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The Behavior of Microdisks and Microring Electrodes. Applications of Neumann's Integral Theorem

by

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Abstract

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It is shown that Neumann's integral theorem can be used to derive the steady-state behavior of microdisk electrodes. Results obtained previously using other methods for uniform surface concentration and uniform flux boundary conditions are derived as limiting cases of a general equation which describes irreversible and quasi-reversible reaction kinetics. It is shown that the approach can be used to assess the effects of the tertiary current distribution and to predict the behavior for electrode reactions which are non-linear in the concentration terms.

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THE BEHAVIOR OF MICRODISK AND MICRORING ELECTRODES. APPLICATION OF NEUMANN'S INTEGRAL THEOREM TO THE PREDICTION OF THE STEADY STATE RESPONSE OF MICRODISKS.

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Introduction

In a series of papers we have recently discussed the steady state behavior of microdisk and microring electrodes(1,2) as well as the chronopotentiometric, chronoamperometric, and A.C. responses of microdisk electrodes(1,3-5) and the determination of the rates of homogeneous reactions (c.e. mechanism) coupled to electrode processes at these electrodes(1,6). Our approach has been based on the use of discontinuous integrals of Bessel functions(7) (for comparable solutions in heat conduction see eg(8,9)). The steady state response, for example, is governed by the solution of the diffusion equation in cylindrical coordinates

$$D \frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D\frac{\partial^2 C}{\partial z^2} = 0 \qquad [1]$$

namely

$$C = C^{\infty} - \int_0^{\infty} f(\alpha) \exp(-\alpha z) J_0(\alpha r)\, d\alpha \qquad [2]$$

where the function $f(\alpha)$ is chosen to satisfy the boundary conditions. The two simplest boundary conditions are those of uniform surface concentration over the disk:

$$C^{s} = \text{constant}, \quad 0 < r < a, \quad z = 0 \qquad [3]$$

$$\frac{\partial C}{\partial z} = 0 \qquad r > a \qquad [4]$$

and of uniform flux:

$$D\frac{\partial C}{\partial z} = Q \text{ (a constant)}, \; 0 < r < a, \; z = 0 \qquad [5]$$

[2], [3], and [4] are combined with the discontinuous integrals

$$\int_0^\infty \sin(\alpha a)\, J_0(\alpha r)\, d\alpha/\alpha = \int_0^\infty \left(\frac{\pi a}{2\alpha}\right)^{1/2} J_{1/2}(\alpha a) J_0(\alpha r)\, d\alpha = \begin{cases} \pi/2, & r < a \qquad [6] \\ \sin^{-1}(a/r), & r > a \qquad [7] \end{cases}$$

associated with

$$\int_0^\infty \sin(\alpha a)\, J_0(\alpha r)\, d\alpha = \int_0^\infty \left(\frac{\pi \alpha a}{2}\right)^{1/2} J_{1/2}(\alpha a) J_0(\alpha r)\, d\alpha = \begin{cases} 1/(a^2 - r^2)^{1/2}, & r < a \qquad [8] \\ 0, & r > a \qquad [9] \end{cases}$$

to give

$$C = C^\infty - \frac{2}{\pi}(C^\infty - C^s)\int_0^\infty \exp(-\alpha z)\, \sin(\alpha a) J_0(\alpha r)\, d\alpha/\alpha \qquad [10]$$

Similarly, [2], [5] and [4] are combined with the discontinuous integral

$$\int_0^\infty J_0(\alpha r)\,J_1(\alpha a)\,d\alpha = \begin{cases} 0, & r>a \quad [11] \\ \frac{1}{2a}, & r=a \quad [12] \\ 1/a, & r<a \quad [13] \end{cases}$$

to give

$$C = C^\infty - \frac{Qa}{D}\int_0^\infty \exp(-\alpha z)\,J_0(\alpha r)\,J_1(\alpha a)\,\frac{d\alpha}{\alpha} \qquad [14]$$

