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Analytical solution of system of coupled non-linear reaction diffusion equations. Part II: Direct reaction of substrate at underlying microdisc surface

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ABSTRACT

An analysis of the reaction and diffusion within polymer-modified ultramicroelectrodes is presented. This analysis contains a non-linear term related to Michaelis–Menten kinetics. In this paper, we obtain approximate analytical solutions for the non-linear equations that describe diffusion and the reaction within the polymer-modified ultramicroelectrode by employing the Homotopy perturbation method (HPM). Approximate analytical expressions for substrate and mediator concentration have been derived for all values of parameter γ_s, γ_E and m. The obtained analytical results are compared with the available limiting case results and are found to be in good agreement.

1. Introduction

Recently, there has been much interest in the development of a theoretical model for ultramicroelectrodes [1–4]. Ultramicroelectrodes (UMEs) are defined as the electrodes with one of its critical dimension less than 20 μm. Upon comparison, UMEs offer several advantages than the conventional sized electrodes. The advantages of the UME include smaller double-layer capacitance, smaller current, and *in vivo* measurements [5]. The small currents observed at UME open up the possibility of analysis in resistive media such as solvents without any electrolytes and super critical fluids [5,6]. Further, the smaller double-layer capacitance of the UME enables them to monitor various complex chemical events in single cells and neuronal region that occur within sub-microsecond time scale [7]. Moreover, UMEs have enhanced fluxes which in turn can enhance the signal-to-noise ratio during trace metal ion analysis [8]. On the other hand, UME can also be employed in scanning electron microscopy (SECM) by combining UME with a micropositioner capable of moving in three dimensions in order to achieve a spatially resolved view of chemical events much like the physical characterization provided by other scanning probe microscopies [9]. Further, UMEs have made great progress in understanding the *in vitro* neurotransmitter release, the dynamics of coupled ion, solvent and electronic transport in conducting electroactive organic thin film materials owing to the utilization of a combination of voltammetric, complex impedance, and probe beam deflection, spectroscopic and gravimetric measurements [10–16]. Moreover, modification of UME with polymers enables specific and selective biosensing.

The theoretical analysis of mediated electron transfer at electroactive polymer film which deposited on the conventional sized electrode surfaces was proposed by Albery and Hillman [17] and Andrieux et al. [18]. Lyons et al. [19,20] have reported the analysis of mediated electroanalysis substrate diffusion, Michaelis–Menten rate equation, electromigration, sensing catalysis, charge percolation and chemical reaction [17,19–22]. Rebouillat et al. [23] have calculated the concentration and current for the limiting cases.

However, to the best of our knowledge, till date there was no general analytical results corresponding to the steady-state substrate, mediator concentrations and current for all values of diffusion parameters γ_s and γ_E have been reported. The purpose of this communication is to derive analytical expressions for steady-state concentrations and current at a polymer-modified ultramicroelectrode based on "Homotopy perturbation method".

2. Assumption and formulation of the boundary value problem of direct reaction of substrate at underlying microdisc surface

In this section we have solved the system of coupled non-linear differential equations using Homotopy perturbation method [24]. Fig. 1 shows the schematic representation of the hemispherical geometry adopted by an electroactive polymer film which has been deposited on an inlaid ultramicrodisc electrode. In the presented analysis we have assumed that the substrate may react

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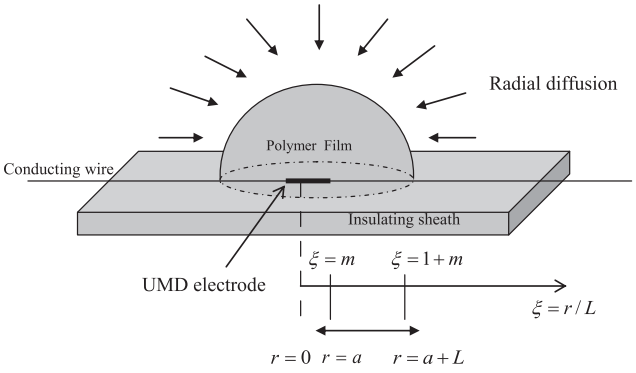

Fig. 1. Schematic representation of the geometry adopted by a polymer-coated ultramicrodisc electrode.

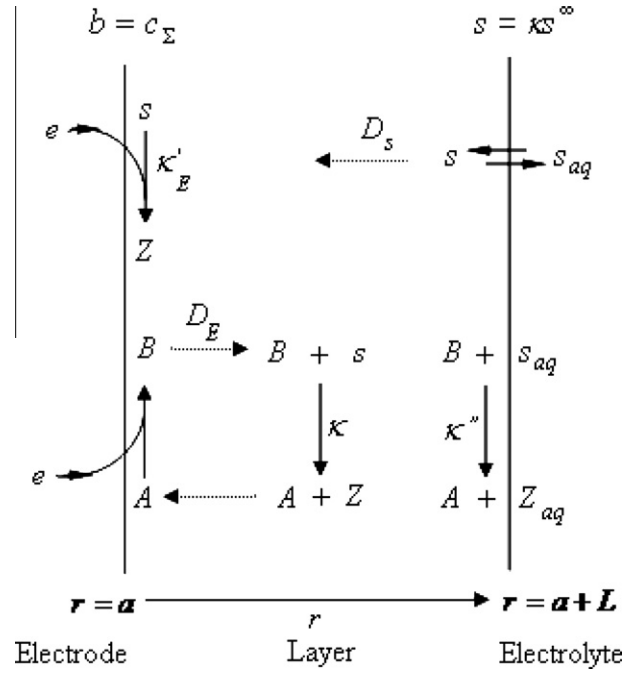

Fig. 2. Schematic representation and a basic notation of a modified electrode.

