Electrochemistry Communications 2 (2000) 679–684

electrochemistry communications

www.elsevier.nl/locate/elecom

Modelling of reaction–diffusion processes: the theory of catalytic electrode processes at hemispheroidal ultramicroelectrodes

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Received 3 July 2000; received in revised form 18 July 2000; accepted 18 July 2000

Abstract

The transient chronoamperometric current for a catalytic electrode reaction (EC′ reaction) at a hemispheroidal Ultramicroelectrode is reported. This simple new approximate multidimensional analytical expression is valid for all values of time and all values of the rate constant. It is more accurate for all times and large K than for short times and small K. The analytical results are compared with recently presented digital simulation results (Galceran and co-workers, J. Electroanal. Chem 466 (1999) 15) for a disc electrode and are found to be in good agreement. © 2000 Published by Elsevier Science S.A.

Keywords: Non-steady state; Reaction-diffusion; EC′ reaction; Ultramicro hemispheroidal electrodes

1. Introduction

Reaction–diffusion models and their study arises in various contexts. Among them mention may be made of $A+A \rightarrow$ products batch reaction [1], bimolecular reaction [2], transport phenomena in solids [3], fractals and quantum mechanics [4], dynamic process in condensed molecular systems [5], coupled chemical/electrochemical processes [6], CE mechanisms [7,8], homogeneous first order reaction regenerating the electroactive species (EC′ mechanism) [9], modelling of catalysis along heterogeneous surface [10], ultramicroelectrodes [11] etc. Diffusion-controlled coagulation reactions were first treated by Smoluchowski [12] and have been of interest in astrophysics [13], material science [14], chemistry [15], biology [16,17] and engineering [18]. Therefore these reactions have been the subject of intense theoretical, numerical and experimental study over the past decades [1,19]. Despite these widespread occurrences, obtaining exact solution of these problems has proved quite formidable in general. In the case of electrochemical transport phenomena involving reaction diffusion of electro active species at ultramicroelectrodes, the mixed nature of the boundary conditions consists of formulating flux at one region and surface concentration c at the other viz.

$$\frac{\partial c(r,t)}{\partial t} = \nabla^2 c(r,t) - Kc(r,t) \tag{1}$$

with $c=f$ on s_1 and $\partial c/\partial n = g$ on s_2 where s_1 and s_2 refer to the electrode and insulated surface respectively, f and g are the functions dictated by the problem under study and ∇^2 is the Laplacian operator in the appropriate co-ordinates. Here c refers to the dimensionless concentration of the electroactive species. K and t denote dimensionless reaction rate and time i.e $K = ka^2/D$ and $t = DT/a^2$. 'a' denotes the characteristic length associated with the geometry under consideration ('a' may be identified as the radius for discs and spheres).

Microelectrodes are powerful tools for understanding the mechanism, behaviour of an electrochemical reaction and kinetics of fast reactions [20]. Recently, there has been much interest in the development of ultramicroelectrodes for electrochemical measurements in view of their advantages such as lower interfacial capacitance, smaller time constant and

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1388-2481/00/$ - see front matter
PII: S1388-2481(00)00103-X

reduced ohmic drop etc. It may also be of advantage in special situation such as in-vivo analysis, where only small perturbation to the system under study are sought or in surface electrochemical studies where an extremely small area may allow for the study of the behaviour of single catalytic centre or the formation and growth of single nuclei. As far back as 1984 Fleischmann et al. [21] used microdisc electrodes to determine the rate constant of coupled homogeneous reactions (CE, EC′, ECE, and DISP mechanisms). Also measurement of the current at micro electrodes in one of the easiest and yet most powerful electrochemical methods for quantitative mechanistic investigations. The use of microelectrodes for kinetic studies has recently been reviewed [22] and the feasibility demonstrated of accessing nano second time scales through the use of fast scan cyclic voltammetry [23]. However, these advantages are earned at the expense of enhanced theoretical difficulties in solving the reaction diffusion equations at these electrodes. Thus it is essential to have theoretical expressions for non steady state currents at such electrodes for all mechanisms.