The total flux to the surface for uniform concentration conditions can be derived from [10] as

$$F = 2\pi D\int_0^\infty \left(\frac{\partial C}{\partial z}\right)_{z=0} r\,dr = 4D(C^\infty - C^S)a \qquad [15]$$

leading to the definition of the mass transfer coefficient

$$\left(k_m\right)_C = 4D/\pi a \qquad [16]$$

Similarly, evaluation of the average surface concentration from [10]

$$C_{Av} = C^\infty - 8Qa/3\pi D \qquad [17]$$

leads to the definition of the mass transfer coefficient for the uniform flux conditions

$$\left(k_m\right)_Q = 3\pi D/8a \qquad [18]$$

Mass transfer to the electrode will be governed by [18] for irreversible and quasi-reversible reactions at low overpotentials and by [16] for all reactions at very high overpotentials. As we have indicated elsewhere(1-3), the effects of the distribution of potential in the solution (the tertiary current distribution) will cause [18] to be the appropriate choice for the bulk of the polarization curves for most conditions; the effects of changing the nature of the assumptions about the magnitude of the mass transfer coefficient are small and near the detection limit for present experiments[1].

The approach we have outlined in Equations [2] - [18] has recently been extended(23) in a discussion of the application of more general boundary conditions such as

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[1] The discontinuous integral [11]-[13] can also be applied to the solution of

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D\frac{\partial^2 C}{\partial z^2} \qquad [19]$$

for a range of non-steady state experiments and for the determination of the rates of homogeneous reactions in solution that are coupled to electrode reactions(1,3-6). Chronoamperometric and chronopotentiometric responses for uniform surface concentration conditions have been investigated using a variety of analytical and simulation techniques eg(10-22). The results of calculations based on the assumption of a uniform flux over the surface are again close to those based on the uniform surface concentration assumption in those cases where comparisons can be made(3,4).

$$\left(\frac{\partial C}{\partial z}\right) = kC, \quad 0 < r < a, \ z = 0 \qquad [20]$$

to the interpretation of the steady state behavior of disk electrodes. By analogy to [14] it was assumed in that work that the weighting function, $f(\alpha)$, is given by a series expansion

$$f(\alpha) = b_0 \frac{J_1(\alpha a)}{(\alpha a)} + b_1 \frac{J_2(\alpha a)}{(\alpha a)^2} + b_2 \frac{J_3(\alpha a)}{(\alpha a)^3} + \cdots = \sum_{n=0}^{\infty} \frac{b_n J_{n+1}(\alpha a)}{(\alpha a)^{n+1}} \qquad [21]$$

(in our notation) at low overpotentials where kinetic control will be dominant and by analogy to [10] by the expansion

$$f(\alpha) = b_0 \frac{J_{1/2}(\alpha a)}{(\alpha a)^{1/2}} + b_1 \frac{J_{3/2}(\alpha a)}{(\alpha a)^{3/2}} + b_2 \frac{J_{5/2}(\alpha a)}{(\alpha a)^{5/2}} + \cdots = \sum_{n=0}^{\infty} \frac{b_n J_{\left(n+\frac{1}{2}\right)}(\alpha a)}{(\alpha a)^{n+1/2}} \qquad [22]$$

at high overpotentials where diffusion will be dominant.

It is evident that the effect of boundary conditions more complicated than [3] or [5] (eg that of [20]) on the behavior of microelectrodes (as well as the influence of non-linearities in the surface reactions including that due to the distribution of potential in the solution) can be readily discussed in terms of Neumann's integral theorem (eg see(7) Chapter 14) and we discuss the application of this theorem to the prediction of the steady-state behavior of microdisk electrodes in this paper.

The Application of Neumann's Integral Theorem

The behavior of microdisk electrodes in the steady-state will be governed in the general case by the differential equation [1] subject to the boundary condition

$$D\frac{\partial C}{\partial z} = Q(\rho), \qquad 0 < \rho < a, \ z = 0 \qquad [23]$$

$$= 0, \qquad \rho > a, \qquad z = 0 \qquad [24]$$

where ρ is the radial position in the plane of the disk. The concentration generated at any position (r,z) by the distribution of sources $Q(\rho)$ can be written down from Neumann's integral as

$$C(r,z) = \int_0^\infty \alpha d\alpha \int_0^a \frac{\exp(-\alpha z)}{\alpha} \frac{Q(\rho)}{D} J_0(\alpha r) J_0(\alpha\rho)\rho d\rho \qquad [25]$$