directly at the underlying support electrode surface. This process will occur at more extreme potentials than that for the mediated reaction and two current plateaus may be noted in the steady-state voltammogram [23]. A brief reaction mechanistic model is shown in Fig. 2. In this type of situation the reaction diffusion equations assume the following forms:

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left\{\xi^2\frac{du}{d\xi}\right\} - \frac{\gamma_s u v}{1+\alpha u} = 0 \tag{1a}$$

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left\{\xi^2\frac{dv}{d\xi}\right\} - \frac{\gamma_E u v}{1+\alpha u} = 0 \tag{1b}$$

where u and v denote the normalized concentrations of the substrate and the oxidized mediator species within the film and we define:

$$u = \frac{s}{ks^\infty};\quad v = \frac{b}{c_\Sigma};\quad \alpha = s^\infty/K_M;\quad \xi = \frac{r}{L};$$
$$\gamma_E = \frac{k\kappa s^\infty a^2}{D_E} = \frac{f_R}{f_E} = \frac{\lambda}{\rho\sigma^2};\quad \gamma_s = \frac{kc_\Sigma a^2}{D_s} = \frac{f_R}{f_s} = \frac{\lambda}{\sigma^2}; \tag{2}$$

The characteristic parameters σ, λ, and ρ introduced many years ago by Andrieux et al. [18]. We note that the parameter $\sigma(=\kappa D_s\delta/D'_sL = f_S/f_D)$ compares the substrate diffusion in the film with the substrate diffusion in the solution. The parameter $\lambda(=\kappa^2 kc_\Sigma D_s\delta^2/D'^2_s = f_R f_s/f_D^2)$ defines the kinetic efficiency of the substrate/mediator reaction in the polymer film and the rate of substrate diffusion in the film, with the rate of diffusion of substrate in the solution adjacent to the polymer-coated microdisc. Finally the parameter $\rho(=\gamma_S/\gamma_E)$ is the ratio of electron diffusion flux in the polymer layer with that of the substrate diffusion flux in the same medium. Also the parameter γ_s represents the catalytic reaction versus substrate diffusion in the film. In an analogous manner the parameter γ_E compares the catalytic reaction versus electron diffusion in the film. Now the boundary conditions become

$$\xi = \frac{a}{L} = m;\quad v = 1;\quad u = 0 \tag{3a}$$

$$\xi = \frac{a+L}{L} = 1+m;\quad \frac{dv}{d\xi} = 0;\quad 1-u = \sigma\left(\frac{du}{d\xi}\right) \tag{3b}$$

The net normalized current density is given by

$$\psi_\Sigma = \psi + \psi_E = \sigma\left\{\left(\frac{du}{d\xi}\right)_m - \rho\left(\frac{dv}{d\xi}\right)_m\right\} \tag{4}$$

2.1. Analytical solution of concentrations of substrate and mediator for all values of the saturation parameter α, ρ and m using HPM

Recently, many authors have applied the HPM to various problems and demonstrated the efficiency of the HPM for handling non-linear structures and solving various physics and engineering problems [24–29]. This method is a combination of Homotopy in topology and classic perturbation techniques. Recently Meena and Rajendran [30] derived analytical expressions for the substrate, product concentrations and current in order to describe and evaluate the performance of amperometric and potentiometric biosensors using Homotopy perturbation method. Also this method is used in Mathematical modeling of disc biosensors [31] and amperometric biosensor [32] at mixed enzyme kinetics and diffusion limitations in the case of substrate inhibition. Using this Homotopy perturbation method (refer Appendix A), we can obtain the following solution to Eq. (1a):

$$u = \frac{\gamma_S(1+m)^2(\xi^2-3m\xi)}{6(1+m+m\sigma)} + \left(\frac{m(1+m)^2}{1+m+m\sigma}+B\right)\left(\frac{1}{m}-\frac{1}{\xi}\right) + \frac{\gamma_s m^2(1+m)^2}{3(1+m+m\sigma)} \tag{5}$$

where

$$B = \frac{\gamma_s m(1+m)^4}{(1+m+m\sigma)^2}\left(\frac{m^2}{3} - \frac{\{(1+m)(2m-1)+\sigma(m-2)\}}{6}\right) \tag{6}$$

Eq. (5) represents the analytical expression of the substrate concentration for all values of the parameters. The solution to Eq. (1b) is as follows

$$v = 1 + \frac{\gamma_E(1+m)^2}{6(1+m+m\sigma)}[(\xi-2m)(\xi-m)] + C\left(\frac{1}{m}-\frac{1}{\xi}\right) \tag{7}$$

where

$$C = \frac{\gamma_E(1+m)^4(m-2)}{6(1+m+m\sigma)} \tag{8}$$

Eq. (7) represents the analytical expression of the mediator concentration for all values of the parameters. Using Eq. (4), we can obtain the normalized current as follows: