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THEORIES OF DIFFUSION AT A MICRORING ELECTRODES: A REVIEW

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Microring electrodes are useful for the investigation of electrode kinetics due to their large perimeter-to-area ratio and compact nature but have hitherto been limited in application due to the absence of the underpinning theory. In this review, the analytical solutions, approximate expressions, and numerical solutions of transient chronoamperometric current at a microring electrode under diffusion control are discussed. The steady and non-steady-state current for microring electrode for an EC' reaction are also discussed. Tabular compilations of dimensionless current are provided.

Keywords: Ring electrodes; chronoamperometry; reaction-diffusion; non-steady state-EC' reaction.

1. Introduction

Microelectrodes have many advantages in electrochemical measurements compared with traditional macroelectrodes. These advantages include enhanced current density, small cell time constants and reduced ohmic drop, etc. Recently, microring electrodes have received significant attention[1–6] because of their wide range of experimental applications. This is primarily because the large perimeter-to-area ratio results in enhanced current density providing an ideal geometry for kinetic measurements. The band and disk microelectrodes can be considered as two limiting cases of a microring electrode.[7] The current on a microring and microdisk electrodes can approach a steady-state value while the current on a band microelectrode decays as the reciprocal logarithm of the time. The ring and disk geometry microelectrodes are particularly attractive since they are easy to make and can be fabricated in compact form. Like the band microelectrode, the ring microelectrode has a higher perimeter-to-area ratio than that of the disk microelectrode.

Table 1. Comparisons of maximum error of various analytical and numerical results for various values of γ.

Publication					
Authors	Ref.	Equation	$\gamma = 1$	$\gamma = 3$	$\gamma = 10$
Wu *et al.*	18	(22)	5.95%	2.76%	0.11%
Rajendran	25	(27)	−0.73%	0.35%	0.19%
Dudko *et al.*	32	(29)	−0.93%	0.65%	2.00%
Cope *et al.* (Integral equation method)	17	—	0.34%	−0.70%	−0.97%
Jin *et al.* (FAM)	23	—	0.70%	−0.30%	−0.39%
Brookes *et al.* (robust finite difference)	24	—	0.04%	−0.57%	−0.15%

Therefore, the significant increasing of mass transport rates to ring geometry compared with that on disks leads to great convenience in analytical applications[8,9] and the measurement of kinetic parameters. As is evident from Table. 1 a substantial amount of work has been done on modeling the microring electrodes.

The rotating disc (RDE) and the rotating ring-disk (RRDE) electrode[10] are very much useful in the studies of coupled homogeneous reaction and catalytic reactions. The important advantage of these electrode is that a steady state is attained rather quickly and measurements can be made with high precision, often without the need for records of oscilloscope. Moreover, at steady state, double layer charging does not enter the measurement. Also, the rates of mass transfer at the electrode surface are typically larger than the rates of diffusion alone, so that the relative contribution of mass transfer to electron-transfer kinetics is often smaller. The theoretical treatments involved in these electrodes are more difficult and involve solving a hydrodynamic problem (e.g. determining solution flow velocity profile as a function of rotation rates, solution viscosities and densities) before the electrochemical one can be tackled. Rarely, closed form or exact solutions can be obtained. This electrode is amenable to rigorous theoretical treatment and is easy to construct with a variety of electrode material. It is the most convenient and widely used electrode by the experiments.[10] This review does not deal with analytical and numerical solutions of RDE (or) RRDE.

However, theoretical studies of electrochemical behavior of microring electrode are complicated by the mixed boundary conditions, which exist on the surface containing the electrodes. As a result, complete analytical solutions to the diffusion problem are extremely difficult or even impossible to obtain. To date such investigations have been based on analytical or semi-analytical approaches. Closed analytical expressions for the electrode current have been published by several authors in the "thin ring" limit,[11−14] following the work of Smythe.[15] 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 the work by Phillips and Stone,[16] Tallman *et al.*,[17] and Wu and Zhang.[18] Tallman reports the most complete set of results using an integral-equation method,[17−19] and details data for chronoamperometry,[27] linear-sweep voltammetry,[20] and even

square-wave voltammetry[22] experiments. Jin *et al.*[23] used the finite analytical numerical method (FAM) to study the diffusion problems at microring electrodes. Kalapathy *et al.*[7] and Cope *et al.*[17] 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.*[24] present a general, robust method for the numerical solutions of steady-state, chronoamperometric, and linear-sweep voltammetry experiments at the ring electrodes of intermediate thickness. Recently, Rajendran[25] derived the transient and steady-state chronoamperometric current for the first-order EC' reactions at microring electrode. A new approach for the numerical solution of the microring electrode problem by the conform mapping technique was introduced in the work of Amatore *et al.*[26] More recently, Svir *et al.*[27] presented the numerical results of chronoamperometric current at microring electrode for ECE mechanism using the same conformal mapping technique.

Since this review aims at the theoretical comprehension of microring electrodes, various detailed numerical techniques are not discussed here. This review describes accurate analytical expression of current for ring electrode for diffusion-limited reaction and EC' reaction. It is our aim that this short review will act as an introduction to the reader who may be interested in pursuing research in this area.

