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The Behavior of Microdisk and Microring Electrodes. Mass Transport to the Disk in the Unsteady State: Chronopotentiometry

by

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The behavior of microdisk and microring electrodes. Mass transport to the disk in the unsteady state

Chronopotentiometry

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ABSTRACT

We describe the time dependent response of a finite disk electrode under conditions of constant applied flux (chronopotentiometry). The exact solution is recovered by solving the differential equations in the circular cylindrical coordinate system with the use of suitable discontinuous integrals. In addition, we present the result for the case of linear sweep amperometry, which will generally be more useful for controlled current experiments with microelectrodes.

INTRODUCTION

There has been much recent work on the analysis of mass transport to finite electrode geometries. One reason for this activity lies in the increased interest in new applications of microelectrodes [1]. The applicability of the preferred spherical microelectrode geometry has so far been somewhat restricted e.g., to the electrodeposition of ensembles [2,3] or single mercury droplets [4–6], the electrolysis of dispersions [7,8], and the dropping mercury microelectrode [9]. Disk, band, and the recently introduced ring microelectrodes [5,10–12], are in general more easily constructed, but the necessary mathematical analysis has so far proved to be rather intractable. The mathematical difficulties are due to the discontinuities at the edges of the electrodes (e.g. constant concentration or flux over the surface of the electrode, zero flux over the adjacent insulating surface). The diffusion limited flux becomes infinite at these discontinuities (the combined effects of the finite rates of the surface reactions and of the distribution of potential and concentration across

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the surface i.e., the "tertiary current distribution," however, will limit the rates at the edges for real systems). Disk and ring microelectrodes have the advantage that quasi-spherical diffusion fields are established at relatively short times; in contrast, diffusion to line or band electrodes does not reach a steady state, the flux varying as $1/\ln t$. Spherical diffusion fields at small electrodes give rise to high rates of mass transport to the surface so that the kinetics of fast heterogeneous reactions and of fast reactions in solution can be studied under steady state conditions (e.g., see the previous analysis, [13]). While it is clear that fast reactions can always be studied by decreasing the size of the electrode, there are some applications that are amenable to study at "larger" microelectrodes. A variety of analytical and simulation procedures have been used in attempts to develop adequate descriptions of the chronoamperometric and chronopotentiometric responses at disk and ring electrodes e.g., see [11,13–26]. In this series of papers, we develop a general approach to the analysis of the non-steady state, and we apply the method here to the chronopotentiometric case for constant and uniform flux over the surface. The result is an exact expression that is valid at all times, and for any size disk, and is therefore applicable to conventional electroanalytical experiments, as well as those at microelectrodes. The approach to the problem is based on the properties of discontinuous integrals (see e.g., refs. 13, 28 and 29) which we have extended from the previous analysis (the prediction of the mass transfer coefficients for constant concentration and constant flux conditions in the steady state) to include time dependent mass transfer. In addition, we include the results for a linearly swept current experiment.

— Please make sure refs 27 & 30 are mentioned

27 and 28

THEORETICAL CONSIDERATIONS

General time dependent solution

For any simple electrochemical experiment involving a single reactant, we must solve the time dependent diffusion equation in circular cylindrical coordinates:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2} + \frac{D}{r}\frac{\partial c}{\partial r} + D\frac{\partial^2 c}{\partial z^2} \tag{1}$$

where c is the concentration of the reactant, and r is the radial distance coordinate measured from the center of the disk electrode which is imbedded in the insulating plane at $z = 0$. The general initial condition is, at

$$r > 0,\ z > 0,\ t = 0 \qquad c = c^{\infty} \tag{2}$$

where c^{∞} is the bulk concentration. Laplace transformation of eqn. (2) gives

$$\frac{\partial^2 \bar{c}}{\partial r^2} + \frac{1}{r}\frac{\partial \bar{c}}{\partial r} + \frac{\partial^2 \bar{c}}{\partial z^2} - q^2\bar{c} + \frac{c^{\infty}}{D} = 0 \tag{3}$$

where

$$q^2 = s/D \tag{4}$$

and s is the Laplace transformation variable. The last term on the LHS of eqn. (3) is a constant and hence determines the particular integral of eqn. (1). We then seek the solution for the complementary function from

$$\frac{\partial^2 \bar{c}_{CF}}{\partial r^2} + \frac{1}{r}\frac{\partial \bar{c}_{CF}}{\partial r} + \frac{\partial^2 \bar{c}_{CF}}{\partial z^2} - q^2 \bar{c}_{CF} = 0 \tag{5}$$