However many electrode processes are complicated, for example, the catalytic electrode process (EC′ reaction) is one among them. With the increasing interest in these reactions [24] for example.

$$A + n\bar{e} \rightarrow B, \quad B + Z \overset{K}{\rightarrow} A + \text{products} \tag{2}$$

there is a need to develop methods for the determination of the kinetics of the coupled chemical reaction and to understand the relationship between the rate constant K, and the limiting current density. In general this process exhibits second-order kinetics by making the amount of Z sufficiently large so that its concentration does not change appreciably in time or space in the course of the experiment. The first order EC′ scheme arises, for instance, in the particularly interesting case of an enzyme system, when there is a high substrate concentration and a low mediator concentration so that the conditions for Pseudo first order reaction in solution are met. One existing method for determining the homogeneous kinetic parameter is to use convolution functions [25]. An accurate model for the transient response can help in the selection of the appropriate experimental time window. If cyclic voltammetry is used at the microdisc electrode, then a description of the history of the flux response is important in the selection of appropriate scan rates for the measurement. More generally a transient analytical model is essential for any model incorporating time variable boundary conditions. The spherical EC′ mechanism was firstly solved by Delmastro and Smith [34]. In electrochemical context Diao et al. [11] derived the chronoamperometric current at hemispherical electrode for EC′ reactions, whereas recently Galceran's et al. [9] evaluated Shifted defacto expression and Shifted asymptotic short-time expression for disc electrodes using Danckwerts relation. Recently the finite element method was used by Galceran's et al. [9] to simulate the current of inlaid and recessed microdisc electrode.

To my knowledge no rigorous analytical solutions for the transient current of this mechanism towards all general ultramicroelectrodes have been reported [9]. The purpose of this communication is to derive accurate polynomial expression for transient current at Hemispheroidal ultramicroelectrode for EC′ reaction.

2. Formulation of the problem and analysis

The origin of rectangular space coordinate (x,y) is located inside the electrode and at the center of electrode exhibiting appropriate symmetries. For two dimensional problems, r denotes $(x^2+y^2)^{1/2}$ and for three dimensional ones it denotes $(x^2+y^2+z^2)^{1/2}$. The required expression for current is [26]

$$\frac{i(t)}{nFD_o} = -\int_A \frac{\partial c}{\partial z}\,\mathrm{d}S \tag{3}$$

Here F is the faraday constant and $\mathrm{d}S$ is an element of surface area. The other conditions pertaining to Eq. (1) are $c=o$ when $t \rightarrow o$ and $c=o$ when $r \rightarrow \infty$. The Laplace transformation of Eq. (1) subject to the this initial condition gives

$$\nabla^2 \bar{c} = (s+K)\bar{c} \tag{4}$$

where s is the Laplace variable. The application of multidimensional theorem employed in soil infiltration studies [27] to analyze mixed boundary value problems of identical nature yields highly accurate expressions of concentration and current. The analytical formula for current is then given by (cf. Appendix A)

$$\frac{i(t)a}{nFD_oC_oA} = i_\infty(K) + K^{1/2}g(K,t) \tag{5}$$

where A is the area of the electrode, $i_\infty(K)$ is the corresponding dimensionless steady state current and

$$g(K,t) = (\pi Kt)^{-1/2}\mathrm{e}^{-Kt} - \mathrm{erfc}(Kt)^{1/2} \tag{6}$$

Eq. (5) represents the most general approximate new expressions for non steady-state current for hemispheriodal electrode for EC′ reaction. The results for a disc and a hemisphere geometries, arising from Eq. (5) is reported below.

2.1. Disc electrodes

Substitution of the appropriate expressions for $A\ (=\pi a^2)$, $i_\infty(K)$ pertaining to the disc electrode in Eq. (5) leads to the chronoamperometric as

$$\frac{i(t)}{4nFD_oC_oa}=\frac{\pi}{4}i_\infty(K)+\frac{\pi}{4}K^{1/2}g(K,t) \tag{7}$$

where the steady state current $i_\infty(K)$ is [28]

$$\frac{\pi}{4}i_\infty(K)=\frac{1+2.0016K^{1/2}+1.8235K+0.96367K^{3/2}+0.307949K^2+0.049925K^{5/2}}{1+1.365K^{1/2}+0.8826K+0.32853K^{3/2}+0.063566K^2} \tag{8}$$

Recently, Rajendran and Sangaranarayanan [28] have presented an exact expression (with accuracy less than 0.01%) Eq. (8) for the steady state current which was originally developed for the scattering of water [29] (where the Helmoholtz equation was solved in oblate spheroidal coordinates) and subsequently adapted to water infiltration [30]. Most recently, Galceran and co-workers [31] presented three new formulae for the steady state current among which they highlighted one Eq. (9)

$$\frac{\pi}{4}i_\infty(K)=\left[1+6K^{1/2}/\pi+3\pi^3K/2^6+\left(\pi K^{1/2}/4\right)^3\right]^{1/3} \tag{9}$$

with an accuracy better than 0.27% over the entire range of rate constant.