2. Mathematical Formulation and Analysis of Non-Steady State Diffusion Limited Current at Microring Electrodes

We consider a simple electron transfer reaction taking place at the ring electrode surface[25]

$$A \pm e^- \rightarrow B \tag{1}$$

with an applied potential step sufficient to achieve diffusion-controlled conditions (viz. $c_A = 0$) at the electrode surface, A being the only species initially present in the solution at the concentration c_0^*. The time-dependent equation, describing the mass-transport of the species B from the electrode surface to the bulk of the solution, is

$$\frac{\partial c}{\partial t} = D \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right], \tag{2}$$

where c denotes the concentration of B. D is the diffusion coefficient of B; t is the time elapsed since the beginning of the potential step; r and z are the cylindrical coordinates describing the semi-infinite space located above the insulating plane in which the electrode is embedded (Fig. 1). The potential step is applied to the electrode at time $t = 0$ and the related initial condition for the concentration of the species B is

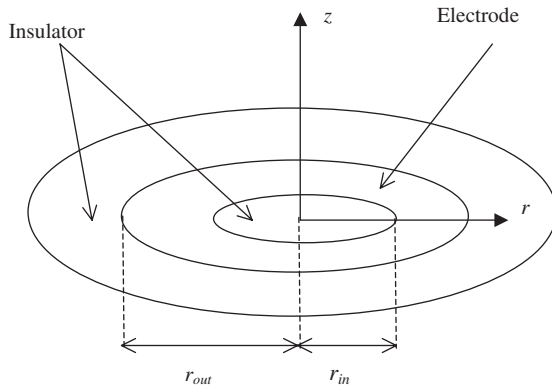$$c(r, z, 0) = 0, \quad 0 \leq r \leq \infty, \ 0 \leq z \leq \infty. \tag{3}$$

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

The boundary conditions to the partial differential equation (2), corresponding to the diffusion-controlled electrolysis,[26] are

$$\left.\frac{\partial c}{\partial z}\right|_{z=0} = 0 \quad 0 < r < r_{\text{in}} \text{ and } r > r_{\text{out}}, \tag{4a}$$

$$c = C_0 \quad r_{\text{in}} \leq r \leq r_{\text{out}}, \tag{4b}$$

$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0 \quad 0 \leq z < \infty, \tag{4c}$$

$$c \to 0 \quad z \to \infty, r \to \infty, \tag{4d}$$

where r_{in} is the inner radius and r_{out} is the outer radius of the ring, C_0 is the concentration of species B at the electrode surface (i.e. $C_0 = c_0^*$ when the two diffusion coefficients of A and B are equal). We normalize the spatial co-ordinates r and z with respect to the outer ring radius:

$$R = \frac{r}{r_{\text{out}}}, \quad Z = \frac{z}{r_{\text{out}}} \tag{5}$$

and As in Ref. 26, a dimensionless time T can be introduced

$$T = \frac{Dt}{r_{\text{out}}^2}. \tag{6}$$

Then, introducing the dimensionless concentration: $C = c/c_0$, we can rewrite Eq. (2) as

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial Z^2}. \tag{7}$$

The initial condition equation (3) becomes

$$C(R, Z, 0) = 0, \tag{8}$$

and the boundary conditions (4a)–(4d) now are

$$\left.\frac{\partial C}{\partial Z}\right|_{Z=0} = 0 \quad 0 < R < a \text{ and } R > 1, \tag{9a}$$

$$C = 1 \quad a \leq R \leq 1, \tag{9b}$$

$$\left.\frac{\partial C}{\partial R}\right|_{R=0} = 0 \quad 0 < Z < \infty, \tag{9c}$$

$$C \to 0 \quad Z \to \infty, \; R \to \infty, \tag{9d}$$

where $a = r_{\text{in}}/r_{\text{out}}$.

We consider a single electron transfer ($n = \pm 1$), so that the current passing at the electrode surface at any time is given by the following expression:

$$I(T) = \pm 2\pi F D \int_{r_{\text{in}}}^{r_{\text{out}}} \left.\frac{\partial c}{\partial z}\right|_{z=0} r\,dr, \tag{10}$$

where the sign "plus" corresponds to a reduction process ($n = 1$), while the sign "minus" corresponds to an oxidation ($n = -1$). The transient current is rewritten as a function of the dimensionless variables as follows:

$$I(T) = \pm 2\pi F D C_0 r_{\text{out}} \int_{a}^{1} \left.\frac{\partial C}{\partial Z}\right|_{Z=0} R\,dR, \tag{11}$$

so that the dimensionless current (flux) is readily expressed as in Ref. 26

$$\psi(\tau = Dt/(r_{\text{out}} - r_{\text{in}})^2) = \frac{|I(\tau)|}{4FDC_0 r_{\text{out}}} = \frac{\pi}{2} \int_{0}^{1} \left.\frac{\partial C}{\partial Z}\right|_{Z=0} R\,dR. \tag{12}$$

2.1. *Short-time current expression*

Short-time diffusion limited current for more planar geometries were determined by Oldham[28] and Phillips and Jansons.[29] The short-time current can be written as

$$i = nFDC_0 \left[\frac{A}{\sqrt{\pi Dt}} + \frac{P}{2} + \frac{1}{2}(m-n)\sqrt{\pi Dt} + \cdots \right] \quad t \to 0, \tag{13}$$

where F is the Faraday's constant, D is the diffusion coefficient of electroactive substrate, n is the charge number of the electrode reaction, and C_0 is the bulk concentration of the electroactive species. A is the area of the electrode, P is the perimeter, and t denotes the time. m is the number of separate pieces it comprises and n denotes the number of "holes" in them. Ring shape (thickness) is denoted[17] by the dimensionless parameter γ, and defined as the ratio of the average of the inner and outer ring radii to the ring thickness.

