Int. J. Electrochem. Sci., 1(**2006**)268-282

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Theories of Ultramicrodisc Electrodes : Review article

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Received: 19 August 2006 / *Accepted:* 10 September 2006 / *Published:* 1 October 2006

This review describes the theory of mass transport at a ultramicrodisc electrodes under diffusion-limited reaction and electrochemical reaction (EC'). The analytical solutions, approximate expressions and simulations of transient current at a ultramicrodisc electrode under diffusion control are discussed. Tabular compilations of dimensionless current are provided. The steady and non-steady state current for disc electrode for EC' reactions are also discussed.

Keywords: Disc electrodes; Chronoamperometry; Reaction-Diffusion; Non-Steady state; Pade approximation; EC' reactions;

1. INTRODUCTION

Microelectrodes are increasingly being used to perform a variety of electrochemical measurements [1-4]. Ultramicroelectrodes offer several advantages in electrochemical measurements such as lower interfacial capacitance, smaller time constants, reduced ohmic drop, enhanced current density, etc. The most commonly used ultramicroelectrode in analytical and molecular electrochemistry involves disc geometry, because of its easier fabrication as well as feasibility for controlled cleaning of their surfaces through simple grinding / polishing procedures [5]. An important consequence of this geometry is that the current density is not uniform across the face of the disc, but is greater at the edge. Further, for quantitative mechanistic investigations, measurement of steady state current of various radii of disc electrodes is one of the easiest electrochemical methods. The methods to simulate current at microdisc electrodes can also be employed in obtaining current pertaining to scanning electrochemical microscope [6-8]. In this technique the response of a microdisc electrode is modified by the presence of a substrate within the diffusion layer arising from electrolysis.

The microdisc electrode is by far the most popular microelectrode geometry as reflected in the volume of electrochemical literature published (refer Table-1). As is evident from Table 2, a substantial amount of work has been done on modelling the microdisc electrode. The disc is by far the most important practical case, but it is complicated theoretically by the fact that diffusion occurs in two dimensions radically with respect to axis of symmetry and normal to the plane of the electrode. Thus it is essential to have exact analytical expressions to describe the current at electrodes of this geometry. Ironically, however, predicting the current at such electrodes remains a particularly vexing problem, even in the simplest circumstances, despite many attempts having been made using a variety of approaches. Generally methods, which have had varied success, fall into three broad categories: elaborate series solution to the boundary value problem [9-19]; digital simulation using varies algorithms [10,20-31,42-49]; and integral equation method [32-40]. More recently Britz et.al [42] provides the reference values of the diffusion-limited current at a disc electrode. Since this review aims

Table 1: Electrochemical literature for the theory of microdisc electrodes

Ref.No	Authors	Title	Editions
[1]	M. Fleischmann, S. Pons, D.R. Rolison & P.P. Schmidt	Ultramicroelectrodes (1987)	P.P.Schmidt
[3]	R.M. Wightman & D.O. Wipf	Elecroanalytical Chemistry Vol.15 (1989)	A.J. Bard
[68]	M.I. Montenegro, M.A. Queiros & J.L. Daschbach	Microelectrodes Theory and Application (1991)	-
[4]	B.R.Scharifker	Microelectrodes Techniques in Electrochemistry (1992)	J.O.M.Bockris
[2]	C.Amatore	Physical Electrochemistry (1995)	I. Rubinstien
[69]	B. Speiser	Elecroanalytical Chemistry Vol.19 (1996)	A.J. Bard & I. Rubinstien
[70]	J.A.Alden	Computational Electrochemistry D.Phil Thesis (1998)	-
[71]	A.J. Bard & L.R. Faulkner	Elecrochemical Methods. (2001)	-
[72]	L.K. Bieniasz	Modern Aspects of Electrochemistry (2002)	B.E. Conway & R.E. White
[43]	D.Britz	Digital Simulation in Electrochemistry (2005)	-

Table 2: Voltammetric theory for microdisc electrodes.