Separations of variables of the form

$$c_{CF} = v \exp[-f(\lambda, q)z] \tag{6}$$

simplify the differential equation (5) to the familiar Bessel form

$$\frac{d^2\bar{v}}{dr^2} + \frac{1}{r}\frac{d\bar{v}}{dr} + \alpha^2 \bar{v} = 0 \tag{7}$$

where

$$\alpha^2 = [f(\lambda, q)]^2 - q^2 \tag{8}$$

For instance, we can choose the simple form

$$f(\lambda, q) = (\alpha^2 + q^2)^{1/2} \tag{9}$$

so that

$$\bar{c}_{CF} = \bar{v} \exp\left[-(\alpha^2 + q^2)^{1/2} z\right] \tag{10}$$

and eqn. (7) is recovered from eqn. (5) with α independent of q. (The factors involved when considering a choice for this function will be discussed elsewhere.) Therefore, the solution to Bessel's differential equation (3) becomes

$$\bar{c} = \frac{c^\infty}{s} - \int_0^\infty g(\lambda, q) \exp(-f(\lambda, q)z) J_0(\alpha r)\, d\alpha \tag{11}$$

where J_0 is the Bessel function of the first kind, order 0, and we choose $g(\lambda, q)$ to satisfy the boundary conditions.

Chronopotentiometry

We consider here the solution for eqn. (11) for the chronopotentiometry problem for a constant a constant uniform flux $-Q$(mol cm^{-2} s^{-1}) over the surface at all $t > 0$. The boundary conditions at the surface of the electrode become

$$\begin{aligned} &0 \leq r < a,\ z = 0,\ t > 0 \qquad D\left[\frac{\partial c}{\partial z}\right] = -Q \\ &r > a,\ z = 0,\ t > 0 \qquad D\left[\frac{\partial c}{\partial z}\right] = 0 \end{aligned} \tag{12}$$

[illegible] eqn
[illegible] eqn
[illegible]

We take the Laplace transform of eqns. (12), and substitute in eqn. (11) after differentiation under the integral and obtain, for $t > 0$,

$$D\left[\frac{\partial \bar{c}}{\partial z}\right] = -\frac{Q}{s} = -\int g(\lambda, q) f(\lambda, q) J_0(\alpha r)\, d\alpha \qquad 0 < r < a,\ z = 0 \tag{13}$$

and

$$D\left[\frac{\partial \bar{c}}{\partial z}\right] = 0 \qquad r > a,\ z = 0 \tag{14}$$

The boundary conditions suggest that we can apply the discontinuous integrals

$$\int_0^\infty J_0(\alpha r) J_1(\alpha a)\, \mathrm{d}\alpha = \begin{cases} 0 & r > a \quad (15) \\ 1/2a & r = a \quad (16) \\ 1/a & r < a \quad (17) \end{cases}$$

in the solution of the problem. We determine the conditions for which $g(\lambda, q)$ fits the boundary conditions (13) and (14). From eqn. (13), we see that

$$\int_0^\infty g(\lambda, q) f(\lambda, q) J_0(\alpha r)\, \mathrm{d}\alpha = \frac{Q}{Ds} \qquad 0 < r < a,\ z = 0 \tag{18}$$

or

$$\frac{Ds}{Qa}\int_0^\infty g(\lambda, q) f(\lambda, q) J_0(\alpha r)\, \mathrm{d}\alpha = \frac{1}{a} \tag{19}$$