$$\gamma = \frac{r_{\text{out}} + r_{\text{in}}}{2(r_{\text{out}} - r_{\text{in}})}. \tag{14}$$

This γ variable was first introduced by Cope *et al.*[17] A disc has $\gamma = 1/2$ and a band has $\gamma = \infty$. If appropriate values for A and P pertaining to ring geometry are substituted in Eq. (13), we obtain the first two terms of short-time expression. For ring electrodes $A = \pi(r_{\text{out}}^2 - r_{\text{in}}^2)$ and $P = 2\pi(r_{\text{in}} + r_{\text{out}})$ and $m = n = 1$. Consequently, Eq. (13) becomes

$$\psi(\tau = D_{\text{B}}t/(r_{\text{out}} - r_{\text{in}})^2) = a_0\tau^{-1/2} + a_1 \quad \tau \to 0, \tag{15}$$

where

$$a_0 = \sqrt{\pi}\gamma/(2\gamma + 1), \quad a_1 = \pi\gamma/(2\gamma + 1). \tag{16}$$

2.2. *Long-time current expression*

For long time, Szabo's result[13] is expressed as

$$i(t)/nFDC_0 = l_0 + l_0^2\Big/(4\pi^3 Dt)^{1/2}, \tag{17}$$

where l_0 is the steady-state limit of the electrode. Phillips[30] has reported the next term in Eq. (17) using the method of matched asymptotic expansions. Equation (17) can be written in the form

$$\psi(\tau = Dt/(r_{\text{out}} - r_{\text{in}})^2) = b_0 + b_1\tau^{-1/2}, \tag{18}$$

where

$$b_0 = l_0/4r_{\text{out}}, \quad b_1 = (2\gamma + 1)b_0^2\Big/\pi^{3/2}, \tag{19}$$

where the steady-state value of l_0 for thin ring is[15]

$$\left(\frac{l_0}{r_{\text{out}}}\right)_{\text{exact}} = \frac{2\pi^2\gamma}{(\gamma + 1/2)\text{In}(32\gamma)} \quad \text{where } \gamma > 1/2. \tag{20}$$

For ring of arbitrary thickness, Szabo's[13] approximate version of Eq. (20) is reformulated as

$$\left(\frac{l_0}{r_{\text{out}}}\right)_{\text{empirical}} = \frac{4\pi^2\gamma/(2\gamma + 1)}{\text{In}[32(\gamma - 1/2) + \exp(\pi^2/4)]} \quad \forall\, \gamma. \tag{21}$$

2.3. *All time current expression*

Some analytical work has also been published for chronoamperometric current for all time and all values of γ for ring electrode. Wu *et al.*[18] states that Eq. (22) is applicable to any radius of ring and at any time.

$$\psi(\tau) = \frac{\pi\gamma}{2\gamma + 1}\left[\frac{1}{\sqrt{\pi\tau}} + \frac{H\sqrt{\tau} + \gamma + 0.5}{\sqrt{\pi\tau} + \gamma + 0.5}\right], \tag{22}$$

where

$$H = \pi^{3/2}/\mathrm{In}[32\gamma] \quad \text{where } \gamma > 1/2 \tag{23}$$

H equates to Szabo's l_0 in Eq. (21) as

$$H = \sqrt{\pi} l_0 / r_{\text{out}}. \tag{24}$$

Rajendran and Sangaranarayanan[31] using the previous asymptotic expressions (15) and (18), constructed the following Pade approximation:

$$\psi(\tau) = \left[\frac{p_0 + p_1 \tau^{-1/2} + p_2 \tau^{-1} + p_3 \tau^{-3/2}}{1 + q_1 \tau^{-1/2} + q_2 \tau^{-1}} \right], \tag{25}$$

where

$$p_0 = b_0, \quad p_1 = a_0 + a_1 q_1, \quad p_2 = a_0 q_1 + a_1 q_2, \quad p_3 = a_0 q_2,$$
$$q_1 = \frac{a_0 - b_1}{b_0 - a_1}, \quad q_2 = q_1^2. \tag{26}$$

Among several options available for constructing a suitable function, given partial information, the Pade approximation is one of the simplest and is easy to implement. Pade approximate gives a remarkable good representation of the whole current function for all values of time. Hence Pade approximation is a closed an accurate, and a powerful but in the end still mysterious mathematical technique. Hence this technique is widely analyzed in phase transitions and critical phenomena, viral equations of state, quadratic anharmonic oscillators and ultramicroelectroded.[31] Recently, Rajendran[25] constructed a simple and closed empirical expression (Eq. (27)) of current for all time and for all values of γ.

$$\psi(\tau) = A_1 + B_1 \tau^{-1/2} + C_1 \exp(-D_1 \tau^{-1/2}), \tag{27}$$

where

$$A_1 = a_1, \quad B_1 = a_0, \quad C_1 = b_0 - a_1, \quad D_1 = \left| \frac{a_0 - b_1}{b_0 - a_1} \right|. \tag{28}$$

The accuracy of rational function approximation given above (Eq. (25)) can be improved by considering higher order terms in short and long time solutions. But this is not possible in the above empirical expression (Eq. (27)). More recently Dudko *et al.*[32] obtained the analytical expression (Eq. (29)) of current for microring electrode.