Publication		Experimental Techniques	Kinetics	Modelling Method
Authors	Ref			
Alden& Compton	JPC, 101, (1997), 9606.	Steady state linear current	E,ECE,EC$_2$E, DISPI,DISP2,EC’	Finite difference & Conformal mapping PKS
Alden et.al	JPC, 101, (1997), 949.	Chronoamperometry & Cyclic Voltammetry	E,EC,EC2	Finite difference SIP
Amatore & Fosset	JEC, 328, (1992), 21.	Chronoamperometry& Steady state linear current	E	Finite difference & Conformal mapping Hopscotch
Aoki & Osteryoung	JEC, 122, (1981), 19. JEC, 160, (1984), 335	Chronoamperometry	E	Analytical
Aoki et.al	JEC 235, (1987), 87.	Steady state Voltammetry	E	Analytical
Baker & Verbrugge	JES, 137, (1990), 205.	Steady state Voltammetry	E	Analytical
Bartlett &Taylor	JEC, 453, (1998), 49.	Chronoamperometry	E	FEM
Bond et.al	JEC, 245, (1988), 71.	Steady state Voltammetry	E	Analytical , Num.Int.
Bond et.al	AC, 64, (1992), 1014.	Linear Sweep Voltammetry & Steady state Voltammetry	Square scheme	Finite difference FQEFD
Britz	JEC, 406, (1996), 15.	Chronoamperometry	E	Finite Difference, LU fact.
Britz,Poulsen & Strutwolf	E.Acta, 50, (2004), 107.	Chronoamperometry	E	Conformal mapping
Carofiglio et.al	JEC, 373, (1994),11	Steady state linear current	CE	Finite difference & Conformal mapping Hopscotch
Ciolkowski et.al	AC, 66, (1994), 3611	Chronoamperometry & Cyclic Voltammetry	DISP1	Finite difference Hopscotch
Cope & Tallman	JEC, 285, (1990), 79 & 95. JEC, 396, (1995), 265.	Chronoamperometry	E	Integral Equation Laplace
Daniele et.al.	JEC, 404, (1996), 105.	Steady state linear current	CE	Finite Difference, Hopscotch
Ferrigno et.al.	E.Acta,42(12), (1997),1895	Chronoamperometry	E	Finite Element
Flanagan& Marcoux	JPC, 122, (1973), 1051.	Chronoamperometry		Finite difference Explicit
Fleischmann et.al.	JEC, 263, (1989), 189. JEC, 263, (1989), 225.	Steady state Voltammetry	E,EC,CE	Analytical Numann Integral Theorem
Galceran, Taylor & Bartlett	JEC, 466, (1999), 15.	Steady state Voltammetry	EC’	Finite difference Danckwerts
Gavaghan	JEC,420,(1997),147	Steady state linear current	E	Finite difference SOR
Gavaghan	JEC,456 ,(1998),1.	Chronoamperometry & Steady state linear current	E	Exponentially expanding Mesh/Expanding Grid
Gavaghan	JEC, 456,(1998),13.	Chronoamperometry	E	Exponentially expanding Mesh/Expanding Grid
Gavaghan	JEC ,456, (1998),25.	Linear Sweep Voltammetry	E	ADI FIRM