Therefore if we let

$$g(\lambda, q) = \frac{J_1(\alpha a)}{f(\lambda, q)} \tag{20}$$

the complete solution to eqn. (3) having boundary conditions (13) and (14) is

$$\bar{c} = \frac{c^\infty}{s} - \frac{Qa}{Ds}\int_0^\infty \exp[-f(\lambda, q)z]\, J_0(\alpha r) J_1(\alpha a) \frac{\mathrm{d}\alpha}{f(\lambda, q)} \tag{21}$$

and at $z = 0$,

$$\bar{c} = \frac{c^\infty}{s} - \frac{Qa}{Ds}\int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{\mathrm{d}\alpha}{f(\lambda, q)} \tag{22}$$

[29]

We point out here that the interpretation of the arguments of the Bessel functions depends on the nature of the assumption of the form of $f(\lambda, q)$ and, indeed, on the nature of the experiment (e.g. compare with the discussion of the chronoamperometric case [31]). The use of the simple form (9) gives

$$\bar{c} = \frac{c^\infty}{s} - \frac{Qa}{Ds}\int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{\mathrm{d}\alpha}{(\alpha^2 + q^2)^{1/2}} \tag{23}$$

for galvanostatic conditions with α now independent of q; we can therefore invert immediately to the t-domain:

$$c = c^\infty - \frac{Qa}{D}\int_0^\infty J_0(\alpha r) J_1(\alpha a)\, \mathrm{erf}(D^{1/2}\alpha t^{1/2}) \frac{\mathrm{d}\alpha}{\alpha} \tag{24}$$

where $\mathrm{erf}(y)$ denotes the error function.

We can evaluate the average concentration at $z = 0$ by integrating eqn. (24) over the surface of the disk:

$$c_{Av} = c^{\infty} - \frac{2Q}{D} \int_0^{\infty} [J_1(\alpha a)] \operatorname{erf}(D^{1/2} \alpha t^{1/2}) \frac{d\alpha}{\alpha^2} \qquad (25)$$

With the substitutions

$$l^2 = Dt \qquad (26)$$

$$\beta = \alpha l \qquad (27)$$

eqn. (25) can be written in terms of dimensionless variables and parameters

$$c_{Av} = c^{\infty} - \frac{2Qa}{D} \cdot \frac{l}{a} \int_0^{\infty} \left[J_1\left(\frac{\beta a}{l}\right) \right]^2 \operatorname{erf}(\beta) \frac{d\beta}{\beta^2}$$

Av

$$= c^{\infty} - \frac{2Qa}{D} \cdot \Phi_1\left(\frac{Dt}{a^2}\right) \qquad (28)$$

The function Φ_1 is tabulated in Table 1 as a function of the dimensionless parameter (Dt/a^2).

At long times and sufficiently small values of the flux, we do not observe a transition time and always reach the steady state value [13]

$$c_{Av} = c^{\infty} - \frac{8Qa}{3\pi D} \qquad (29)$$

If Q is sufficiently large we will get a sharp transition time as the surface concentration of the reactant approaches zero; for this condition eqn. (28) can be written

$$\frac{2Qa}{Dc^{\infty}} \cdot \frac{l}{a} \int_0^{\infty} \left[J_1\left(\frac{\beta a}{l}\right) \right]^2 \operatorname{erf}(\beta) \frac{d\beta}{\beta^2} = \frac{2Qa}{Dc^{\infty}} \cdot \Phi_1\left(\frac{Dt}{a^2}\right) = 1 \qquad (30)$$

from which the transition time can be obtained. The problems to be discussed in this series of papers are always cast in the form of such definite integrals, and these frequently converge slowly. Accurate evaluation is readily obtained, however, through the use of standard Bulirsch–Stoer numerical integration methods. In addition, convergence can always be speeded by suitable rearrangements. For instance, eqn. (30) can be rewritten in the equivalent form

$$\frac{2Qa}{Dc^{\infty}} \cdot \frac{l}{a} \left\{ \int_0^{\infty} \left[J_1\left(\frac{\beta a}{l}\right) \right]^2 \frac{d\beta}{\beta^2} + \int_0^{\infty} \left[J_1\left(\frac{\beta a}{l}\right) \right]^2 (\operatorname{erf}(\beta) - 1) \frac{d\beta}{\beta^2} \right\} \qquad (31)$$