$$\psi(\tau) = \frac{1}{4} \left[\frac{l_0}{r_{\text{out}}} + \left(\frac{4\pi\gamma}{1 + 2\gamma} - \frac{l_0}{r_{\text{out}}} \right) e^{N^2 T_D} \operatorname{erfc}(N\sqrt{T_D}) + \frac{\sqrt{\pi} 8 \gamma^2}{\sqrt{T_D}(1 + 2\gamma)^2} \right], \tag{29}$$

where

$$|N| = \frac{2\pi \left[\left(\dfrac{4\pi\gamma}{1 + 2\gamma} \right) - \dfrac{l_0}{r_{\text{out}}} \right]}{\left[\dfrac{l_0^2}{r_{\text{out}}^2} - \left(\dfrac{16\pi^2\gamma}{(1 + 2\gamma)^2} \right) \right]} \tag{30}$$

and

$$T_D = \frac{4\tau}{(1 + 2\gamma)^2}.$$ (31)

2.4. *Numerical solutions*

The application of numerical solutions and digital simulations to electrochemical problems are discussed in Refs. 33 and 34. The integral equation approach has been consistently taken by the Cope and Tallman group for the modeling of microring electrode behavior; this work continues,[17] also elsewhere.[35] The potential advantage of the method are high efficiency (due to direct calculation of the flux at the electrode surface rather than the intermediate calculation of concentration over the cell interior, with further simplification because only the integral of the flux is needed) and a unified numerical approach to a broad range of electrochemical diffusion-problems. Jin *et al.*[23] used the finite analytical numerical method (FAM) combined with a conformal map to study the diffusion problem, at microring electrode. As a result, this method has the flexibility to adapt to a number of electrode geometries and exhibits high computational efficiency. Brookes *et al.*[24] presented a robust finite difference numerical method for the simulation of electrochemical processes at microring electrode of intermediate thickness. This method relies on a meshing strategy to minimize the electrode flux errors (Table 2).

2.5. *Discussion*

Tables 3–5 indicate the dimensionless chronoamperometric current for ring electrode using Eq. (25) together with the analytical results of (i) Wu and Zhang,[18] (ii) Rajendran,[25] (iii) Dudko *et al.*[32] and numerical results of (iv) Cope *et al.*,[17] using integral equation method (v) Jin *et al.*,[23] using FAM method and (vi) Brookes *et al.*[24] using robust finite difference method. All these data are compared in Figs. 2–4. The data are shown using the differences from the Pade approximation results of Rajendran and Sangaranarayanan.[31] The maximum error of all the analytical and numerical results are given in Table 1.

3. Mathematical Formulation and Analysis of Non-Steady- and Steady-State Current at Microring Electrodes for An Ec' Reaction

As a representative example of the reaction-diffusion problems considered, the standard pseudo-first-order catalytic reaction scheme.[36]

$$\mathrm{A} \pm e^- \rightarrow \mathrm{B},$$
$$\mathrm{B} + \mathrm{Z} \xrightarrow{K} \mathrm{A} + \mathrm{Products}$$ (32)
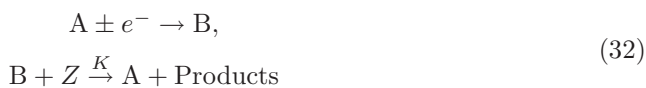
has been chosen, with initial and boundary conditions corresponding to potential-step method for the ring electrode.

Table 2. Voltammetric theory for microring electrode.

Publication		Experimental		Modeling
Authors	Ref.	Technique	Kinetics	Method
Amatore *et al.*	26	Chronoamperometry and linear sweep voltammetry	E	Conformal mapping
Brookes *et al.*	24	Steady state chronoamperometry and linear sweep voltammetry	E	Robust finite difference numerical method
Cope *et al.*	19, 20	Chronoamperometry	E	Integral equation
Dudko *et al.*	32	Chronoamperometry	E	Analytical
Oldham	JEC, 297, (1991), 3117	Voltammetry	E	Analytical
Fleishmann	11, 12.	Chronoamperometry	E	Analytical Neumann integral theorem
Gavaghan	JEC, 456, (1998), 1.	Chronoamperometry	E	Exponential expanding mesh/Expanding grid
Irina Svir *et al.*	JEC, 578, (2005), 289.	Chronoamperometry	ECE	Conformal mapping
Kalapathy *et al.*	7	Linear sweep voltammetry	E	Integral equation
Phillips *et al.*	JEC, 303, (1991), 1. 29	Chronoamperometry	E	Analytical
Rajendran and Sangaranarayanan Rajendran	25, 31, E. Analysis, 10, (1998), 506.	Chronoamperometry Chronoamperometry (reversible electron transfer reaction) Diffusion limited current	E E EC'	Pade approximation Pade approximation Danckwerts' expression
Smythe *et al.*	15	Chronoamperometry	E	Analytical
Symanski *et al.*	JEC. Soc, 135, (1988), 1985. 14	Chronoamperometry	E	Experimental
Szabo	13	Chronoamperometry	E	Analytical
Tallman	22	Square wave voltammetry	E	Integral equation
Wu *et al.*	18	Chronoamperometry	E	Analytical