where integration over ρ has been restricted to $0 < \rho < a$ in view of [24]. The derivation of the complete solution therefore depends on the evaluation of $Q(\rho)$ using the appropriate boundary condition.[2] For electrochemical experiments we are concerned with a distribution of sinks over the surface of the disk; a convenient distribution of such sinks can be based on the truncated Fourier series

$$-Q(\theta) = \frac{-1}{a\cos(\theta)}\left\{c_0 + c_1\cos(\theta) + c_2\cos(2\theta) + \cdots + c_n\cos(n\theta)\right\} \qquad [26]$$

where

$$\rho = a\sin(\theta) \qquad [27]$$

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[2] Time-dependent problems can be discussed in terms of a distribution of sources $Q(\rho,s)$ where s is the variable of the Laplace transformation (for an application to heat conduction see (24)).

The number of terms, n+1, in the series is chosen so that C(r,z) converges to values independent of n. It may be noted that a choice of coefficients

$$c_1 = c_2 = c_3 = \cdots = c_n = 0 \qquad [28]$$

gives

$$-Q(\theta) = \frac{-c_0}{a\cos(\theta)}$$

$$= \left(\frac{-c_0}{(a^2-\rho^2)^{1/2}} \text{ cf. Equation [8]}\right) \qquad [29]$$

[27] and [29] in [1] give

$$C(r,z) = -\frac{c_0}{D}\int_0^{\infty}\exp(-\alpha z)\, J_0(\alpha r)d\alpha \int_0^{\pi/2} a\sin(\theta)\, J_0(a\sin(\theta))d\theta$$

$$= -\frac{c_0}{D}\int_0^{\infty}\left(\frac{\pi a}{2\alpha}\right)^{1/2}\exp(-\alpha z)\, J_0(\alpha r)J_{1/2}(\alpha a)d\alpha \qquad [30]$$

and, with [6] and

$$c_0 = 2D/\pi\ (C^{\infty}-C^{s}) \qquad [31]$$

we recover [10]. Similarly, the choice of the coefficients

$$c_0 = c_2 = c_3 = \cdots = c_n = 0 \qquad [32]$$

gives

$$-Q(\theta) = -c_1/a \qquad [33]$$

Thus we can write

$$C(r,z) = -\frac{1}{D}\int_0^\infty \exp(-\alpha z)\ J_0(\alpha r)d\alpha \int_0^a c_1 J_0(\alpha\rho)\frac{\rho d\rho}{a}$$

$$= -\frac{c_1}{D}\int_0^\infty \exp(-\alpha z)\ J_0(\alpha r)J_1(\alpha a)\frac{d\alpha}{\alpha} \qquad [34]$$

and, with [13] and

$$c_1 = Qa \qquad [35]$$

we recover [14]. Thus the first two terms of the series [26] give respectively the diffusion controlled limit at high overpotentials and the kinetically controlled limit at low overpotentials. It would be expected, therefore, that a relatively short truncated Fourier series will adequately represent the behavior at intermediate overpotentials.

At these intermediate overpotentials we need to evaluate the integral

$$\int_0^{\pi/2} a\sin(\theta)J_0(\alpha a\sin(\theta))\left\{c_0 + c_1\cos(\theta) + c_2\cos(2\theta) + \cdots + c_n\cos(n\theta)\right\}d\theta \qquad [36]$$

It is convenient to express the terms $c_j\cos(j\theta)$ in this series in terms of powers of $\cos(\theta)$ using

$$\cos(j\theta) = \text{Real part of } (\exp(ij\theta)) = \text{Real part of } (\cos(\theta) + i\sin(\theta))^j \qquad [37]$$

and Q(q) can be reexpressed as a series in $\cos^j q$

$$-Q(\theta) = \frac{-1}{a\cos(\theta)}\left\{d_0 + d_1\cos(\theta) + d_2\cos^2(\theta) + \cdots + d_n\cos^n(\theta)\right\} \qquad [38]$$

where the coefficients d_j are expressed in terms of c_j. The nature of the coefficients d_j therefore depends on the length of the Fourier series [26] chosen to represent $Q(\theta)$; values of the coefficients for n up to 10 are listed in Table 1. The advantages of using the particular series expansion [38] to represent the flux will be discussed elsewhere(26).