[27] The value of the first integral is known to be $4a/3\pi l$ [2[illegible]]. The second integral converges rapidly since the error function approaches 1 with increasing β. Figure 1 illustrates the square root of the dimensionless transition times $D\tau/a^2$ as a function of the inverse of the dimensionless flux $2Qa/Dc^{\infty}$. The values are close to those predicted by Aoki and Osteryoung [18] even though these authors based their analysis on a uniform surface concentration boundary condition; the expressions

TABLE 1

Values of the function $\Phi_1(Dt/a^2)$

Dt/a^2	$\Phi_1(Dt/a^2)$	Dt/a^2	$\Phi_1(Dt/a^2)$
4.0000×10^{6}	2.1217×10^{-4}	2.7778	2.0533×10^{-1}
2.7778×10^{6}	2.5460×10^{-4}	2.0408	2.3064×10^{-1}
2.0408×10^{6}	2.9702×10^{-4}	1.5625	2.5372×10^{-1}
1.5625×10^{6}	3.3944×10^{-4}	1.2346	2.7473×10^{-1}
1.2346×10^{6}	3.8186×10^{-4}	1.0000	2.9381×10^{-1}
1.0000×10^{6}	4.2427×10^{-4}	2.5000×10^{-1}	4.1045×10^{-1}
2.5000×10^{5}	8.4826×10^{-4}	1.1111×10^{-1}	4.5961×10^{-1}
1.1111×10^{5}	1.2720×10^{-3}	6.2500×10^{-2}	4.8524×10^{-1}
6.2500×10^{4}	1.6954×10^{-3}	4.0000×10^{-2}	5.0085×10^{-1}
4.0000×10^{4}	2.1185×10^{-3}	2.7778×10^{-2}	5.1132×10^{-1}
2.7778×10^{4}	2.5414×10^{-3}	2.0408×10^{-2}	5.1883×10^{-1}
2.0408×10^{4}	2.9640×10^{-3}	1.5625×10^{-2}	5.2448×10^{-1}
1.5625×10^{4}	3.3863×10^{-4}	1.2346×10^{-2}	5.2888×10^{-1}
1.2346×10^{4}	3.8083×10^{-3}	1.0000×10^{-2}	5.3240×10^{-1}
1.0000×10^{4}	4.2300×10^{-3}	2.5000×10^{-3}	5.4828×10^{-1}
2.5000×10^{3}	8.4318×10^{-3}	1.1111×10^{-3}	5.5358×10^{-1}
1.1111×10^{3}	1.2605×10^{-2}	6.2500×10^{-4}	5.5623×10^{-1}
6.2500×10^{2}	1.6751×10^{-2}	4.0000×10^{-4}	5.5783×10^{-1}
4.0000×10^{2}	2.0868×10^{-2}	2.7778×10^{-4}	5.5889×10^{-1}
2.7778×10^{2}	2.4957×10^{-2}	2.0408×10^{-4}	5.5964×10^{-1}
2.0408×10^{2}	2.9018×10^{-2}	1.5625×10^{-4}	5.6021×10^{-1}
1.5625×10^{2}	3.3051×10^{-2}	1.2346×10^{-4}	5.6065×10^{-1}
1.2346×10^{2}	3.7055×10^{-2}	1.0000×10^{-4}	5.6101×10^{-1}
1.0000×10^{2}	4.1032×10^{-2}	2.5000×10^{-5}	5.6260×10^{-1}
2.5000×10^{1}	7.9259×10^{-2}	1.1111×10^{-5}	5.6313×10^{-1}
1.1111×10^{1}	1.1472×10^{-1}	6.2500×10^{-6}	5.6340×10^{-1}
6.2500	1.4749×10^{-1}	4.0000×10^{-6}	5.6356×10^{-1}