3.1. *Non-steady-state current at microring electrodes*

The initial boundary value problem which has to be solved in this case can be written in dimensionless forms as follows:[36]

$$\frac{\partial c_{\mathrm{B}}}{\partial T} = \frac{\partial^2 c_{\mathrm{B}}}{\partial r^2} + \frac{1}{r}\frac{\partial c_{\mathrm{B}}}{\partial r} + \frac{\partial^2 c_B}{\partial z^2} - Kc_{\mathrm{B}}, \tag{33}$$

where c_{B} $(= C_{\mathrm{B}}/c_{\mathrm{A}}^*)$ denotes the dimensionless concentration of the electro-active species B, K and T denotes the dimensionless reaction rate and time, i.e. $K = kr_{\mathrm{in}}^2/D_{\mathrm{B}}$ and $T = D_{\mathrm{B}}t/r_{\mathrm{out}}^2$ (r_{in} and r_{out} may be identified as the inner and outer radius for a ring electrode). z and r are the cylindrical coordinates normalized with

Table 3. Comparison of various results for dimensionless current for ring electrode for various values of τ when $\gamma = 1$.

|	Analytical				Numerical Solution		
$\text{Log}(\tau)$	Pade Appr.[31] Eq. (25)	Wu *et al.*[18] Eq. (22)	Ref. 25 Eq. (27)	Dudko *et al.*[32] Eq. (29)	Integral Equation Method[17]	FAM[23]	Robust Finite Difference[24]
−2.00	41.730	41.600	41.731	41.932	41.740	41.520	41.867
−1.50	26.208	26.000	26.223	26.296	26.160	26.118	26.249
−1.00	17.454	17.151	17.482	17.573	17.300	17.244	17.374
−0.50	12.468	12.084	12.538	12.737	12.210	12.138	12.205
0.00	9.516	9.146	9.713	9.693	9.305	9.282	9.320
0.25	8.538	8.171	8.789	8.779	8.418	8.376	8.445
0.50	7.824	7.423	8.090	8.087	7.789	7.752	7.811
0.75	7.320	6.850	7.560	7.562	7.327	7.320	7.347
1.00	6.954	6.410	7.160	7.163	6.986	6.960	7.005
1.25	6.696	6.074	6.857	6.860	6.734	6.702	6.752
1.50	6.504	5.818	6.629	6.631	6.535	6.510	6.563
1.75	6.360	5.624	6.457	6.459	6.398	6.384	6.423
2.00	6.252	5.476	6.328	6.329	6.290	6.270	6.318

Table 4. Comparison of various results for dimensionless current for ring electrode for various values of τ when $\gamma = 3$.

	Analytical				Numerical Solution		
$\text{Log}(\tau)$	Pade Appr.[31] Eq. (25)	Wu *et al.*[18] Eq. (22)	Ref. 25 Eq. (27)	Dudko *et al.*[32] Eq. (29)	Integral Equation Method[17]	FAM[23]	Robust Finite Difference[24]
−2.00	125.118	124.829	125.192	124.778	125.300	124.782	125.375
−1.50	78.442	78.013	78.619	77.729	78.750	78.372	78.649
−1.00	51.940	51.049	52.065	51.237	52.490	52.276	52.387
−0.50	36.526	36.041	36.452	35.938	37.480	37.380	37.439
0.00	27.202	26.874	26.983	26.811	28.430	28.392	28.399
0.25	23.968	23.695	23.745	23.692	25.110	25.032	25.073
0.50	21.420	21.151	21.230	21.252	22.310	22.218	22.237
0.75	19.432	19.098	19.288	19.338	19.960	19.908	19.891
1.00	17.892	17.433	17.795	17.850	18.120	18.004	18.095
1.25	16.716	16.084	16.653	16.699	16.790	16.702	16.786
1.50	15.834	14.994	15.784	15.817	15.850	15.778	15.837
1.75	15.148	14.122	15.124	15.147	15.160	15.092	15.142
2.00	14.644	13.429	14.625	14.640	14.630	14.560	14.627

respect to the electrode outer radius r_{out}. The conditions pertaining to Eq. (33) are $c_B = 0$ when $T \to 0$ and $c_B = 0$ when $r \to \infty$. 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

Table 5. Comparison of various results for dimensionless current for ring electrode for various values of τ when $\gamma = 10$.

