Journal of Theoretical and Computational Chemistry
Vol. 6, No. 2 (2007) 301–307

World Scientific
www.worldscientific.com

THE THEORY OF REACTION-DIFFUSION PROCESSES AT CYLINDRICAL ULTRAMICROELECTRODES

G. RAHAMATHUNISSA*, C. A. BASHA* and L. RAJENDRAN†

*Central Electrochemical Research Institute
Karaikudi — 630 003, Tamilnadu, India

†SMSV Higher Secondary School
Karaikudi — 630001, Tamilnadu, India
raj_sma@rediffmail.com

Received 14 November 2006
Accepted 9 January 2007

The transient chronoamperometric current for a catalytic reaction mechanism (EC' reaction) at cylindrical ultramicroelectrodes is derived using Danckwerts' expression for short time and slow reaction rate. The transient current for an EC' reaction at cylindrical microelectrodes for all time and all reaction rate is also reported.

Keywords: Reaction–diffusion; EC' reaction; ultramicrocylindrical electrode; non-steady state; Danckwert's expression.

1. Introduction

Ultramicroelectrodes are widely used for a variety of electrochemical measurement techniques and exhibits several advantageous properties compared with conventional electrodes.[1] Ultramicroelectrodes are of small size. The latter property enables ultramicroelectrodes to be used as probes to monitor chemical events inside single biological cells[2] or to monitor chemical events with very high spatial resolution, as evidenced by the increasing utilization of scanning tunneling microscopy and atomic force microscopy methodology in electrochemical investigations.[3–6] It is also established that the ratio of the faradaic to the charging current is improved as the electrodes size decreased. These are often used in electroanalysis, due to such reasons as higher current densities, faster response times and lower IR drops than planar electrodes.[1] Additionally, electrodes of a small size can be positioned close to cellular events[7] or used *in vivo*.[8] The development of ultramicroelectrodes has expanded the scope of electrochemical studies in recent years.[9,10]

The advantages of using a very small electrode have gradually been recognized for the last 10 years as our understanding of the properties of microdisks,

†Tel.: +91-4565-220126; Fax: +91-4565-38108.

microspheres, microcylinders, microband and ensembles of microelectrodes has increased. Among the possible microelectrode geometries, microcylinders such as carbon fibers[11] and platinum[12] are often used. This is because they are cheap and readily available. Their form is suited to implantation[13] and because much is known about their surface characteristics.[14]

In response to the widespread use of cylindrical ultramicroelectrode system, a considerable theoretical knowledge of their operating characteristics has been built up over recent years. Tokuda *et al.*[15] described the theory of ac voltammetry for reversible processes at microcylinder electrodes. Fahidy and Sioda[16] have analyzed time variant and steady state concentration profiles of electrochemically generated unstable radical of ions in cylindrical cells. Recently Somasundrum and Aoki[11] presented a kinetic-diffusion model of the steady state at an enzyme-modified microcylinder electrodes. More recently, Galceran *et al.*[17] presented the transient limiting current for an EC' reaction at an inlaid and recessed microdisc electrodes using Danckwert's expression.[26]

However, to the best of the author's knowledge, no purely rigorous analytical or numerical solutions for the transient current of this mechanisms (EC' reaction) towards cylindrical microelectrodes have been reported. The purpose of this communication is to derive accurate analytical expression for the current at cylindrical electrodes for an EC' reactions for short time and slow reaction rate, using Danckwert's expression.[26] The transient current for an EC' reaction at a cylindrical electrodes for all time and all reaction rate is also reported.

2. Formulation of the Problem

As a example of the reaction–diffusion problems considered, the standard pseudo first-order catalytic reaction scheme

$$\begin{gathered} \mathrm{A} \pm e^{-} \rightarrow \mathrm{B} \\ \mathrm{B} + \mathrm{Z} \xrightarrow{K} \mathrm{A} + \mathrm{Products} \end{gathered} \tag{1}$$

has been chosen, with initial and boundary conditions corresponding to potential-step methods for the cylindrical electrode. The initial boundary value problem which has to be solved in this case can be written in dimensionless forms as follows:

$$\frac{\partial c_B}{\partial \tau} = \frac{\partial^2 c_B}{\partial r^2} + \frac{1}{r}\frac{\partial c_B}{\partial r} - K c_B \tag{2}$$

where c_B denotes the dimensionless concentration of the electro-active species B, K and τ denotes dimensionless reaction rate and time, i.e. $K = ka^2/D_B$ and $\tau = D_B t/a^2$."a" denotes the characteristic length associated with the geometry under consideration ("a" may be identified as the radius of cylindrical electrode). r is the cylindrical coordinates normalized with respect to radius a. The Laplacian (here $\nabla^2 c_B = \frac{\partial^2 c_B}{\partial r^2} + \frac{1}{r}\frac{\partial c_B}{\partial r}$) takes different forms varying with coordinates, on which the characteristics of microelectrodes are reflected. The coordinates are selected so that the largest time variation of the diffusion layer is expressed by