they derived could not be inverted exactly over the entire time range whereas eqn. (30) is exact. It should be noted that the constant flux condition is more likely to apply for most of the duration of the experiment rather than the constant surface concentration condition, the actual behavior lying between these two limiting conditions. A more correct formulation of the boundary condition on the disk for an irreversible reaction, say, would be

$$\partial c/\partial z = kc \qquad 0 < r < a,\ z = 0 \tag{32}$$

For a cathodic reaction, say, we would write

$$k = k_0 \exp[\alpha EF/RT] = \text{constant} \qquad 0 < r < a \tag{33}$$

provided we neglect the effects of the distribution of potential in the solution k, i.e. we neglect the primary or secondary current distribution. Equation (32) shows that we cannot strictly speaking assume either the flux or the concentration to be constant over the surface of the disk. However, the close agreement of the transition

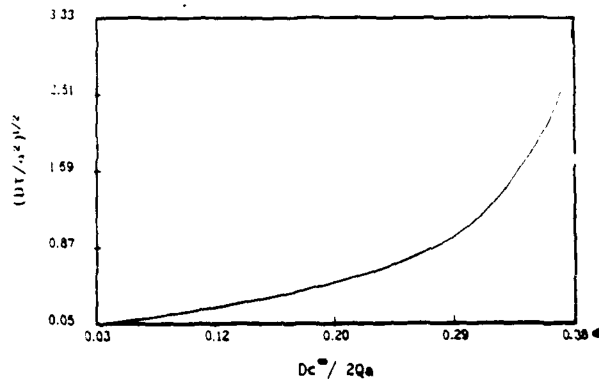

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Fig. 1. Plot of the square root of the dimensionless transition time $(D\tau/a^2)^{1/2}$ as a function of the inverse of the dimensionless flux $(2Qa/Dc^\infty)$.

[29] times derived using there two approaches shows that the interpretation is not very sensitive to the nature of the assumptions; subsequent papers [31] will show that this is also the case for other types of experiment. We note that the constant flux condition will hold at low current densities (as in relaxation experiments) while the constant concentration condition may be approached in the limiting current region (see, however, below) so that the actual behavior must lie between these two limits. Thus, while it would be possible to develop the conditions (31) and (32), it is unlikely that the accuracy of the experimental data would allow an assessment of the range of validity of the various assumptions. Furthermore, the application of eqn. (31) would also require the consideration of the distribution of the potential in the solution, i.e. we have to consider the tertiary current distribution. We can predict, to some extent, the probable outcome of such analyses: it is unlikely that the "throwing power" of any practicable system would ever be sufficiently low that the current density could deviate appreciably from uniformity over the surface of a microdisk (note that an infinite flux to the edge of the disk is clearly impossible even on the limiting current plateau!). We therefore consider that the constant flux boundary condition will hold under most experimental conditions.

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Figure 1 shows the expected linear dependence at high values of $2\cancel{0}Qa/Dc^\infty$ where we observe essentially linear diffusion to the electrode followed by a rapid rise at low values of $2Qa/Dc^\infty$ as this parameter approaches the condition required for the observation of a steady state

$$\frac{2Qa}{Dc^\infty} \leqslant \cancel{\frac{4}{3\pi} = 0.4244} \qquad \frac{3\pi}{4} \approx 2.3562 \tag{34}$$

The calculated values of $c_{\ast}$ may be used to derive the potential–time curves for appropriate models of the electrode reactions. For instance, in the case of simple Butler–Volmer kinetics, we obtain

$$\frac{FQ}{i_0} + \frac{2Qa}{Dc^\infty}\Phi_2\left(\frac{Dt}{a^2}\right)\left\{\exp\left(\frac{-\alpha\eta F}{RT}\right) + \exp\left(\frac{(1-\alpha)\eta F}{RT}\right)\right\}$$

$$= \exp\left(\frac{-\alpha\eta F}{RT}\right) - \exp\left(\frac{(1-\alpha)\eta F}{RT}\right) \tag{35}$$

which shows that the transients are a function of α, FQ/i_0 and $2Qa/Dc^\infty$.