For non-steady state current, Galceran and his co-workers [9] have derived exact analytical solutions to the inlaid microdisc problems using Danckwerts expression. The Shifted asymptotic short-time current can be written as [9]

$$\frac{i(t)}{4nFD_oC_oa}=(\pi/4)\left[1+\left(K^{1/2}+1/4K^{1/2}\right)\mathrm{erf}(Kt)^{1/2}+\mathrm{e}^{-KT}/(\pi t)^{1/2}\right] \tag{10}$$

Galceran and his co-workers [9] have also presented shifted defacto expression in the following form

$$\frac{i(t)}{4nFD_oC_oa}=0.7854(1-\mathrm{e}^{-KT})+0.4431(\pi K)^{1/2}\mathrm{erf}(Kt)^{1/2}+0.2146K\int_o^t\mathrm{e}^{-0.39115/u^{1/2}-Ku}\mathrm{d}u$$
$$+\mathrm{e}^{-Kt}\left[0.7854+0.2146\mathrm{e}^{-0.39115t^{-1/2}}+0.4431t^{-1/2}\right] \tag{11}$$

Among the approximations of Eqs. (7) and (11), our approximation Eq. (7) is found to be the simplest one. Substituting $K=0$ (without reaction) in Eq. (7), we obtain the familiar first term in the asymptotic expansion for inlaid disc electrodes (Eq. (44) of Ref. [35]).

Table 1 indicates the dimensionless chronoamperometric current for disc electrode evaluated using Eq. (7) with the simulation results of Galceran et al. [9] calculated using Finite element method (FEM). The average relative difference between our Eq. (7) and Galceran et al. [9] is about 0.61%. Column 1, in Table 1 contains less accurate values than previously reported values [36]. The deviation from simulated values is due to both the approximate nature of the new suggested approach and the simulation error. In fact Eqs. (10) and (11) may be of the same order of accuracy as that or the new approximation (7)

2.2. Hemispherical electrode

If the appropriate values for $A\ (2=\pi a^2)$ and $i_\infty(K)\ (=1+K^{1/2})$ pertaining to hemispherical electrode are substituted in Eq. (5) the chronoamperometric current for hemishperical electrode can be obtained as

$$\frac{i(t)a}{nFD_oC_oA}=1+K^{1/2}+K^{1/2}\left[(\pi kt)^{-1/2}\mathrm{e}^{-Kt}-\mathrm{erfc}(Kt)^{1/2}\right]=1+K^{1/2}\mathrm{erf}(Kt)^{1/2}+(\pi t)^{-1/2}\mathrm{e}^{-Kt} \tag{12}$$

The above given Eq. (12) is identical with Eq. (19) of Ref. [11].

Table 1
Transient chronoamperometric current $i(t)/4nFD_oC_oa$ at a disc electrode for different values of K [a]

t	$K=0$		$K=1$		$K=5$		$K=10$		$K=50$		$K=100$		$K=500$	
	Eq. (7)	simulation [b]	Eq. (7)	simulation [b]	Eq. (7)	simulation [b]	Eq. (7)	simulation [b]	Eq. (7)	simulation [b]	Eq. (7)	simulation [b]	Eq. (7)	simulation [b]
10^{-3}	15.013	14.797 (1.46)	14.938	14.806 (0.89)	14.947	14.862 (0.57)	15.000	14.932 (0.44)	15.506	15.487 (0.12)	16.234	16.171 (0.38)	21.323	21.269 (0.25)
10^{-2}	5.4310	5.2207 (4.02)	5.3788	5.2702 (2.06)	5.4998	5.4453 (1.00)	5.7147	5.6611 (0.95)	7.3011	7.2706 (0.42)	9.0526	9.0378 (0.16)	18.386	18.346 (0.21)
10^{-1}	2.4010	2.2489 (6.76)	2.4458	2.3751 (2.97)	2.8962	2.878 (0.63)	3.4468	3.4309 (0.46)	6.3743	6.3543 (0.31)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)
1	1.4431	1.3736 (5.05)	1.7285	1.7155 (0.76)	2.6151	2.6038 (0.43)	3.3220	3.3130 (0.27)	6.3649	6.3536 (0.18)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)
10	1.1411	1.1152 (2.32)	1.6890	1.6824 (0.39)	2.6121	2.6036 (0.32)	3.3220	3.3130 (0.27)	6.3649	6.3536 (0.18)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)
10^{2}	1.0443	1.0361 (0.79)	1.6890	1.6824 (0.39)	2.6121	2.6036 (0.32)	3.3220	3.3130 (0.27)	6.3649	6.3536 (0.18)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)
10^{3}	1.0140	1.0114 (0.26)	1.6890	1.6824 (0.39)	2.6121	2.6036 (0.32)	3.3220	3.3130 (0.27)	6.3649	6.3536 (0.18)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)
10^{4}	1.0044	1.0036 (0.08)	1.6890	1.6824 (0.39)	2.6121	2.6036 (0.32)	3.3220	3.3130 (0.27)	6.3649	6.3536 (0.18)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)
10^{5}	1.0014	1.0011 (0.03)	1.6890	1.6824 (0.39)	2.6121	2.6036 (0.32)	3.3220	3.3130 (0.27)	6.3649	6.3536 (0.18)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)
10^{6}	1.0004	1.0004 (0.00)	1.6890	1.6824 (0.39)	2.6121	2.6036 (0.32)	3.3220	3.3130 (0.27)	6.3649	6.3536 (0.18)	8.658	8.6461 (0.14)	18.356	18.344 (0.07)