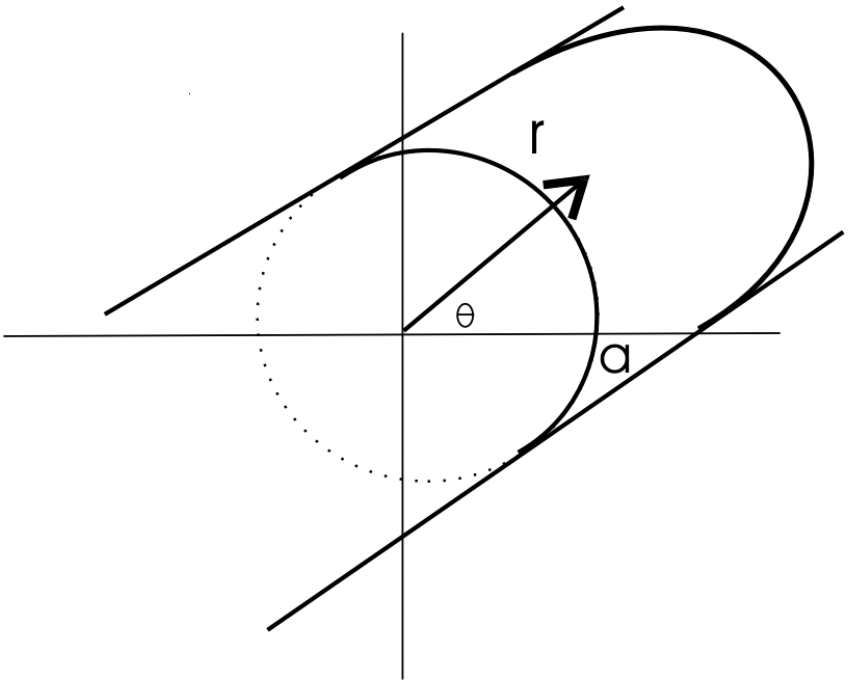

Fig. 1. Coordinates appropriate to a cylindrical electrodes.

only one dependent variable. For example, the best choice at a sufficiently long cylinder electrode is the cylindrical coordinates consisting of the radial length (r in Fig. 1) and the rotation around the axis (θ in Fig. 1). Since θ has no influence on the equiconcentration contour, the current is uniform over the electrode surface.[20]

The conditions pertaining to Eq. (2) are $c_B = 0$ when $\tau \to 0$ and $c_B = 0$ when $r \to \infty$. The mixed boundary conditions are $c_B = c_A^*$ on the electrode and $(\partial_{C_B}/\partial r)_{r=0} = 0$ on the insulated base. Here c_A^* denotes the initial bulk concentration of species A. Assuming $D_B = D_A$ and semi-infinite diffusion leads to $c_A + c_B = c_A^*$. This means that we only need solve the system for c_B. For cylindrical electrodes, normalized current is obtained by dividing the measured current by steady state current expected at the cylindrical electrode with the same bulk conditions and no homogeneous reaction.

$$\phi \equiv \frac{I(\tau)a}{4nFD_A c_A^* A} = \pm \int_0^1 \left[\frac{\partial c}{\partial r}\right]_{r=0} r dr \tag{3}$$

where F is the Faraday constant, D_A is the diffusion coefficient of species A and A is the area of the electrode. The sign "plus" corresponds to a reduction process ($n = 1$) while the sign "minus" corresponds to an oxidation process ($n = -1$).

3. Analytical Solution of the Current Using Danckwert's Expression[26] to First Order EC' Reaction

A general relationship [Danckwert's expression Eq. (4)] allows the computation of the transient limiting current for first-order EC' reaction, from the limiting currents at the same electrode when there is a no homogeneous reaction. In terms of normalized parameter, the shifting formula of Danckwert's expression is[17,26]

$$\phi(\tau) = K \int_0^\tau e^{-Ku} \phi^0(u) du + e^{-K\tau} \phi^0(\tau) \tag{4}$$