Continue				
Harriman, Gavaghan & Süli	EC, 5,(2003), 519.	Chronoamperometry	E	Finite difference AFEM
Harriman et.al.	EC, 2, (2000), 150.	Steady state Voltammetry	E	AFEM
Harriman et.al.	EC, 2, (2000), 163.	Chronoamperometry	EC	AFEM
Heinze	JEC, 124, (1981), 73.	Chronoamperometry	E	Finite difference ADI
Heinze & Storzbach	Ber.Bunsenges.Phys. Chem.,90, (1986), 1043	Cyclic Voltammetry	E, EC,EC_2	Finite difference ADI
Jin et.al.	JEC, 411, (1996), 19.	Chronoamperometry & Linear Sweep Voltammetry	E	Other Numerical Fin.Analyt
Kakihana et.al.	JEC, 117, (1981), 201.	Chronoamperometry	E	Finite difference Explicit
Lavagnini et.al.	JEC, 358, (1993), 193.	Steady state Voltammetry	EC,CE, EC'	Finite difference Hopscotch
Lavagnini et.al.	JEC, 316, (1991), 37.	Linear Sweep Voltammetry		Finite Element, Conformal mapping, Expanding Grid Hopscotch
Michael et.al.	JEC, 267, (1989),33.	Cyclic Voltammetry	E, EC	Finite difference & Conformal mapping Hopscotch
Mirkin & Bard	JEC, 323, (1992), 1.	Chronoamperometry & Cyclic Voltammetry		Integral Equation
Mahon & Oldham	E.Acta, 49, (2004), 5041.	Choroamperometry	E	Finite difference& Integral. Equation Cope-Tallman method
Oldham	JEC, 122, (1981), 1.	Steady state Voltammetry	E	Analytical
Phillips	JEC, 296, (1990), 255.	Steady state linear current	1st order EC'	Analytical Transient Analogy
Phillips	JEC, 291, 1990), 251.	Steady state linear current	E	
Rajendran et.al.	JEC, 392, (1995),75. JPC,101,(1997).4583	Chronoamperometry	E	Analytical Padé approximation
Rajendran	EC, 2, (2000), 679.	Chronnoamperometry	EC'	Analytical
Rajendran	JPC B,103,(1999),1518 JTCC,5 (2006)11.	Steady state chronoamperometry	EC' EC'	Padé approximation Analytical
Saito	Rev.polarogr., 15, (1968),177.	Steady state linear current	E	Analytical
Shoup & Szabo	JEC, 140, (1982), 237.	Chronoamperometry	E	Analytical & Finite difference Hopscotch
Shoup & Szabo	JEC, 160, (1984), 1.	Choroamperometry	E, 1st order EC'	Finite Difference, Hopscotch
Speiser et.al.	Can. JC ,62,(1984),716.	Cyclic Voltammetry	EC	Other Numerical & Expanding Grid, OC
Taylor et.al.	JEC, 293, (1990), 19.	Choroamperometry & Cyclic Voltammetry	E	Finite difference& Expanding Grid, ADI
Tutty	JEC, 377, (1994), 39.	Steady state linear current	EC'	ADI
Verbrugge & Baker	JPC, 96, (1992), 4572.	Chronoamperometry	E	Finite difference Explicit
Zhuang & Sun	JEC, 440, (1997), 103.	Steady state linear current	EC_2,EC_2E, DISP1	Analytical Rxn Layer

at the theoretical comprehension of ultramicrodisc electrodes, various detailed numerical techniques are not presented here.

This review describes accurate analytical expressions for current for a disc electrodes for diffusion-limited reaction and EC' reaction. It is our aim that this short review will act as an introduction to readers who may be interested in either pursuing research in this area or in exploiting these rapidly developing technologies.

2. Mathematical formulation and analysis of non steady state current at ultramicrodisc electrodes

The non-steady state diffusion equation governing the transport of electroactive species along with the boundary condition are as follows:

$$\frac{\partial^2 c(r,z,t)}{\partial t} = D_0\left[\frac{\partial^2 c(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c(r,z,t)}{\partial r} + \frac{\partial^2 c(r,z,t)}{\partial z^2}\right] \tag{1}$$

where c is the concentration, D_0 is the diffusion coefficient of electroactive substrate, t the time, r the radical distance from the central axis of the cylindrical system and z the vertical distance from the disc. The initial condition is given by $c=1$ at $t = 0$. The mixed boundary conditions are given by $c(r, 0, t) = 0$ on the electrode surface and $\partial c / \partial z \,|_{z=0} = 0$ on other regions. The other condition pertaining to Eq(1) is $c = 1$ when $z, r \to \infty$ [43]. Let us define $\tau = 4D_0 t/a^2$. The current time curve is

$$i/i_{ss} = f(\tau) \tag{2}$$

where $i_{ss}(= 4nFD_0 c_0^b a)$ is the steady state diffusion current at disc electrode which was first derived by Saito [6]. Here F is the Faraday's constant and D_0 is above , n is the charge number of the electrode reaction and c_0^b is the bulk concentration. The function $f(\tau)$ was determined as two power series applicable in different domains of τ [9,10,12] .

2.1. Short-time current expression

Short time diffusion limited current for more planar geometries were determined by Oldham [17] and by Phillips and Jansons [14]. The short-time current can be written as

$$f(\tau) = \frac{1}{4a}\left[\frac{A}{\sqrt{\pi Dt}} + \frac{P}{2} + \frac{\sqrt{\pi Dt}}{2} + \ldots\right] \tag{3}$$

where A is the area of the electrode, P is the perimeter and t denotes the time. From the above expression, it follows that the short-time response generally has the following components: (i) An evanescent term ($t^{-1/2}$) that decreases with increase in time.(ii) A time-independent prompt component and (iii) augmentative components whose magnitude increase with time, as $t^{1/2}$, t , $t^{3/2}$ etc. If appropriate values for A and P pertaining to disc geometry are substituted in Eq. (3), we obtain the first three terms of short-time expression. Using Wiener-Hopf technique, Aoki and Osteryoung [12] provide the short time solution

