CHAPTER – II

THE THEORY OF REACTION–DIFFUSION PROCESSES AT

CYLINDRICAL ULTRA–MICRO–ELECTRODES

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2.1 INTRODUCTION

Ultra-micro-electrodes are widely used for a variety of electrochemical measurement techniques and exhibits several advantageous properties compared to conventional electrodes [1]. Ultra-micro-electrodes are of small size. The latter property enables ultra-micro-electrodes 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 electro analysis, due to such reasons as higher current densities, faster response times and lower IR drops than planar electrodes [1]. Additionally, electrodes of small size can be positioned close to cellular events [7] or used in vivo [8]. The development of ultra-micro-electrodes has expanded the scope of electrochemical studies [9, 10].
The advantages of using very small electrode have gradually been recognized for the last 10 years as our understanding of the properties of micro-disks, micro-spheres, micro-cylinders, micro-band and ensembles of microelectrodes has increased. Among the possible microelectrode geometries, micro-cylinders 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], because of their well known surface characteristics [14].

In response to the widespread use of cylindrical ultra-micro-electrode system, a considerable theoretical knowledge of their operating characteristics was 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. Somasundrum and Aoki [11] presented a kinetic-diffusion model of the steady state at an enzyme-modified micro cylinder electrode. Recently, Galceran et al [17]
presented the limiting current transient for an EC’ reaction at an inlaid and recessed micro-disc electrodes using Danckwerts’ expression [26]. However, there is no purely rigorous analytical or numerical solutions for the transient current of this mechanisms (EC’ reaction) towards cylindrical microelectrodes have been reported.

In this chapter an accurate analytical expression for the current at cylindrical electrodes for an EC’ reactions for short duration and reaction rate using Danckwerts’ expression [26] is derived. The transient current for an EC’ reaction at a cylindrical electrode for whole duration and all reaction rates is also reported.

2.2 FORMULATION OF THE PROBLEM

As a representative example of the reaction-diffusion problems considered, the standard pseudo first-order catalytic reaction scheme was chosen, with initial and boundary conditions corresponding to potential-step methods for the cylindrical electrode.

\[ A \pm e^- \rightarrow B, \quad B + Z \xrightarrow{k} A + \text{Products} \]  \hspace{1cm} (1)
The initial boundary value problem which has to be solved in this case can be written in dimensionless forms as follows:

\[
\frac{\partial c_B}{\partial \tau} = \frac{\partial^2 c_B}{\partial r^2} + \frac{1}{r} \frac{\partial c_B}{\partial r} - Kc_B
\]

where \( c_B \) denotes the dimensionless concentration of the electroactive species \( B \), \( K \) and \( \tau \) denote dimensionless reaction rate and time, i.e. \( \tau = D_B \alpha^2 \), \( K = k_\alpha^2 / D_B \) and \( \alpha \) denotes the characteristic length associated with the geometry under consideration (\( \alpha \) may be identified as the radius of cylindrical electrode). ‘\( r \)’ is the cylindrical coordinate normalized with respect to radius \( \alpha \). 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 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 Figure 1) and the rotation around the axis (\( \theta \) in Figure 1). Since \( \theta \) has no
influence on the equi-concentration contour, the current is uniform over the electrode surface [20].

![Fig. 1 Coordinates appropriate to a cylindrical electrode](image)

The conditions pertaining to equation (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 on the insulated base $\left(\frac{\partial c_A}{\partial r}\right)_{r=0} = 0$. 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 need to solve the system only 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 same bulk conditions and no homogeneous reaction.

\[
\phi \equiv \frac{I(\tau) a}{4nFD_A c_A A_e} = \pm \int_0^r \left[ \frac{\partial c_A}{\partial r} \right]_{r=0} \, rdr
\]  

(3)