where $\phi^0(\tau)$ refers to normalized current for the system without coupled reaction. K and τ denotes dimensionless reaction rate and time [defined below the Eq. (2)]. Danckwertss' expression[17,26] makes no assumptions about the particular size or electrode geometry. Thus, Eq. (4) can be used for micro- or macro-electrodes, planar electrodes (disc, ring, band, elliptic, irregular etc.) or other three-dimensional shapes (spherical, oblate, prolate, cylindrical, conical, or irregular), for individual electrodes and for arrays of electrodes. Thus if an analytical expression (either exact or approximate) is available for $\phi^0(\tau)$ in any given problem, then Eq. (4) can readily yield the analytical solution for the associated first order problem. Recently, Galceran, Taylor and Bartlett[17] derived the transient currents at an inlaid and recessed microdisc electrodes for first order EC' reaction using Danckwert's method.[26] To our knowledge, no rigorous analytical solution for the transient current towards the cylindrical microelectrodes has been reported. Many workers have made contribution to the current understanding of the asymptotic behaviour at short time.[18−22] In terms of normalized parameters, the limiting current at the cylindrical electrode at short time where there is no homogeneous reaction is[22]

$$\phi^0(\tau) = \frac{1}{\sqrt{\pi\tau}} + \frac{1}{2} - \frac{1}{4}\sqrt{\frac{\tau}{\pi}}. \tag{5}$$

Upon application of the shifting formula [Eq. (4)], we obtain

$$\phi = \frac{I(\tau)a}{4nFD_A c_A^* A} = \frac{1}{2} + \frac{1}{\sqrt{\pi\tau}} e^{-K\tau} + \left(\sqrt{K} - \frac{1}{8\sqrt{K}}\right) erf(\sqrt{K\tau}). \tag{6}$$

The closed form of an approximate expression of limiting current without homogeneous reaction for long time[10] is not integrated easily. Szabo *et al.*[22] have given an expression of the limiting current at the cylindrical electrodes when there is no homogeneous reaction for all time

$$\phi^0(\tau) = \frac{\exp(-\sqrt{\pi\tau}/10)}{\sqrt{\pi\tau}} + \frac{1}{\ln[(4e^{-\gamma}\tau)^{1/2} + e^{5/3}]}. \tag{7}$$

Using the shifting formula [Eq. (4)], we obtain the current for all time and all reaction rate for an EC' reaction

$$\left[K\int_0^{\tau} e^{-Ku}\left(\frac{e^{-\sqrt{\pi u/10}}}{\sqrt{\pi u}}+\frac{1}{\ln[(4e^{-\gamma}u)^{1/2}+e^{5/3}]}\right)du\right] + e^{-K\tau}\left[\frac{e^{-\sqrt{\pi\tau/10}}}{\sqrt{\pi\tau}}+\frac{1}{\ln[(4e^{-\gamma}\tau)^{1/2}+e^{5/3}]}\right]. \tag{8}$$

Substituting the numerical values of the constants we obtain

$$\phi=\left[K\int_0^{\tau} e^{-ku}\left(0.5642u^{-1/2}\exp(-0.1772u^{1/2})+\frac{1}{\ln[1.4986u^{1/2}+5.2945]}\right)du\right] + e^{-K\tau}\left[0.5642\tau^{-1/2}\exp(-0.1772\tau^{1/2})+\frac{1}{\ln[1.4986\tau^{1/2}+5.2945]}\right]. \tag{9}$$

Equation (8) or Eq. (9) represents the transient current for an EC' reaction at a cylindrical electrode for all time and all reaction rates. The first term of the Eq. (8) or Eq. (9) is not integrated analytically. Therefore it can be evaluated numerically using any mathematical software. When $K = 0$, Eq. (8) is equal to Eq. (7).

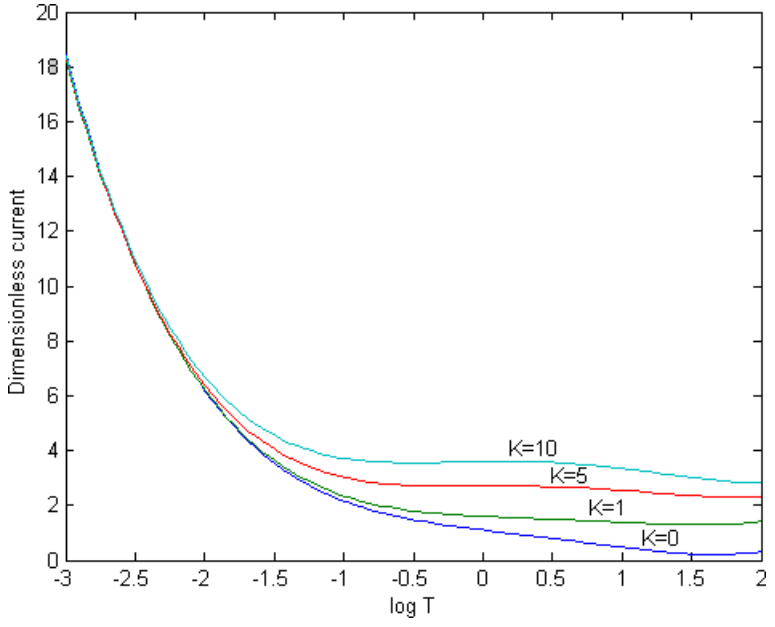

Fig. 2. Dimensionless current ϕ for varies values of $\tau$and K.