Linear sweep amperometry

It is clear that since there is rapid attainment of steady state diffusion to microdisk electrodes, constant current experiments may not be generally useful. It is difficult to determine the appropriate galvanostatic condition that will give a transition time within a convenient experimental time scale. It is therefore more straightforward to apply time dependent fluxes to the surface. It we consider, for example, the simplest case of a linear current ramp

$$Q(t) = \gamma t \tag{36}$$

we can immediately rewrite eqn. (23) in the general form [1,13,~~31~~]

[1,13,29]

$$\bar{c} = \frac{c^\infty}{s} - \frac{\gamma a}{Ds^2}\int_0^\infty J_0(\alpha r) J_1(\alpha a)\frac{\mathrm{d}\alpha}{(\alpha^2+q^2)^{1/2}} \tag{37}$$

and by the same methods obtain the transition time

$$\frac{4\gamma t a}{Dc^\infty}\cdot\frac{l}{a}\int_0^\infty\left[J_1\left(\beta\frac{a}{l}\right)\right]^2\left[\int_0^\beta y\,\mathrm{erf}(y)\,\mathrm{d}y\right]\frac{d\beta}{\beta^4} = 1 \tag{38}$$

or

$$\frac{4\gamma t a}{Dc^\infty}\cdot\Phi_3\left(\frac{Dt}{a^2}\right) = 1 \tag{39}$$

If now the current is swept from zero, a very sharp transition is observed in the potential–time plot. For simple Butler–Volmer kinetics, the shape of the response can be determined from

$\frac{F\gamma t}{i_0} +$

$$\frac{FQ}{i_0} + \frac{4\gamma t a}{Dc^\infty}\cdot\Phi_3\left(\frac{Dt}{a^2}\right)\left\{\exp\left(\frac{-\alpha\eta F}{RT}\right) + \exp\left(\frac{(1-\alpha)\eta F}{RT}\right)\right\}$$

$$= \exp\left(\frac{-\alpha\eta F}{RT}\right) - \exp\left(\frac{(1-\alpha)\eta F}{RT}\right) \tag{40}$$

Table 2 gives values of Φ_3 as a function of Dt/a^2.

The application of other boundary conditions representing other electrochemical experiments (e.g. cyclic amperometry, ac impedance measurments, and to cases involving reactions in solution coupled to the electrode processes) to this form of