|	Analytical				Numerical Solution		
$\text{Log}(\tau)$	Pade Appr.[31] Eq. (25)	Wu *et al.*[18] Eq. (22)	Ref. 25 Eq. (27)	Dudko *et al.*[32] Eq. (29)	Integral Equation Method[17]	FAM[23]	Robust Finite Difference[24]
−2.00	417.270	416.781	417.312	417.850	417.700	416.64	416.080
−1.50	262.038	261.198	262.243	260.917	262.500	261.786	260.800
−1.00	174.451	173.222	174.916	172.696	175.000	174.258	173.661
−0.50	124.698	122.942	125.512	121.620	125.100	124.572	124.249
0.00	95.298	93.398	95.841	92.093	95.540	94.920	94.756
0.25	84.840	83.204	84.806	81.749	85.090	84.174	84.296
0.50	76.104	74.961	75.609	73.227	76.470	75.978	75.723
0.75	68.628	68.115	67.666	66.188	69.230	68.670	68.574
1.00	62.076	62.275	60.931	60.232	63.080	62.664	62.505
1.25	56.406	57.178	55.313	55.163	57.730	57.372	57.220
1.50	51.618	52.670	50.710	50.862	52.920	52.626	52.468
1.75	47.670	48.669	47.003	47.267	48.670	48.384	48.215
2.00	44.520	45.143	44.064	44.327	45.050	44.814	44.672
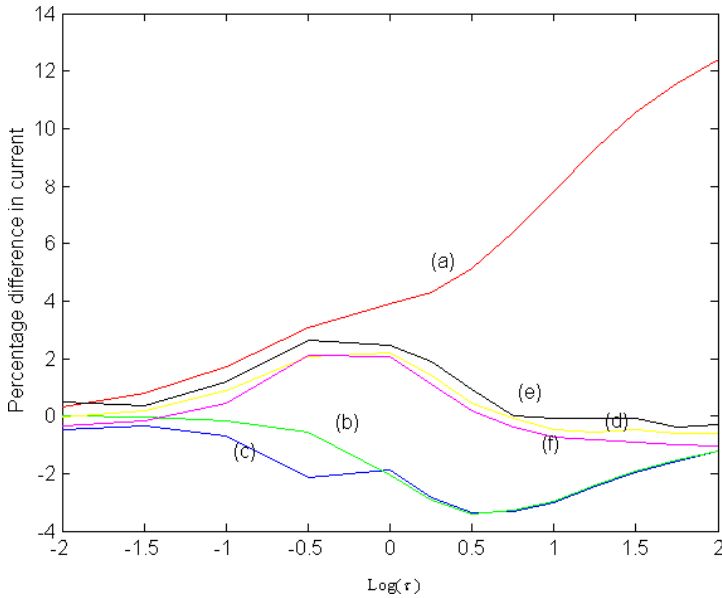
Fig. 2. Comparison of percentage difference in dimensionless diffusion limited current with Pade approximation (Eq. (25)) when $\gamma = 1$. (a) Wu *et al.*[17] Eq. (22), (b) Eq. (27), Ref. 24, (c) Dudko *et al.*[31] (Eq. (29)), (d) integral equation method,[16] (e) FAM,[22] (f) robust finite difference.[23]

current expected at very thick ring electrode ($r_{\text{in}} \to 0$) with same bulk conditions and no homogeneous reaction.[36]

$$\phi \equiv \frac{I}{4nFD_A c_A^* r_{\text{out}}} = \pm \frac{\pi}{2} \int_{r_{\text{in}}/r_{\text{out}}}^{1} \left[\frac{\partial c_B}{\partial z} \right]_{z=0} r\, dr, \qquad (34)$$
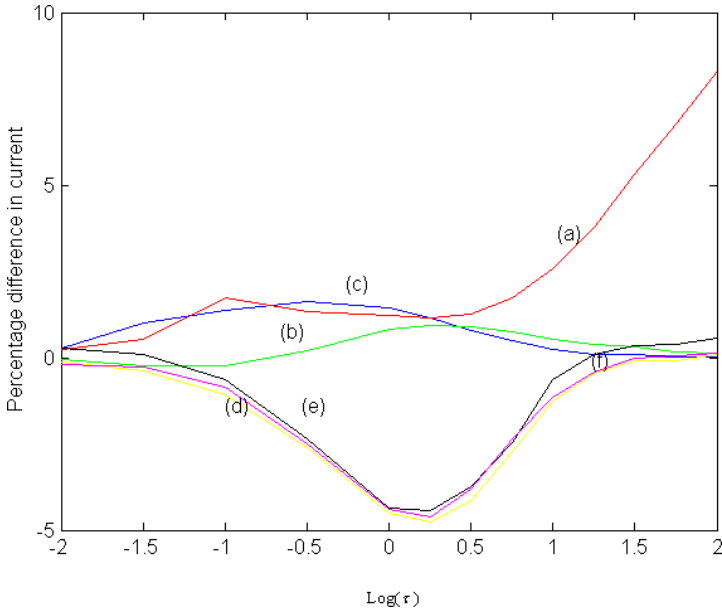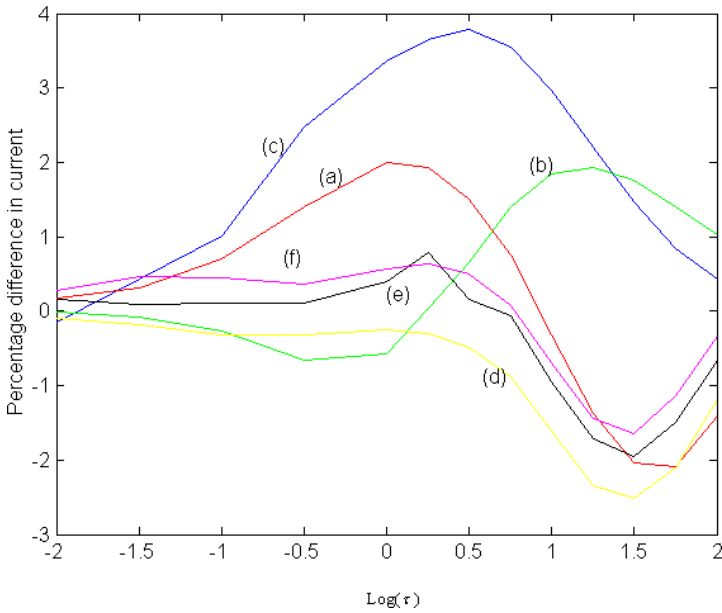
Fig. 3. Comparison of percentage difference in dimensionless diffusion limited current with Pade approximation (Eq. (25)) when $\gamma = 3$. (a) Wu *et al.*[17] Eq. (22), (b) Eq. (27) Ref. 24, (c) Dudko *et al.*[31] (Eq. (29)), (d) integral equation method,[16] (e) FAM,[22] (f) robust finite difference.[23]