The Neumann integral can be rewritten using [38] giving

$$C(r,z) = -\frac{a^2}{D}\int_0^\infty \exp(-\alpha z)J_0(\alpha r)d\alpha \sum_{j=0}^{n}\int_0^{\pi/2} Q(\theta)J_0(\alpha a\sin(\theta))\sin(\theta)\cos^j(\theta)\cos(\theta)d\theta$$

$$= -\frac{a}{D}\int_0^\infty \exp(-\alpha z)J_0(\alpha r)d\alpha \sum_{j=0}^{n}\int_0^{\pi/2} d_j J_0(\alpha a \sin(\theta))\sin(\theta)\cos^j(\theta)d\theta \quad [39]$$

Using the known result (compare eg(7,25)

$$\int_0^{\pi/2} J_0(\alpha a \sin(\theta))\sin(\theta)\cos^j(\theta)d\theta = \frac{2^{((j-1)/2)}\Gamma((j+1)/2)}{(\alpha a)^{((j+1)/2)}} J_{\left(\frac{j+1}{2}\right)}(\alpha a) \qquad [40]$$

we derive the values of the integrals listed in Table 2; we express these terms as $\left(e_j J_{\left(\frac{j+1}{2}\right)}(\alpha a)\right) \Big/ \left(\alpha a\right)^{(j+1)/2}$ and note that these values are independent of the length of the Fourier series. [26]. We combine the appropriate choice of the coefficients in Table 1 with the coefficients in Table 2 to give

$$C(r,z) = -\frac{a}{D}\sum_{j=0}^{n}\int_0^\infty d_j e_j \exp(-\alpha z)J_0(\alpha r)\frac{J_{\left(\frac{j+1}{2}\right)}(\alpha a)}{(\alpha a)^{((j+1)/2)}}\,d\alpha \qquad [41]$$

In the application of [41] we are especially interested in the values of the concentration at the surface of the electrode where

$$C(r) = -\frac{a}{D}\sum_{j=0}^{n} d_j e_j \int_0^\infty J_0(\alpha r)\frac{J_{\left(\frac{j+1}{2}\right)}(\alpha a)}{(\alpha a)^{((j+1)/2)}}\,d\alpha \qquad [42]$$

The Weber-Schaftheitlin-Sonine type integrals can be conveniently evaluated in terms of hypergeometric (Gauss) series (7,25) (compare (2)) using

$$\int_0^\infty J_0(\alpha r)\frac{J_{\left(\frac{j+1}{2}\right)}(\alpha a)}{(\alpha a)^{((j+1)/2)}}d\alpha = \frac{\pi^{1/2}}{2^{((j+1)/2)}\Gamma((j+2)/2)a}\,{}_2F_1\left\{\frac{1}{2},-\frac{j}{2};\ 1;\ \frac{r^2}{a^2}\right\} \qquad [43]$$

As can be seen, the value of any particular integral at a position r/a depends on j and we denote this value by $f_j(r/a)$, see Table 2. We can therefore write [42] as

$$C(r) = -\frac{a}{D}\sum_{j=0}^{n} d_j e_j f_j\left(\frac{r}{a}\right)$$

$$= -\frac{\pi^{1/2}}{2D}\sum_{j=0}^{n} d_j \frac{\Gamma\left(\frac{j+1}{2}\right)}{\Gamma\left(\frac{j+2}{2}\right)}\,{}_2F_1\left\{\frac{1}{2},-\frac{j}{2};\ 1;\ \frac{r^2}{a^2}\right\} \qquad [44]$$

Equation [44] provides the link between the assumed form of the flux [26] (or [38]) and the concentration. In the case of relatively simple boundary conditions such as [20], evaluation of the concentration at (n+1) radial positions denoted by r_k provides the (n+1) linear equations required to determine the (n+1) coefficients $(d_0 \ldots d_n)$ or $(c_0 \ldots c_n)$. For simplicity, we write the set of equations in term of the coefficients d_j

$$D\left(\frac{\partial C}{\partial z}\right)_{r=r_k} = Q(\theta_k) = \frac{1}{a\cos(\theta_k)}\left(d_0 + d_1\cos(\theta_k) + \cdots + d_n\cos^n(\theta_k)\right)$$

$$= \frac{1}{\left(a^2-r_k^2\right)^{1/2}}\left[d_0 + d_1\left(\frac{a^2-r_k^2}{a^2}\right)^{1/2} + d_2\left(\frac{a^2-r_k^2}{a^2}\right) + \cdots + d_n\left(\frac{a^2-r_k^2}{a^2}\right)^{n/2}\right]$$

$$= kC^{\infty} - \frac{ak}{D}\sum_{j=0}^{n} d_j e_j f_j\left(\frac{r_k}{a}\right) \qquad [45]$$