TABLE 2

Values of the funcuon $\Phi_1(Dt/a^2)$

Dt/a^2	$\Phi_1(Dt/a^2)$	Dt/a^2	$\Phi_1(Dt/a^2)$
2.0000×10^{-2}	7.5112×10^{-5}	5.0000	3.6511×10^{-1}
3.1623×10^{-2}	1.8778×10^{-4}	7.0711	3.9321×10^{-1}
3.5355×10^{-2}	2.3473×10^{-4}	1.0000	4.0842×10^{-1}
3.7796×10^{-2}	2.6826×10^{-4}	1.1180	4.1155×10^{-1}
4.4721×10^{-2}	3.7556×10^{-4}	1.1952	4.1313×10^{-1}
5.0000×10^{-2}	4.6945×10^{-4}	1.4142	4.1631×10^{-1}
7.0711×10^{-2}	9.3831×10^{-4}	1.5811	4.1792×10^{-1}
1.0000×10^{-1}	1.8728×10^{-3}	2.2361	4.2116×10^{-1}
1.1180×10^{-1}	2.3385×10^{-3}	3.1623	4.2277×10^{-1}
1.1952×10^{-1}	2.6706×10^{-3}	3.7796	4.2327×10^{-1}
1.4142×10^{-1}	3.7299×10^{-3}	4.4721	4.2360×10^{-1}
1.5811×10^{-1}	4.6526×10^{-3}	5.0000	4.2376×10^{-1}
2.2361×10^{-1}	9.2073×10^{-3}	7.0711	4.2409×10^{-1}
3.1623×10^{-1}	1.8023×10^{-2}	1.0000×10^{2}	4.2425×10^{-1}
3.5355×10^{-1}	2.2285×10^{-2}	1.1180×10^{2}	4.2428×10^{-1}
3.7796×10^{-1}	2.5269×10^{-2}	1.1952×10^{2}	4.2430×10^{-1}
4.4721×10^{-1}	3.4486×10^{-2}	1.4142×10^{2}	4.2433×10^{-1}
5.0000×10^{-1}	4.2138×10^{-2}	1.5811×10^{2}	4.2435×10^{-1}
7.0711×10^{-1}	7.4851×10^{-2}	2.2361×10^{2}	4.2438×10^{-1}
1.0000	1.1751×10^{-1}	3.1623×10^{2}	4.2440×10^{-1}
1.1180	1.3151×10^{-1}	3.5355×10^{2}	4.2440×10^{-1}
1.1952	1.3971×10^{-1}	3.7796×10^{2}	4.2440×10^{-1}
1.4142	1.5820×10^{-1}	4.4721×10^{2}	4.2440×10^{-1}
1.5811	1.7040×10^{-1}	5.0000×10^{2}	4.2441×10^{-1}
2.2361	2.2654×10^{-1}	7.0711×10^{2}	4.2441×10^{-1}
3.1623	2.9695×10^{-1}	1.0000×10^{3}	4.2441×10^{-1}
3.5355	3.1727×10^{-1}	3.1623×10^{3}	4.2441×10^{-1}
4.4721	3.5219×10^{-1}	1.0000×10^{4}	4.2441×10^{-1}

Please replace with new values Attached.

[30] analysis, as well as extension of the analysis to include the ring geometry will be discussed elsewhere [3~~2~~].

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GLOSSARY OF SYMBOLS USED

a	Radius of disk, cm
c	Concentration, mol cm^{-3}
c^{∞}	Bulk concentration, mol cm^{-3}
c_{Av}	Average concentration, mol cm^{-3}
c_{CF}	Concentration complementary function
c^{s}	Surface concentration, mol cm^{-3}

D	Diffusion coefficient, $\mathrm{cm^2\,s^{-1}}$
E	Electrode potential, V
F	Faraday constant, 96485 $\mathrm{C\ mol^{-1}}$
i_0	Exchange current density, $\mathrm{A\ cm^{-2}}$
J_0, J_1	Bessel functions
k	Heterogeneous rate constant, $\mathrm{cm\ s^{-1}}$
k^0	Heterogeneous standard rate constant, $\mathrm{cm\ s^{-1}}$
l	$(Dt)^{1/2}$
q	$(s/D)^{1/2}$
Q	Flux, $\mathrm{mol\ cm^{-2}\ s^{-1}}$
R	Gas constant, 8.314 $\mathrm{J\ mol^{-1}\ K^{-1}}$
r	Radial coordinate, cm
s	Laplace transform variable
t	Time, s
T	Temperature, K
v	Concentration amplitude
z	Coordinate normal to plane of disk, cm
α	Transfer coefficient (when in exponent)
α	Continuous dummy integration variable
β	αl
γ	Flux sweep rate, $\mathrm{mol\ cm^{-2}\ s^{-2}}$
λ	Continuous dummy integration variable
η	Overpotential, V
Φ_1	$\frac{l}{a}\int_0^\infty\left[J_1\left(\frac{\beta a}{l}\right)\right]^2 \mathrm{erf}(\beta)\frac{\mathrm{d}\beta}{\beta^2}$
Φ	$\frac{l}{a}\int_0^\infty\left[J_1\left(\beta\frac{a}{l}\right)\right]^2\left[\int_0^\beta y\,\mathrm{erf}(y)\,\mathrm{d}y\right]\frac{\mathrm{d}\beta}{\beta^4}$
τ	Transition time, s

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