-potential response have been derived for all the values of reaction diffusion parameters using the new homotopy perturbation method (NHPM).The current-potential response in osmium redox polymer mediated glucose oxidase enzyme electrodes is discussed. The analytical results for the concentrations are also compared with numerical results and a satisfactory agreement is noted. The influence of diffusion coefficient of mediator, thickens of the film, turnover rate of Gluocose Oxidase and Michaelis-Menten constant on current-potential curve is also analyzed.

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1. Introduction

Enzymatic fuel cell convert the chemical energy of biofuel into electrical energy. Enzymatic biofuel cells are the electricity generating devices that mimic this process by using enzyme-modified electrons using oxygen as the final electrodes acceptor [1–6]. These devices have the potential to provide a flexible, compact, and inexpensive micropower sources [7]. Glucose oxidizing enzyme electrodes have long been studied for their application to biosensors and, more recently, anodes in biofuel cells [8].

Theoretical models in biofuel cells are useful to identify and optimize important experimental parameters such as film thickness, diffusivity of mediators, loading of biocatalysts, kinetic parameters, amount of substrates, mediators and inhibitors etc. Mathematical models must incorporate consideration of various processes like electron and species transport, reaction mechanism and experimental techniques etc, which controls the overall performance [9]. Interesting approach for the theoretical modeling of enzymatic approach is discussed by Glykys et al. [10]. Paul Kavanagh et al. recently analyzed mediated electron transfer processes for glucose oxidizing enzyme electrodes based on anodes in a biofuel cell [8]. In the literature contains several modeling of enzymatic electrodes [10–13] and enzymatic biosensors [14], the modeling of enzymatic electrodes has been more attractive due to the consideration of the enzymatic reaction and the material balance of species which are participating in the enzymatic reaction. Andrieux and Saveant [15] have reported kinetics of electrochemical reactions mediated by redox polymer films for stationary voltammetry techniques. Bartlett *et al.* [16,17] presented the analysis by considering Michaelis-Menten enzyme kinetics and stated one dimensional catalytic film model for steady state conditions. Gallaway *et al.* [3] used this approach to obtain the kinetic information of oxygen reducing laccase-based electrodes, having different osmium redox polymers mediated through redox hydrogels. For the enzyme kinetics problem, approximate analytical solutions have been developed by Elaedel *et al.* [18], Kulys *et al.* [19] and Bartlett and Whitaker [20] only forthe limiting cases (saturated and unsaturated). The applications of numerical and approximate analytical methods have been reported by Barlett and Pratt [16].

Senthamarai and Rajendran [21] derived the approximate analytical expressions for the concentration of substrate, mediator

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http://dx.doi.org/10.1016/j.electacta.2017.01.149
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Nomenclature

Symbol	Description
$[M_{ox}](mol\,cm^{-3})$	Concentration of mediator
$[S](mol\,cm^{-3})$	Concentration of substrate
$[O_2](mol\,cm^{-3})$	Concentration of oxygen
$[M_T]_\infty(mol\,cm^{-3})$	Bulk Concentration of Oxidized mediator
$[S]_\infty(mol\,cm^{-3})$	Bulk Concentration of substrate
$[O_2]_\infty(mol\,cm^{-3})$	Bulk Concentration of oxygen
$K_S(mol\,cm^{-3})$	Michaelis constant of substrate
$k_o(cm^3\,mol^{-1}s^{-1})$	Second-order reaction rate constant between enzymeand oxygen
$L(cm)$	Thickness of the hydrogel
$k_m(cm^3\,mol^{-1}s^{-1})$	Second-order reaction rate constant between enzymeand mediator
$k_{cat}(s^{-1})$	Turnover number of enzyme GOx
p_a	Partition coefficient of mediator
p_S	Partition coefficient of substrate at the film solution interface
p_O	Partition coefficient of oxygen at the film solution interface
$D_m(cm^2s^{-1})$	Diffusivities of mediator
$D_S(cm^2s^{-1})$	Diffusivities of substrate
$D_O(cm^2s^{-1})$	Diffusivities of oxygen
$x(cm)$	Distance
$D_1(cm^2s^{-1})$	Glucose diffusion coefficient in bulk solution
$D_2(cm^2s^{-1})$	Oxygen diffusion coefficient in bulk solution
$\nu(cm^2s^{-1})$	Kinematic viscosity of electrolyte
$\omega(rpm)$	Rotation of electrode
E_{red}	Reduced form of enzyme
E	Potential at electrode surface
$E_T(mol\,cm^{-3})$	Total concentration of immobilized enzyme
E^0	Formal potential of mediator couple
N	Number of electrons transferred by mediator
F	Faraday constant
R	Universal gas constant
T	Absolute temperature
a	Dimensionless concentration of substrate
s	Dimensionless concentration of mediator
o	Dimensionless concentration of oxygen
$d, \beta, \beta, \eta, \mu, \kappa$	Dimensionless parameter
χ	Dimensionless distance
δ_1	Diffusion layer thickness of glucose at the film-solution interface
δ_2	Diffusion layer thickness of oxygen at the film-solution interface
σ_1	Dimensionless parameter
σ_2	Dimensionless parameter
a_e	Dimensionless mediator concentration at electrode surface
ε	Dimensionless potential
J_{obs}	Flux mediator at electrode surface
j_{obs}	Dimensionless flux mediator at electrode surface
i	Current density per projected surface area