The coefficients d_j (or c_j) can therefore be determined by a set of equations such as [45] and the behavior of the system is then fully specified. Thus the local flux is given by any of the equivalent forms [26], [38], or

$$Q\left(\frac{r}{a}\right) = \frac{1}{\left(a^2-r_k^2\right)^{1/2}}\left[d_0 + d_1\left(\frac{a^2-r^2}{a^2}\right)^{1/2} + d_2\left(\frac{a^2-r^2}{a^2}\right) + \cdots + d_n\left(\frac{a^2-r^2}{a^2}\right)^{n/2}\right] \qquad [46]$$

while the total flux is given by any of the relations

$$2\pi D\int_0^a \left(\frac{\partial C}{\partial z}\right) r\,dr = 2\pi Da \sum_{j=0}^{n} \int_0^{\pi/2} c_j \cos(j\theta)\sin(\theta)\,d\theta$$

$$= 2\pi a \sum_{j=0}^{n} \int_0^{\pi/2} d_j \cos^j(\theta)\sin(\theta)\,d\theta$$

$$= 2\pi \sum_{j=0}^{n} \int_0^a d_j \left(\frac{a^2-r^2}{a^2}\right)^{1/2} \frac{r\,dr}{\left(a^2-r^2\right)^{1/2}}$$

$$= 2\pi a \sum_{j=0}^{n} \frac{d_j}{j+1} \qquad [47]$$

The concentration distribution C(r,z) is given by an equation such as [41] while the surface concentration is given by

$$C(r) = C^{\infty} - \frac{a}{D} \sum_{j=0}^{n} d_j e_j f_j\left(\frac{r}{a}\right) \qquad [48]$$

(or by equivalent forms written in terms of θ).

More Complex Boundary Conditions

Quasi-reversible Reactions

Certain examples of the application of more complex boundary conditions can be analyzed by closely similar methods to those outlined above. For example, for a redox couple following quasi-reversible Butler-Volmer kinetics

$$i = i_0\left[\left(\frac{C_O^\infty - C_O(r)}{C_O^\infty}\right)\exp\left(\frac{-\alpha\eta F}{RT}\right) - \left(\frac{C_R^\infty + C_R(r)}{C_R^\infty}\right)\exp\left(\frac{(1-\alpha)\eta F}{RT}\right)\right] \qquad [49]$$

we obtain

$$\frac{F}{i_0}Q\left(\frac{r_k}{a}\right) = \exp\left(\frac{-\alpha\eta F}{RT}\right)\left[1 - \exp\left(\frac{\eta F}{RT}\right)\right]$$

$$- \left(\frac{a}{D_O C_O^\infty} + \frac{a}{D_R C_R^\infty}\right)\left(\sum_{j=0}^{n} d_j e_j f_j\left(\frac{r_k}{a}\right)\exp\left(\frac{-\alpha\eta F}{RT}\right)\left[1 + \exp\left(\frac{\eta F}{RT}\right)\right]\right) \qquad [50]$$

We therefore again obtain a set of (n+1) linear equations which can be solved for the coefficients d_j (or c_j). Once these coefficients have been determined, the concentration distributions and total current at any given overpotential follow as above from [41], [48], and [47].

The Tertiary Current Distribution

Analysis of the behavior of microdisk electrodes based on the solution of the diffusion equation above (i.e. neglecting the effects of the distribution of potential in the solution) lead to the conclusion that the flux at the edge of the disk becomes infinite in the limiting current region, cf. Equation [8]. Such infinities are impossible, however, as the local overpotential would then also have to become infinite. In reality, the "throwing power" of the system in this potential region must be sufficiently high to make the current distribution much more uniform than that given by [8]. We have pointed out that a consequence of the tertiary current distribution therefore is that the solutions based on a model of a uniform flux over the surface, equations [14], [17], and [18], is more likely to apply over the bulk of the polarization curve than solutions based on a model of a uniform surface concentration over the surface, Equations [10] and [16](3). It is clear that an adequate analysis of the behavior of microdisk electrodes at high overpotentials must take due account of the tertiary current distribution.