$$f(\tau) = 0.88623\tau^{-1/2} + 0.7854 + 0.094\tau^{1/2} \tag{4}$$

However, this approximation is not quit correct [43]. Aoki and Osteryoung state [12] that they have adjusted the third coefficient (0.094) so that the approximation meshes better with their long-time approximation [43]. This was pointed out by Phillips and Jansons [14], who then presented the correct series

$$f(\tau) = 0.88623\tau^{-1/2} + 0.7854 + 0.111\tau^{1/2} \tag{5}$$

This slightly extends the range of applicability of the approximation [43]. Rajendran et.al. [18] obtained a much improved short time non-steady state diffusion limited current from steady state current for EC' reaction as in Eq.(6) .

$$f(\tau) = \frac{\pi^{1/2}}{2}\tau^{-1/2} + \frac{\pi}{4} + \frac{\pi^{1/2}}{16}\tau^{1/2} - \frac{\pi}{128}\tau + \frac{\pi^{1/2}}{384}\tau^{3/2} + O(\tau^2)$$

$$= 0.88623\tau^{-1/2} + 0.7854 + 0.11078\tau^{1/2} - 0.0245\tau + 0.00462\tau^{3/2} + O(\tau^2) \tag{6}$$

This is the accurate analytic expression of current for short time. More recently Mahon and Oldham [19] obtained the short time current (Eq. (7)) using “Cope and Tallman” method.

$$f(\tau) = 0.88623\tau^{-1/2} + 0.7854 + 0.11078\tau^{1/2} - 0.0236\tau + 0.0013\tau^{3/2} \tag{7}$$

The coefficients of fourth and fifth term of Eq.(6) and Eq.(7) are slightly different.

2.2. Long-time current expression

For long time, Szabo's result [41] is expressed as

$$f(\tau) = \frac{1}{4a}\left[l_0 + l_0^2 / (4\pi^3 Dt)^{1/2}\right] \tag{8}$$

where l_0 is the steady state limit of the electrode. Phillips [15] has reported the next term in Eq. (8) using the method of matched asymptotic expansions. For long times, a complicated expression was derived by Aoki and Osteryoung [9] , but it was incorrect, as pointed out Shoup and Szabo [10] who gave the corrected expression, also given by Aoki [42], with one more term [43].

$$f(\tau) = 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2} + O(\tau^{-7/2}) \quad (9)$$

For very large τ , this becomes the steady state value of Saito [43]. Aoki and Osteryoung [12] short and long time curve overlap in the domain $0.82 \le \tau \le 1.44$. Recently Rajendran and Sangaranarayanan [18] also derived Eq(10) for non steady state diffusion limited current for long time.

$$f(\tau) = 1 + 4\pi^{-3/2}\tau^{-1/2} - 32\left(\frac{1}{\pi^2} - \frac{1}{9}\right)\pi^{-3/2}\tau^{-3/2} + 48\left(\frac{16}{\pi^4} - \frac{8}{3\pi^2} + \frac{71}{675}\right)\pi^{-3/2}\tau^{-5/2} + O(\tau^{-7/2}) =$$
$$1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2} + O(\tau^{-7/2}) \quad (10)$$

More recently Mahon and Oldham [19] obtained the much improved long time current (Eq.(11)) using “Cope and Tallman” method.

$$f(\tau) = 1 + 0.7183\tau^{-1/2} + 0.0563\tau^{-3/2} - 0.0065\tau^{-5/2} - 0.0224\tau^{-7/2} + 0.0444\tau^{-9/2} \quad (11)$$

This slightly extends the range of applicability of the approximation for long time. Rajendran and Sangaranarayanan in 1999 [18] and Mahon and Oldham in 2004 [19] generated concordant results although the approaches are somewhat different. Unlike the approximation of Aoki and Osteryong or the universal approximation of Shoup and Szabo, Mahon and Oldham’s [19] short time and long time solution yield accurate current values over the whole time scale without a gap [43].

2.3. All-time current expression

Shoup and Szabo’s [10] general approximation for all values of time

$$f(\tau) = 0.7854 + 0.8862\tau^{-1/2} + 0.2146\exp(-0.7823\tau^{-1/2}) \quad (12)$$

yields results within 0.6% of Heinze’s [20] simulated data. Rajendran and Sangaranarayanan [18], using their previous asymptotic expressions (6) and (10), constructed the following [5/4] Pade approximation.

$$f(\tau) = \frac{1 + 2.5929x + 3.9686x^2 + 4.51506x^3 + 3.47861x^4 + 1.34989x^5}{1 + 1.87459x + 2.62197x^2 + 2.57529x^3 + 1.52319x^4} \quad (13)$$

where x= $\tau^{-1/2}$. We reiterate here that Eq (13) represent the most accurate expression (average error is 0.006 %.) for diffusion limited current for all time at an ultramicrodisc electrodes.

3. Discussion

Table-3A indicates the dimensionless chronoamperometric current for disc electrodes evaluated using equation (13) together with the simulation results of (i) Heinze [20] calculated using the Alternating direction method, (ii) Shoup and Szabo [10] employing the Hopscotch method, and (iii) Amatore [31] using a combination of conformal maps and the Hopscotch algorithm method, (iv) Jin et.al [25] using Finite analytical and numerical (FAM) methods, (v) Gavaghan [28,29] using the Fully-implicit finite difference (FIFD) method, and (vi) analytical results of Mahon and Oldham [19] using the Cope and Tallman method. The average relative difference between Padé approximant (Eq. (13)) and Heinze's numerical results is ca. 0.006%. Shoup and Szabo's [10] de facto expression (Eq.(12)) is within 0.6% of Heinze's simulated data. Eq.(13) is a more convenient analytical expression of chronoamperometric current for disc electrodes for all time .

Table **3A:** Transient Chronoamperometric current at ultramicrodisc electrodes $f(\tau)$ where $\tau = 4D_0 t / a^2$. The number in parenthesis denotes the magnitude of the percentage deviation from the values estimated by Eq. (13).

τ	[5/4] Pade Eq (13)	Digital Simulation of Heinze [20]	Digital Simulation of Szabo [10]	Digital Simulation of Amatore et.al [31]	Digital Simulation of Jin et.al [25]	Digital Simulation of Gavaghan et.al [28]	Cope-Tallman Method [19]	Eq (6) or Eq (7) Short time	Eq (11) Long time
0.01	9.659	9.660 (0.01)	9.632 (0.28)	9.653 (0.06)	9.673 (0.14)	9.657 (0.02)	9.658 (0.01)	9.658 (0.01)	-
0.04	5.238	5.237 (0.02)	5.226 (0.23)	5.236 (0.04)	5.242 (0.07)	5.235 (0.06)	5.237 (0.02)	5.237 (0.02)	-
0.09	3.771	3.772 (0.03)	3.768 (0.08)	3.768 (0.08)	3.771 (0.00)	3.767 (0.11)	3.771 (0.00)	3.771 (0.00)	-
0.25	2.609	2.609 (0.00)	2.601 (0.30)	2.605 (0.15)	2.606 (0.11)	2.605 (0.15)	2.608 (0.04)	2.608 (0.04)	-
0.64	1.969	1.969 (0.00)	1.969 (0.00)	1.966 (0.15)	1.965 (0.20)	1.965 (0.20)	1.967 (0.10)	1.967 (0.10)	-
1.21	1.688	1.688 (0.00)	1.678 (0.47)	1.678 (0.59)	1.684 (0.23)	1.685 (0.18)	1.686 (0.12)	1.686 (0.12)	1.685 (0.18)
2.25	1.495	1.495 (0.00)	1.488 (0.27)	1.488 (0.47)	1.490 (0.33)	1.493 (0.13)	1.494 (0.07)	1.494 (0.07)	1.494 (0.07)
4.00	1.367	1.367 (0.00)	1.366 (0.07)	1.367 (0.00)	1.363 (0.29)	1.367 (0.00)	1.366 (0.07)	1.367 (0.00)	1.366 (0.07)
6.76	1.280	1.280 (0.00)	1.279 (0.00)	1.279 (0.00)	1.276 (0.31)	1.279 (0.08)	1.279 (0.08)	1.278 (0.16)	1.279 (0.08)

Digital simulation of this problem also has been performed by many different techniques. More recently Britz et.al [42] provides reference values of the diffusion-limited current at a disc electrode. This reference values in the form of a discrete set of current values is very much useful to find the current at any time using interpolation [42]. In Table 3B Shoup and Szabo's [10] general approximation (Eq(12)) and Rajendran and Sangaranarayanan [18] two point Pade approximation (Eq(13)) for all values of time are compared with reference values of Britz et.al [42]. The average relative error between Shoup and Szabo's results and simulation results of Britz et.al [42] is 0.49 % whereas the average relative error between Rajendran and Sangaranarayanan [18] two point Pade approximation and simulation results of Britz et.al [42] is 0.04 %.

Table 3B: Comparison of all time current expressions (Eq (13) and Eq (12)) with Britz et-al [42] reference values of diffusion limited current at disc electrodes. The number in parenthesis denotes the magnitude of the percentage deviation from the values estimated by reference values

$\tau/4$	Britz et.al [42] Reference values	Rajendran et.al [18] Pade approximation Eq [13]	Shoup and Szabo [10] general approximation Eq [12]
0.010	5.2377.	5.2378 (0.00)	5.2207 (0.32)
0.020	3.9481	3.9483 (0.00)	3.9321(0.41)
0.030	3.3793	3.3795 (0.01)	3.3661 (0.40)
0.040	3.0416	3.0419 (0.01)	3.0313 (0.34)
0.050	2.8120	2.8124 (0.02)	2.8043 (0.27)
0.070	2.5125	2.5131 (0.02)	2.5091 0.14)
0.100	2.2477	2.2486 (0.04)	2.2489 (0.05)
0.150	2.0020	2.0032 (0.05)	20076 (0.28)
0.200	1.8577	1.8590 (0.07)	1.8657 (0.43)
0.250	1.7606	1.7618 (0.07)	1.7697 (0.52)
0.275	1.7226	1.7239 (0.08)	1.7321 (0.55)
0.300	1.6896	1.6909 (0.08)	1.6994 (0.58)
0.325	1.6607	1.6620 (0.07)	1.6707 (0.60)
0.350	1.6351	1.6363 (0.07)	1.6451 (0.62)
0.400	1.5915	1.5926 (0.07)	1.6016 (0.63)
0.450	1.5556	1.5567 (0.07)	1.5657 (0.65)
0.500	1.5255	1.5265(0.07)	1.5355 (0.65)
0.550	1.4997	1.5007 (0.07)	1.5095 (0.65)
0.600	1.4774	1.4782 (0.06)	1.4869 (0.65)
0.650	1.4578	1.4586 (0.05)	1.4671 (0.64)
0.700	1.4404	1.4411 (0.05)	1.4494 (0.63)
0.800	1.4108	1.4114 (0.04)	1.4193 (0.61)
0.900	1.3864	1.3869 (0.03)	1.3945 (0.58)
1.000	1.3659	1.3664 (0.03)	1.3736 (0.56)

Alden et.al [44] applied the strongly implicit procedure (SIP) to this problem. Gavaghan and Rollett [45] performed the simulation of the Finite element method with a uniform rectangular mesh by correcting the boundary singularities and Galceran et.al. [46] applied the same method but used the non uniform triangular mesh. Harriman et.al. [47] applied the adaptive finite element method to this problem and gave the results in the form of figures. Qian et.al. [48] gave the results of this problem as an extreme of an oblate hemispherical microelectrodes. Bartlett and Taylor [49] used finite element method to this problem. Non steady-state diffusion limited current can also been obtained using various numerical methods (Refer Table-1 and Table-2)

4. Mathematical formulation and analysis of steady and non steady state current at ultramicrodisc electrodes for EC' reaction

As a representative example of the reaction-diffusion problems considered, the standard pseudo-first-order catalytic reaction scheme [50]

$$\begin{aligned} &A + e \rightarrow B \\ &B + Z \xrightarrow{k} A + products \end{aligned} \qquad (14)$$

has been chosen, with initial and boundary conditions corresponding to potential step method for the disc electrode.

4.1. Steady state current at ultramicrodisc electrodes

The initial boundary value problem which has to be solved in this case can be written in dimensionless form as follows

$$\nabla^2 c(r,z) - Kc(r,z) = 0 \qquad (15)$$

where c refers to the dimensionless concentration of the electroactive species B, K denotes dimensionless reaction rate i.e, $K = ka^2 / D_B$ and 'a' denotes the characteristic length associated with the geometry under consideration ('a' may be identified as the radius for disc). The condition pertaining to Eq. (15) is c=0 when $r \rightarrow \infty$.

