Available online at www.sciencedirect.com
SCIENCE DIRECT
Electrochimica Acta 51 (2006) 4439–4446
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Microring electrode: Transient and steady-state chronoamperometric current for first-order EC reactions

L. Rajendran *

Department of Mathematics, SMSV Higher Secondary School, Karaikudi 630001, Tamil Nadu, India

Received 14 September 2005; received in revised form 14 December 2005; accepted 14 December 2005
Available online 26 January 2006

Abstract

The transient diffusion-limited current at the ring electrode is calculated over significant time intervals and reaction rates for the full range of significant ring sizes using Danckwerts' expression [J. Galceran, S.L. Taylor, P.N. Bartlett, J. Electroanal. Chem. 466 (1999) 15]. The steady state current for a ring electrode for EC reaction for all reaction rate is also derived. Limiting case results are compared with digital simulation results and are found to be in good agreement.

Keywords: Microring electrode; Steady state; Non-steady state; EC reaction; Chronoamperometric

1. Introduction

Recently, there has been much interest in the development of microelectrodes for electrochemical measurement [1–3]. Microelectrodes have many advantages in electrochemical measurement compared with a traditional macroelectrodes. These advantages include enhanced current density, small cell time constants and reduced ohmic drop, etc. The ring and disk microelectrodes are particularly attractive since they are easy to make and can be fabricated in compact form. Recently microring electrodes mounted on an insulating plane (Fig. 1) have received significant attention because of their increasingly wide range of experimental applications [4–10]. This is primarily because the larger perimeter-to-area ratio results in enhanced current density providing an ideal geometry for kinetic measurements and analytical applications [11,12].

Also the band and disk microelectrodes can be considered as two limiting cases of a microring electrode [13–16]. Because the limiting geometries of zero and infinite interior radius (corresponding to microdisk and microband electrodes, respectively) exhibit such dissimilar transient and steady-state behavior, a full theoretical description of the microring response poses a challenging problem. To date such investigations have been based around analytical or semi analytical approaches. Closed analytical expressions for the electrode current have been published by several authors in the "thin ring" limit [17–20], following the work of Smythe [21]. The majority of these methods implement a constant flux approximation at the electrode surface. Results that do not use this assumption have been presented recently in work by Philips and Stone [22], Tallman and coworkers [23], and Wu and Zhang [24]. Tallman reports the most complete set of results using an integral equation method [23,25], and details data for chronoamperometry [26], linear-sweep voltammetry [27], and even square-wave voltammetry [28] experiments. Jin et al. [29] used the finite analytical numerical method (FAM) to study the diffusion problems at microring electrodes. Kalapathy et al. [13] and Cope et al. [23] have calculated the transient diffusion-limited current by integral equation method over significant time intervals for the full range of significant ring sizes. Recently Brookes et al. [30] presents a general, robust method for the simulation of steady-state, chronoamperometric and linear-sweep voltammetry experiments at ring electrodes of intermediate thickness.

However, to the best of the author's knowledge, no purely numerical or analytical results have been published for electrodes of this geometry for EC reactions. The purpose of this communication is to derive asymptotic approximate expressions for the current at a ring electrodes for EC reaction for steady and non-steady state. The transient current for EC reaction at a ring microelectrodes is derived using Danckwerts' expression [31]

* Tel.: +91 4565 220126; fax: +91 4565 238108.
E-mail address: raj_sms@rediffmail.com.

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2005.12.033

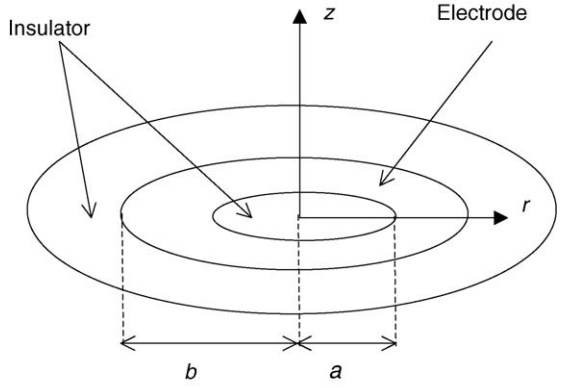

Fig. 1. Diagram illustrating the geometry of the microring electrode.

and steady state current for EC reaction at a ring microelectrodes is derived using equivalent approximation [31,32].