and current for the non-linear Michaelis–Menten kinetic scheme by solving a system of non-linear coupled reaction-diffusion using the variational iteration method. Logambal et al. [22] presented the approximate analytical expressions for the concentrations of the mediator and substrate using homotopy perturbation methods. Rasi et al. [23] presented a theoretical model describing the transient response of electroreduction of oxygen to water in the presence of laccase enzyme, interacting via ping-pong kinetic scheme. Mathematical modelling of non-linear reaction and diffusion processes in a biofuel cell were also discussed [24]. A novel graphical procedure for estimating the Michaelis-Menten constants and turnover rate solely fromthe current-potential curve is suggested in this manuscript. Influence of the controllable parameters such as diffusion of the mediator, Michaelis-Menten constant for substrate, second-order rate constant, thickness of the film, turnover rate and initial substrate concentration on the current density are also presented. Bambhania [9] developed the kinetics of osmium redox polymer mediated glucose oxidase electrodes. To the best our knowledge, no analytical expression for the concentration of mediator, oxygen and substrate has been derived. In this paper we have derived for the first time the simple and closed-form of an approximate analytical expressions for the concentration of mediator, oxygen and substrate in terms of kinetic parameters. This modeling approach is useful to understand and optimize the kinetics behavior of the enzymatic fuel cells.

2. Analytical expressions of concentrations using a new approach to the new homotopy perturbation method

Fig. 1 shows the general kinetic scheme of reaction rate in the redox hydrogel film-modified enzyme electrodes, which may be limited and affected by several factors such as: electron transport via mediator, enzyme kinetics, substrate transport and by the presence of oxygen for the GOx based electrodes. The one-dimensional steady state equations for the reduced form of GOx (Appendix A) can be written as follows [9]:

$$\frac{d^2a}{d\chi^2} = \frac{\kappa^2 as}{\gamma a\,(1+\mu s)+s} \tag{1}$$

$$\frac{d^2o}{d\chi^2} = \frac{\kappa^2 os\eta^{-1}\beta d}{\gamma a\,(1+\mu s)+s} \tag{2}$$

$$\frac{d^2s}{d\chi^2} = \frac{\kappa^2 as\eta^{-1}\gamma}{\gamma a\,(1+\mu s)+s} \tag{3}$$

Dimensionless boundary conditions for eqns. (1)-(3) are as follows:

$$\begin{aligned} &a = a_e;\ \ \frac{do}{d\chi} = 0;\ \ \frac{ds}{d\chi} = 0; \qquad when\ \ \chi = 0 \\ &\frac{da}{d\chi} = 0\ ;\ \ o = 1-\sigma_2\left(\frac{do}{d\chi}\right);\ \ \ s = 1-\sigma_1\left(\frac{ds}{d\chi}\right); \qquad when\ \chi = 1 \end{aligned} \tag{4}$$

Eqs (1)-(3) are nonlinear differential equations.Non linear differential equations play a crucial role in many branches of physical sciences. Solving systems of nonlinear differential equations have gained importance and popularity in recent years, mainly due to the necessity of analytical solutions in diverse fields of science and engineering.

Many authors have paid attention to study the solutions of non linear differential equations by using various advanced analytical methods such asHomotopy perturbation method [25], Homotopy analysis methods [26], variational iteration methods [27], Laplace

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