Some theoretical work has also been published for the first order EC' scheme at disc and hemispherical electrodes. Delmastro and Smith [51] solved the mass transport equations at a dropping mercury electrode for the pseudo-first order reaction. Fleischmann et.al. [52] adapted this to give an expression for a spherical electrode, as in Eq.(16).

$$I / I_0 = 1 + \frac{\pi}{4} K^{1/2} \qquad (16)$$

Dayton et.al [53] also derived the spherical response using Neumann's integral theorem. Denuault et.al. [54,55] derived an analytical expression for the steady-state at a spherical electrode due to a second-order EC' process. Oldham [56] has derived the current for pseudo-first order kinetics at a microdisc electrodes using the 'equivalent sphere' approximation, in Eq. (17).

$$I / I_0 = 1 + \frac{2}{\pi} K^{1/2} \qquad (17)$$

Bender and Stone [57] tackled the problem of finding an exact expression for steady-state current for disc electrode by means of integral equation. Zhuang and Chen [58] have derived the current equation for EC' reaction at spherical electrodes for steady state conditions using the concept of the steady-state reaction-diffusion layer. Phillips [59] derived a pair of asymptotic equations for the pseudo-first order EC' behavior at a microdisc electrode without resorting to a spherical approximation. The first expression is valid at small rate constants, in Eq. (18). The second expression is valid at large rate constants in Eq. (19).

$$I/I_0 = 1 + \frac{2}{\pi}K^{1/2} + \left(\frac{4}{\pi^2} - \frac{1}{3}\right)K \qquad K \to 0 \qquad (18)$$

$$I/I_0 = \frac{\pi}{4}\left(K^{1/2} + 1 + \frac{1}{4K^{1/2}}\right) \qquad K \to \infty \qquad (19)$$

Most recently Galceran and Co-workers [61] obtained the current of inlaid and recessed microdisc electrodes using finite element method. Rajendran et.al [60] have derived an exact analytical expression Eq. (20) (with accuracy less than 0.01%) for steady-state current for all K using two-point Pade approximation. Here the accuracy of steady state current for disc electrode is calculated by taking the Galceran et.al [61] simulations values as exact.

$$I/I_0 = \frac{1 + 2.0016K^{1/2} + 1.8235K + 0.96367K^{3/2} + 0.307949K^2 + 0.049925K^{5/2}}{1 + 1.365K^{1/2} + 0.8826K + 0.32853K^{3/2} + 0.063566K^2} \qquad (20)$$

Most recently Galceran and Co-workers [61] presented three new formula for steady state current among which they highlighted one in Eq. (21)

$$I/I_0 = \left[1 + 6K^{1/2}/\pi + 3\pi^3 K/2^6 + (\pi K^{1/2}/4)^3\right]^{1/3} \qquad (21)$$

with accuracy better than 0.27%. More Recently Rajendran derived the chronoamperometric current [62] for the disc electrode

$$I/I_0 = 0.7854 + 0.7854K^{1/2} + 0.2146\exp(-0.6934K^{1/2}) \qquad (22)$$

Among the approximation of Eqs. (16) to (22), Eq. (22) to be the simplest one with 0.22% average relative error. Table 4 indicates the dimensionless chronoamperometric current for disc electrodes evaluated using Eq.(22) together with the analytical results of (i) Oldham [56] (error 3% for $K<1$), (ii) Fleischman [52], employing equivalent sphere approximation (error 3% for $K<0.07$), (iii) Galceran [61], using asymptotic expression (error 0.27% for all K), (iv) Rajendran [60], calculated using two-point Pade approximation (error 0.01% for all K).

This result is also compared with the simulation results of (i) Lavagnini et.al [63], employing hopscotch method, (ii) Galceran et.al. [61], using finite element method. The average relative error between our new Eq. (22) and Galceran et.al. [61] simulations results is about 0.22%. Numerical simulation of currents, for disc electrode can also be obtained from hopscotch method [63], adaptive moving-grid technique [64], ILU (Incomplete LU factorization) preconditioned Krylov subspace methods [65] and adaptative finite element method [66]. These involve considerable computational effort.