As has been shown, the use of the Neumann integral [25] coupled to a suitable Fourier series expansion of the local flux [26] leads to a formal solution [41] or [42] which links the distribution of the flux over the surface to the local concentration. The coefficients in the Fourier expansion can therefore be determined by applying the relevant boundary conditions at a sufficient number of positions on the surface. This procedure can evidently be extended to take into account the effects of the distribution of potential in the solution especially that at the surface of the disk.

In the presence of excess support electrolyte, the potential in the solution will be governed by

$$\kappa \frac{\partial^2 \phi}{\partial r^2} + \frac{\kappa}{r} \frac{\partial \phi}{\partial r} + \kappa \frac{\partial^2 \phi}{\partial z^2} = 0 \qquad [51]$$

which is entirely analogous to the differential equation [1] governing diffusion. We take

$$\phi = 0,\ r = \infty,\ z = \infty \qquad [52]$$

and note that the local current density at the surface of the disk can be written

$$I = zFQ(\rho) \qquad [53]$$

The potential at any position in the solution can therefore be written as

$$\phi(r,z) = \frac{zF}{\kappa}\int_0^\infty \alpha d\alpha \int_0^a \frac{\exp(-\alpha z)}{\alpha}\, Q(\rho)J_0(\alpha r)J_0(\alpha\rho)\rho d\rho \qquad [54]$$

and at the surface of the disk we have

$$\phi(r) = \frac{zF}{\kappa}\int_0^\infty J_0(\alpha r)d\alpha \int_0^a Q(\rho)J_0(\alpha\rho)\rho d\rho \qquad [55]$$

Again, using the representation of the local flux by [26] and [28] we obtain by the same methods as those used to discuss the concentration distribution [48]

$$\phi(r) = \frac{zFa}{\kappa} \sum_{j=0}^{n} d_j e_j f_j \left(\frac{r}{a}\right) \qquad [56]$$

In this paper we will restrict attention to the generalization of the boundary condition [20] to take account of the potential distribution [56]. We now regard the rate constant k as the appropriate value uniform over the surface of the disk provided we can neglect the potential distribution in the solution, i.e.

$$k = k_0 \exp\left(\frac{-\alpha\eta F}{RT}\right), \quad \phi(r) = 0, \quad 0 < r < a \qquad [57]$$

For such a cathodic Tafel-type relation we can therefore write

$$\begin{aligned} k(r) &= k \exp\left(\frac{-\alpha\phi(r)F}{RT}\right) \\ &= k \exp\left[\frac{-\alpha zF^2 a}{\kappa RT} \sum_{j=0}^{n} d_j e_j f_j \left(\frac{r}{a}\right) \right] \end{aligned} \qquad [58]$$

As before, the (n+1) coefficients of the Fourier series must be determined by the application of the boundary condition [20] in this case modified by [58]. For example we can use

$$D\left(\frac{\partial C}{\partial z}\right)_{r=r_k} = \frac{1}{\left(a^2-r_k^2\right)^{1/2}}\left[d_0 + d_1\left(\frac{a^2-r_k^2}{a^2}\right)^{1/2} + d_2\left(\frac{a^2-r_k^2}{a^2}\right) + \cdots + d_n\left(\frac{a^2-r_k^2}{a^2}\right)^{n/2}\right]$$

$$= k\left\{\exp\left[\frac{-\alpha zF^2 a}{\kappa RT}\sum_{j=0}^{n} d_j e_j f_j\left(\frac{r_k}{a}\right)\right]\right\}\cdot\left\{C^{\infty} - \frac{a}{D}\sum_{j=0}^{n} d_j e_j f_j\left(\frac{r_k}{a}\right)\right\} \qquad [59]$$

For small perturbations of the bulk concentration and small values of the potential in solution (i.e. for the low overpotential region) sets of equations such as [59] can be linearized and solutions for the coefficients d_j can therefore again be obtained by matrix methods. At high overpotentials it is however necessary to solve the set of non-linear equations. This can be done iteratively, the set of the coefficients d_j in the argument of the exponential function being determined by the previous cycle of the calculation; the same matrix methods can therefore still be applied. Values of the concentration and total current are derived as in the other cases when convergence of the coefficients has been achieved; equally, potential distributions, average potential drops, etc. can be predicted using [56].