4. Discussion

The evolution of the current with time can been seen in Fig. 2 for several K values. Qualitatively the behaviour with increasing K is as expected. At short time ($\tau \leq 0.1$), the values of the current tend to the same value, regardless the value of K. The value of the current is increasing at all times due to that the catalytic reaction and the asymptotic approach to steady state appears sooner as K increases. From Fig. 2, it is inferred that the current reaches almost steady state value when $K\tau \geq 10$. Also the value of the current is independent of K when $K\tau < 0.1$. It is also known that the relative error between Eqs. (6) and (9) is very negligible for short time and slow reaction rate. Hence the closed form of an analytical expressions [Eq. (6)] may be regarded as a *de facto* solution of the of this problem.

5. Conclusion

Recently the transient chronoamperometric current for catalytic electrode reaction mechanisms, at hemispheroidal (disc, hemisphere)[23] and at hemi-oblate and prolate electrodes[24] and ring electrodes[25] is discussed. The theory of the catalytic electrode processes at cylindrical microelectrodes has been obtained in this paper. The primary result of this work is the first accurate calculation of non–steady state current at cylindrical ultramicroelectrode for an EC' mechanism over significant time intervals and reaction rates. The integral expression of current for an EC'reaction at cylindrical microelectrodes for all times and all reaction rates using Danckwert's expression is also presented.

Acknowledgments

The author is very thankful to the referees for their valuable suggestions. The work was supported by the Department of Science and Technology (DST), Government of India. The authors also thanks Director, CECRI, Karaikudi for his encouragement.

References

1. Fleischmann M, Pons S, Rolison D, Schmidt PP (eds.), *Ultramicroelectrodes Data Tech Systems*, Morganton, NC, 1987.
2. Chien JB, Wallingford RA, Ewing AG, *J Neurochem* **54**:633, 1990.
3. Bard AJ, Fan FRF, Kwak J, Lev O, *Anal Chem* **61**:132, 1989.
4. Bard AJ, Fan FRF, Pierce DT, Unwin PR, Wipf DO, Zhou F, *Science* **254**:68, 1991.
5. Mirkin M, Fan FRF, Bard AJ, *Science* **257**:364, 1992.
6. Bard AJ, Denuault G, Lee G, Mandler D, Wipf DO, *Acc Chem Res* **23**:357, 1990.
7. Huang L, Kennedy T, *Trans Anal Chem* **14**:58, 1995.
8. Llaudet E, Botting MP, Crayston JA, Dale N, *Biosens Bioelectron* **18**:43, 2003.
9. Wightman RM, Wipf DO, *Electroanalytical Chemistry*, Vol. 15, ed. Bard Aj,Marcel Dekker, New York, p. 267, 1989.
10. Amatore C Rubinstein I (eds.), *Physical Electrochemistry: Principles, Methods and Applications*, Marcel Dekker, New York, p. 131, 1995.
11. Somasundram M, Aoki K, *J Electroanal Chem* **530**:40, 2002.

12. Descroix S, Bedioui F, *Electroanalysis* **13**:131, 2001.
13. Gonon F, Suaud MF, Changny, Buda M, *Proceedings of Satellite Symposium on Neuroscience and Technology*, eds. Dittmar A, Foment JC, Lyon, p. 215, 1992.
14. Donnet JB, Basal RC, *International Fiber Science and Technology*, Vol. 3, Carbon Fibers, Dekker, New York, 1984.
15. Tokuda K, Kitamura E, Kumagai A, Ohsaka T, *J Electroanal Chem* **396**:365, 1995.
16. Fahidy TZ, Sioda RE, *J Electroanal Chem* **481**:95, 2000.
17. Galceran J, Taylor SL, Bartlett PN, *J Electroanal Chem* **15**:466, 1999.
18. Shoup D, Szabo A, *J Electroanal Chem* **140**:237, 1982.
19. Oldham KB, *J Electroanal Chem* **122**:1, 1981.
20. Aoki K, *Electroanalysis* **5**:627, 1993.
21. Philips CG, Jansons KM, *Proc R Soc Lond Ser* A **428**:431, 1990.
22. Szabo A, Cope DK, Tallman DE, Kovach PM, Wightman RM, *J Electroanal Chem* **217**:417, 1987.
23. Rajendran L, *Electrochem Commun* **2**:679, 2000.
24. Rajendran L, Ananthi SP, *Electrochem Commun* **4**:72, 2002.
25. Rajendran L, *Electrochimica Acta* **51**:4439, 2006.
26. Danckwerts PV, *Trans Faraday Soc* **47**:1014, 1951.