4.2 Non steady state current at ultramicrodisc electrodes

In the previous section 4.1, various analytical and numerical results of steady state current of EC' reaction for disc electrodes are completely discussed. The initial boundary value problem which has to be solved for the case of non steady state can be written in dimensionless form as follows

$$\frac{\partial c(r,z,t)}{\partial t} = \nabla^2 c(r,z,t) - Kc(r,z,t) \tag{23}$$

Table 4. Theoretical and simulated for steady state current in a disc electrode for various rate constants K

K	Oldham et.al [56] Eq.(17)	Fleischmann et. al [52] Eq.(16)	Phillips et. al [59]		Galceran et.al [61] Eq.(21)	Rajendran et.al [60] Eq.(20)	Raiendran [62] Eq.(22)	Hopscotch Method [63]	Finite Element Method [67]
			Small K Eq.(18)	Large K Eq.(19)					
10^{-4}	1.006	1.008	1.006		1.006	1.006	1.006	1.010	1.003
10^{-3}	1.020	1.025	1.020		1.020	1.020	1.020	1.023	1.016
10^{-2}	1.064	1.079	1.064		1.064	1.064	1.064	1.066	1.060
10^{-1}	1.201	1.248	1.209		1.208	1.208	1.206	1.209	1.203
1	1.637	1.785	1.709	1.767	1.692	1.689	1.678	1.689	1.682
10^{1}	3.013	3.484		3.331	3.329	3.322	3.293	3.320	3.313
10^{2}	7.366	8.854		8.659	8.662	8.658	8.640	8.620	8.646
10^{3}	21.132	25.836		25.628	25.629	25.628	25.622	25.480	25.617
10^{4}	64.662	79.540		79.327	79.328	79.328	79.325	79.088	79.335

where c refers to the dimensionless concentration of the electroactive species, K and t denotes 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 disc). The conditions pertaining to Eq. (23) are $c(r,z,0) = 1$ and $c(r,0,t)=0$ on the electrode surface. For non-steady state current, Galceran and his co-workers [67] have derived exact analytical solutions to the inlaid microdisc problems using Danckwerts expression. The shifted asymptotic short-time current can be written as [67]

$$\frac{i(t)}{4nFD_0C_0a} = (\pi/4)\left[1 + (K^{1/2} + 1/4K^{1/2})erf(Kt)^{1/2} + e^{-Kt}/(\pi t)^{1/2}\right] \tag{24}$$

Galceran and his co-workers [67] have also presented shifted defacto expression in the following form

$$\frac{i(t)}{4nFD_0C_0a} = 0.7854(1 - e^{-Kt}) + 0.4431(\pi K)^{1/2} erf(Kt)^{1/2} + 0.2146K\int_0^t e^{-0.39115u^{-1/2} - Ku}du$$
$$+ e^{-Kt}[0.7854 + 0.2146e^{-0.39115t^{-1/2}} + 0.4431t^{-1/2}] \tag{25}$$

Recently Galceran et.al. [67] derived the simulation results for disc electrodes using finite element method. For K=10, the difference between Eq. (25) and the simulation results remains under 0.17%. For K=1 the limit is 0.81% and for K=100 the maximum difference is 0.03%. Rajendran [50] also derived the transient chronoamperometric current for a catalytic electrode reaction (EC' reaction) at a disc electrodes as in Eq(26).

$$\frac{i(t)}{4nFD_0C_0a} = \frac{\pi}{4}i_\infty(K) + \frac{\pi}{4}K^{1/2}g(K,t) \tag{26}$$

where $(\pi/4)I_\infty(K)$ is the steady state current (Eq.(20) and

$$g(K,t) = (\pi Kt)^{-1/2}e^{-Kt} - erfc(Kt)^{1/2} \qquad (27).$$

The average relative error between Eq. (26) and simulation results of Galceran et.al. [67] is about 0.61%.

5. Conclusion

Thus it can be seen that in the past decade, considerable progress has been made in the understanding of diffusion process at ultramicrodisc electrodes. This paper has reviewed the theory of mass transport at ultramicrodisc electrodes under diffusion -limited reaction and electrochemical reaction.

The non-steady state current at ultramicrodisc 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 ultramicrodisc electrodes for EC' reaction have also been reviewed. This article is very useful for the application of ultramicrodisc electrodes in analytical and molecular electrochemistry.

ACKNOWLEDGEMENTS

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

6. References

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