Fig. 4. Comparison of percentage difference in dimensionless diffusion limited current with Pade approximation (Eq. (25)) when $\gamma = 10$. (a) Wu *et al.*[17] Eq. (22), (b) Eq. (27), Ref. 24, (c) Dudko *et al.*[31] (Eq. (29)), (d) integral equation method,[16] (e) FAM,[22] (f) robust finite difference.[23]

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 is the diffusion coefficient of species A. A general relationship, arising from Danckwerts'[36] expression 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. Using the Danckwerts' expression, Rajendran[25] obtain the current for EC' reaction for ring electrode

$$\phi(\tau) = a_1 + a_0\left[\sqrt{\pi K}\,\mathrm{erf}(\sqrt{K\tau}) + e^{-K\tau}\tau^{-1/2}\right] \quad \tau \to 0, \tag{35}$$

$$\phi(\tau) = b_0 + b_1\left[\sqrt{\pi K}\,\mathrm{erf}(\sqrt{K\tau}) + e^{-K\tau}\tau^{-1/2}\right] \quad \tau \to \infty, \tag{36}$$

$$\phi(\tau) = A_1 + B_1[\sqrt{\pi K}\,\mathrm{erf}(\sqrt{K\tau}) + e^{-K\tau}\tau^{-1/2}] + C_1\left[K\int_0^\tau \exp(-D_1/u^{1/2}\right.$$

$$\left. - Ku)du + \exp(-D_1\tau^{-1/2} - K\tau)\right] \text{ all } \tau. \tag{37}$$

The values of $a_0, a_1, b_0, b_1, A_1, B_1, C_1$ and D_1 are given in Eqs. (16), (19) and (28), respectively. Equations (35) and (36) represents the transient current for EC' reaction for ring electrode. When $\gamma = 0.5$ (disc electrode), Eq. (37) becomes

$$\phi(\tau) = 0.7854 + 0.4431\left[\sqrt{\pi K}\,\mathrm{erf}(\sqrt{K\tau}) + e^{-K\tau}\tau^{-1/2}\right]$$

$$+ 0.2146\left[K\int_0^\tau \exp(-0.39115/u^{1/2} - Ku)du\right.$$

$$\left. + \exp(-0.39115\tau^{-1/2} - K\tau)\right]. \tag{38}$$

It is the chronoamperometric current for disc electrode for EC' reaction. Equation (38) is identical with Eq. (40) of Ref. 33.

3.2. *The steady-state current at a microring electrodes*

The initial boundary value problem which has to be solved in this case can be written in dimensionless form as follows[36,37]:

$$\frac{\partial^2 c_B}{\partial r^2} + \frac{1}{r}\frac{\partial c_B}{\partial r} + \frac{\partial^2 c_B}{\partial z^2} = Kc_B, \tag{39}$$

where c_B refers to the dimensionless concentration of the electroactive species B and K denotes the dimensionless reaction rate ($K = kr_{in}^2/D_B$). The mixed boundary conditions are given by $c_B(r, 0) = 1$ on the electrode surface and $(\partial c_B/\partial z)_{z=0} = 0$ on the insulated surface. The other condition pertaining to Eq. (39) is $c_B(\infty, z) = 0$. The current for the diffusion-limited case is evaluated from Eq. (39). The calculation of the current for a pseudo-first-order EC' process, where the electroactive species is regenerated by a chemical reaction following the electron transfer process is mathematically equivalent to the calculation of the Laplace transform of the current in a transient problem.[34] Using this equivalence, from known solutions for the

short- and long-time transients of the diffusion limited current for a disc electrode in the absence of chemical reactions, Phillips derived the asymptotic expression for the steady-state current for a pseudo-first-order EC' reactions, when the dimensionless reaction rate is either very large or very small. Using the same equivalence, Rajendran obtain the steady-state current for ring electrode for EC' reaction for large and small values of K.[25]

$$\phi_{\mathrm{ss}}(K) = \frac{I}{4nFD_A c_A^* r_{\mathrm{out}}} = a_0\sqrt{\pi K} + a_1 + O(K^{-1/2}) \quad K \to \infty, \tag{40}$$

$$\phi_{\mathrm{ss}}(K) = \frac{I}{4nFD_A c_A^* r_{\mathrm{out}}} = b_0 + b_1\sqrt{\pi K} + O(K) \quad K \to 0, \tag{41}$$

where a_0, a_1, b_0, b_1 are defined in Eqs. (16) and (19). When $\gamma = 1/2$ (disc) the above equation are identical with Eqs. (20) and (19) of Ref. 34. It is of interest to devise a simple analytic expression for $\phi_{\mathrm{ss}}(K)$ which is accurate for all values reaction rate. The empirical expression[25]

$$\phi_{\mathrm{ss}}(K) = \frac{I}{4nFD_A c_A^* r_{\mathrm{out}}} = A + BK^{1/2} + C\exp(-DK^{1/2}), \tag{42}$$