[a] The number in parentheses denotes the magnitude of the percentage deviation from the values estimated by Eq. (7).

[b] Digital simulation of Galceran et al. [9].

The reversible, quasi-reversible and irreversible reactions have the following relation, with diffusion limited reaction [32]

$$i_{\mathrm{R}} = i_{\mathrm{d}}/\theta \tag{13}$$

$$i_{\mathrm{QR}} = (i_{\mathrm{d}}/\theta)\left[1 + \frac{\pi}{\kappa\theta}\left(\frac{2\kappa\theta + 3\pi}{4\kappa + 3\pi^2}\right)\right]^{-1} \tag{14}$$

$$i_{\mathrm{IR}} = i_{\mathrm{d}}\left[1 + \frac{\pi}{\kappa}\left(\frac{2\kappa + 3\pi}{4\kappa + 3\pi^2}\right)\right]^{-1} \tag{15}$$

where

$$\theta = 1 + \exp[(nF/RT)(E - E^o] \tag{16}$$

$$\kappa = \kappa^o \exp[(-\alpha nF/RT)(E - E^o)] \tag{17}$$

Using the above relations the current for catalytic reversible [11], quasi-reversible and irreversible reactions also can be obtained. Recently Diao and Zhang [11] obtained the reversible catalytic reaction current for hemi-spherical electrode.

3. Conclusions

The transient chronoamperometric current of the catalytic electrode process at a spheriodal ultramicroelectrode has been reported and compared with numerical results. A good agreement with digital simulation data is noticed. The extension of procedure to other limiting cases of spheroidal geometries such as hemi-prolate, hemi-oblate and Whisker (needle or sessile hemishpere) electrodes etc apart from the study of scanning electrochemical microscope (SECM) response for different tip shapes [33] seems possible.

Acknowledgements

The author would like to thank Dr. P.N. Bartlett for kindly providing numerical values in Fig. 2 of Ref. [9]. The author also thanks Dr. M.V. Sangaranarayanan, Department of Chemistry, IIT, Chennai, India and Prof. R.G. Compton, Physical and Theoretical Chemistry Laboratory, Oxford University, Oxford for his encouragement and useful suggestions during the preparations of this paper. The author is very thankful to the referees for giving their valuable suggestions.

Appendix A.

The general solution of Eq. (4) using the Laplace transform method is given by [27]

$$c(r,K,t) = \sum_{n=0}^{\infty} L^{-1}\left\{K_m\left[(s+K)^{1/2} r\right]/sK_m\left[(s+K)^{1/2}\right]\right\} c_\infty(r,K) \tag{A.1}$$

where K_m is the modified Bessel function of second kind of order m. ($m = n$ for two dimensions and $m = n + 1/2$ for three dimensions geometry) and $c_\infty(r,K)$ is the corresponding steady state solution of the problem. Using the theorems in soil infiltration literature [27], Eq. (A.1) becomes

$$c(r,K,t) \approx G(r,K,t)\, c_\infty(r,K) \tag{A.2}$$

where

$$G(r,K,t) = G(\rho,\gamma) = \tfrac{1}{2}\left[\mathrm{erfc}\left((\rho/2 - \gamma)/\gamma^{1/2}\right) + \mathrm{e}^{2\rho}\mathrm{erfc}\left((\rho/2 + \gamma)/\gamma^{1/2}\right)\right] \tag{A.3}$$

where $\gamma = Kt$ and $\rho = K^{1/2}(r-1)$. The approximate expression (A.2) is more accurate for all times and large K. It is less accurate for short times and small K. The asymptotic expansion of the current in the closed form is, in the present notation (Eq. (52) of Ref. [27])

$$\frac{i(t)\,a}{nFD_oC_o A} = i_\infty(K) + K^{1/2} g(K,t) \tag{A.4}$$

where $g(K,t)$ is given in Eq. (5).

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