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

2.3 ANALYTICAL SOLUTION OF THE CURRENT USING DANCKWERTS' EXPRESSION TO FIRST ORDER EC' REACTION

A general relationship (Danckwerts’ Equation (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 Danckwerts’ expression is [17, 26].
\[ \phi(\tau) = K \int_0^\tau e^{-K\tau} \phi'(u)\,du + e^{-K\tau} \phi'(\tau) \]  

(4)

Where \( \phi'(\tau) \) refers normalized current for the system without coupled reaction. \( K \) and \( \tau \) denote dimensionless reaction rate and time (defined below the equation (2)). Danckwerts’ expression [17, 26] makes no assumptions about the particular size or electrode geometry. Thus, equation (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) and for individual electrodes or for arrays of electrodes. Thus if an analytical expression (either exact or approximate) is available for \( \phi'^o(\tau) \) any given problem then, equation (4) can readily yield the analytical solution for the associated first order problem. Galceran, Taylor and Bartlett [17] derived the transient current for an inlaid and recessed microdisc electrode for first order EC’ reaction using Danckwerts’ method [26]. There is no rigorous analytical solution for the transient current towards the cylindrical micro-electrodes has been reported. Many workers have made contribution to the current understanding of the
asymptotic behaviour at short interval of time [18–22]. In terms of normalized parameters, the limiting current at the cylindrical electrode for short duration where there is no homogeneous reaction is [26]

\[
\phi^0(\tau) = \frac{1}{\sqrt{\pi \tau}} + \frac{1}{2} - \frac{1}{4} \sqrt{\frac{\tau}{\pi}}
\]  

(5)

Upon application of the shifting formula equation (4) we obtain,

\[
\phi = \frac{I(\tau)d}{4nFD_Ac_A A} = \frac{1}{2} + \frac{1}{\sqrt{\pi \tau}} e^{-k\tau} + (\sqrt{K} - \frac{1}{8\sqrt{K}})erf(\sqrt{K\tau})
\]  

(6)

The closed form of an approximate expression of limiting current without homogeneous reaction at long time [10] can not integrated easily. Szabo et al.[27] have given an expression for the limiting current at the cylindrical electrodes, when there is no homogeneous reaction for whole duration

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

Using the shifting formula (Equation (4)) we obtain the current for whole duration and all reaction rates for an EC' reaction
Substituting the numerical values of the constants we obtain

$$\phi = \left[ K \int_0^\tau e^{-ku} \left( \frac{e^{-\sqrt{\pi}u/10}}{\sqrt{\pi}u} + \frac{1}{\ln[(4e^{-\tau}u)^{1/2} + e^{5/3}]} \right) \, du \right]$$

$$+ e^{-K\tau} \left[ \frac{0.5642u^{-1/2} \exp(-0.1772u^{1/2}) + \frac{1}{\ln[1.4986u^{1/2} + 5.2945]}}{\ln[1.4986u^{1/2} + 5.2945]} \right]$$

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

2.4 DISCUSSION

The evolution of the current with time can be seen in Figure 2 for several $K$–values. Qualitatively the behaviour with increasing $K$ is as expected. At short duration ($\tau < 0.1$), the values of the current tend to be the same, regardless of the value of $K$. The value of the current increases
at whole duration due to the catalytic reaction and the asymptotic approach to steady state appears sooner as $K$ increases. From the Figure 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 equation (6) and equation (9) is very negligible for short duration and reaction rate. Hence the closed form of an analytical expression (equation (6)) may be regarded as a de facto solution of this problem.

2.5 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 at the ring electrodes [25] are discussed. The theory of the catalytic electrode processes at cylindrical micro–electrodes is obtained in this chapter. The primary result of this work is the first accurate calculation of non–steady state current. The integral expression of current for an EC’ reaction at
cylindrical micro–electrodes for whole duration and all reaction rates using Danckwerts’ expression is also presented.

REFERENCES


[22] Szabo A, Cope DK, Tallman DE, Kovach PM and Wightman RM, J