where

$$
\begin{aligned}
A &= a_1 = \pi\gamma/(2\gamma + 1), \\[4pt]
B &= a_0\sqrt{\pi} = \pi\gamma/(2\gamma + 1), \\[4pt]
C &= b_0 - a_1 = \frac{l_0}{4r_{\mathrm{out}}} - \frac{\pi\gamma}{2\gamma + 1}, \\[8pt]
D &= \frac{\sqrt{\pi}(a_0 - b_1)}{b_0 - a_1} = \frac{\dfrac{\pi\gamma}{2\gamma + 1} - \dfrac{(2\gamma + 1)(l_0/r_{\mathrm{out}})^2}{16\pi}}{C}
\end{aligned}
\tag{43}
$$

reproduces the first two terms of large and small K (reaction rate) expression. It is the simple and closed analytical expression of steady-state current for ring electrode for all reaction rate.

4. Conclusions

Thus, it can be seen that in the past decade, considerable progress has been made in the understanding of diffusion process at microring electrodes. This paper has reviewed the theory of mass transport at microring electrodes under diffusion limited reaction and electrochemical reaction. The non-steady-state current at microring electrodes has also been discussed with different headings such as short-time current expression, long-time current expression and all-time current expression. The steady- and non-steady-state current at microring electrodes for EC' reactions have also been reviewed. This article is very useful for the application of microring electrodes in analytical and molecular electrochemistry. This review may be of use to some experimental researchers and few specialized electroanalytical chemists.

Acknowledgments

References

1. Lee Y, Ameniya S, Bard A, *J Anal Chem* **73**:2261, 2001.
2. Pennarun GI, Boxall C, O'Hare D, *Analyst* **121**:1779, 1996.
3. Kuhn LS, Weber A, Weber SG, *Anal Chem* **62**:1631, 1990.
4. Zhung Q, Che H, *Electroanalysis* **6**:485, 1994.
5. Cohen CB, Weber SG, *Anal Chem* **65**:169, 1993
6. Casillas N, James P, Smyrl WH, *J Electrochem Soc* **132**:L16, 1950.
7. Kalapathy U, Tallman DE, Hagen S, *J Electroanal Chem* **325**:65, 1992.
8. Khoo SB, Gunasingham H, Ang KP, Tay BT, *J Electroanal Chem* **216**:115, 1987.
9. Tay BT, Khoo SB, Loh SW, *Analyst* **114**:1039, 1989.
10. Bard AJ, Faulkner LR, *Electrochemical Methods Fundamental and Application*. 2nd edn. Chap. 9.
11. Fleischmann M, Pons S, *J Electronal Chem* **222**:107, 1987.
12. Fleischmann M, Bandyopadhy S, Pons S, *J Phys Chem* **89**:5537, 1985.
13. Szabo A, *J Phys Chem* **91**:3108, 1987.
14. Symanski JS, Bruckenstein S, Extended abstract, in 165th Meeting of the Electrochemical Society, May 1984. Electrochemical Society Penington, NJ., 1984, P. 527.
15. Smythe WR, *J Appl Phys* **22**:1499, 1951.
16. Phillips CG, Stone HA, *J Electroanal Chem* **396**:277, 1995.
17. Cope DK, Scott CH, Tallman DE, *J Electroanal Chem* **285**:49, 1990.
18. Wu Z, Zhang Z, *Acta Chim Sin* **51**:697, 1993.
19. Cope DK, Tallman DE, *J Electroanal Chem* **303**:1, 1991.
20. Cope DK, Scott CH, Tallman DE, *J Electroanal Chem* **289**:49, 1989.
21. Kalapathy U, Tallman DE, *J Electroanal Chem* **325**:65, 1992.
22. Tallman DE, *Anal Chem* **66**:557, 1994.
23. Jin B, Qian W, Zhang Z, Shi H, *J Electroanal Chem* **417**:45, 1996.
24. Brookes BA, Gavaghan DJ, Compton RG, *J Phys Chem B* **106**:4886, 2002.
25. Rajendran L, *Electrochimica Acta* **51**:4439, 2006.
26. Amatore C, Oleinick AI, Svir IB, *J Electroanal Chem* **564**:245, 2004.
27. Svir I, Oleinick A, Yunus K, Fisher AC, Wadhawan JD, Davies TJ, Compton RG, *J Electroanal Chem* **578**:289, 2005.
28. Oldham KB, *J Electroanal Chem* **129**:128, 1982.
29. Phillips CG, Janson KM, *Proc R Soc London* **A428**:431, 1990.
30. Phillips CG, *J Electroanal Chem* **333**:11, 1992.
31. Rajendran L, Sangaranarayanan MV, *J Phys Chem* **101**:4583, 1997, and references therein.
32. Dudko OK, Szabo A, Ketter J, Wightman RM, *J Electroanal Chem* **586**:18, 2006.
33. Bieniasz LK, Britz D, *Polish J Chem* **78**:1195, 2004.
34. Britz D, *Digital Simulation in Electrochemistry*, Springer, 2005.
35. Phillips CG, Stone HA, *J Electroanal Chem* **437**:15, 1997.
36. Galceran J, Taylor SL, Bartlett PN, *J Electroanal Chem* **476**:132, 1999.
37. Rajendran L, Sangaranarayanan MV, *J Phys Chem* **103**:1518, 1999.