2. Formulation of the problem and analysis

As a representative example of the reaction-diffusion problems considered, the standard pseudo first-order catalytic reaction scheme [31].

$$A \pm e^- \rightarrow B$$

$$B + Z \xrightarrow{k} A + \text{products}$$

has been chosen, with initial and boundary conditions corresponding to potential-step method for the ring electrode. The initial boundary value problem which has to be solved in this case can be written in dimensionless forms as follows [31].

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

where $c_B \left(= C_B/c_A^*\right)$ denotes the dimensionless concentration of the electro active species B, K and T denotes dimensionless reaction rate and time, i.e. $K = ka^2/D_B$ and $T = D_B t/b^2$ (a and b may be identified as the inner and outer radii for a ring electrode). z and r are the cylindrical coordinates normalized with respect to the electrode outer radius b. Fig. 1 illustrates the geometry of the problem. Ring shape (thickness) is denoted [26] by the dimensionless parameter γ, defined as the ratio of the average of the inner and outer ring radii to the ring thickness.

$$\gamma = \frac{b + a}{2(b - a)} \tag{2}$$

This γ variable was first introduced by Cope et al. [26]. A disc has $\gamma = 1/2$ and a band has $\gamma = \infty$. The conditions pertaining to Eq. (1) are $c_B = 0$ when $T \rightarrow 0$ and $c_B = 0$ when $r \rightarrow \infty$. The mixed boundary conditions are $c_B = c_A^*$ on the electrode surface and $(\partial c_B/\partial z)_{z=0} = 0$ 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 need only solve the system for c_B.

We now use ϕ to denote the normalized current or flux. For ring electrodes, this is obtained by dividing the measured current by the steady state current expected at very thick ring electrode ($a \rightarrow 0$) with same bulk conditions and no homogeneous reaction [31,42,43].

$$\phi \equiv \frac{I}{4nFD_A c_A^* b} = \pm\frac{\pi}{2}\int_{a/b}^{1}\left[\frac{\partial c_B}{\partial z}\right]_{z=0} r\,dr \tag{3}$$

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

3. Analytical solution of the transient current for first-order EC reactions using Danckwerts' expression

A general relationship, arising from Danckwerts' expression (Eq. (4)), allows the computation of the transient limiting current for an 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

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

where $\phi^0(\tau)$ refers normalized current for the system without coupled reaction. K is the dimensionless reaction rate (defined below the Eq. (1)) and τ the dimensionless time (defined in the Eq. (12)). Dankwerts' expression makes no assumptions about the particular size or electrode geometry. Thus, Eq. (4) can be used for micro or macroelectrodes, planar electrode (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 $\phi^0(\tau)$ for any given problem, then Eq. (4) can readily yield the analytical solution for the associated first-order problem. Recently Galceran et al. [31] derived the transient currents at inlaid and recessed mocrodisc electrodes for first-order EC reaction using Danckwerts' method. To our knowledge no analytical solution for the transient current towards a ring electrode has been reported. Many workers have made contribution to the current understanding of the asymptotic behavior at short time[33–35], long time[19,36] and all times[21,37]. The limiting current at planar ultramicroelectrode at short and long time where there is no homogeneous reaction is [19,21, 33–37]

$$\frac{i(t)}{nFD_A c_A^*} \approx \frac{S}{\sqrt{\pi Dt}} + \frac{P}{2} + \frac{1}{2}(m - h)\sqrt{\pi Dt}; \quad t \rightarrow 0 \tag{5}$$

$$\frac{i(t)}{nFD_A c_A^*} \approx l_0 + \frac{l_0^2}{\sqrt{4\pi^3 Dt}}; \quad t \rightarrow \infty \tag{6}$$