Boundary Conditions Non-linear in the Concentration Terms

The kinetics of electrode reactions are frequently non-linear in the concentration terms either because of the complexities of the reaction mechanism (total order of reaction ≠ 1) or because of adsorption of the reactants. The strategy outlined in the previous section can also be used to derive complete solutions in these cases and we illustrate the approach for the simple example

$$D\frac{\partial C}{\partial z} = kC^2 = kC' \cdot C \qquad [60]$$

We evaluate the set of equations linear in d_j

$$D\left(\frac{\partial C}{\partial z}\right)_{r=r_k} = \frac{1}{\left(a^2-r_k^2\right)^{1/2}}\left[d_0 + d_1\left(\frac{a^2-r_k^2}{a^2}\right)^{1/2} + d_2\left(\frac{a^2-r_k^2}{a^2}\right) + \cdots + d_n\left(\frac{a^2-r_k^2}{a^2}\right)^{n/2}\right]$$

$$= k\left\{C^\infty - \frac{a}{D}\sum_{j=0}^{n} d_j' e_j f_j\left(\frac{r_k}{a}\right)\right\} \cdot \left\{C^\infty - \frac{a}{D}\sum_{j=0}^{n} d_j' e_j f_j\left(\frac{r_k}{a}\right)\right\} \qquad [61]$$

where the concentration C' and the coefficients d_j' have been evaluated in the previous cycle of the calculation.

Discussion

It is apparent that the use of Neumann's integral allows a detailed analysis of the behavior of microdisk electrodes. The choice of the Fourier series [26] (or the equivalent forms [38] or [45]) to express the local reaction rate appears to offer special advantages: the results for the uniform surface concentration [3] and uniform surface flux [5] boundary conditions follow as special cases and a single series such as [41] can be seen to give the concentration distribution under all conditions (rather than the two series [21] and [22] which have been applied to the low and high overpotential regions, respectively$^{(23)}$).[3]

A particular advantage of this approach is that it allows a systematic analysis of boundary conditions non-linear in the concentration terms as well as of the effects of the tertiary current distribution. This latter analysis gives a precise description of the ohmic potential drops in solution: these ohmic potential losses (eg. that to the edge of the disk) will be quite different to those at microspherical electrodes and the magnitudes depend on the disk radii. Such predictions are in line with experimental observations but are contrary to currently accepted views.

The polarization curves for simple irreversible or quasi-reversible reactions derived from the application of [45] or [50] will not differ

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[3] Other series expansions such as

$$Q(\rho) = b_0 + b_1\rho + b_2\rho^2 + \cdots + b_n \qquad [62]$$

which are perhaps more obvious than [26] do not converge well in parts of the concentration / flux range and/or generate infinite series when used in Neumann's integral. Thus each term in the series [62] itself generates an infinite series according to

$$\int_0^a b_k J_0(\alpha\rho)\rho^{n+1}d\rho = \frac{b_n a^{n+1}}{\alpha} \frac{\Gamma\left(\frac{n+2}{2}\right)}{\Gamma\left(-\frac{n}{2}\right)} \sum_{k=0}^{\infty} \frac{(2k+1)\Gamma(k-n/2)}{\Gamma\left(\frac{n+4}{2}+k\right)} J_{2k+1}(\alpha a) \qquad [63]$$

The effects of the truncation of series therefore become difficult to assess. However, it may well be possible to find series even more convenient than [26].

markedly from those predicted using the mass transfer coefficient [18] based on the uniform flux approximation$^{(1)}$ except in the high overpotential region where the polarization plots will be more drawn out than those given by simple theory. The effect of including the potential drop in solution (using [59]) will be to further draw out the polarization curves, a behavior which is again in line with experimental observations: well defined limiting currents are difficult to observe. It is likely therefore, that the major application of the approach outlined here will be in the analysis of data in the high overpotential region and to the prediction of polarization curves for complex reaction mechanisms.

In this paper we have applied the method to the prediction of the behavior of simple electrode reactions in the steady state. Numerical data, applications to more complex reactions as well as to the prediction of the behavior for a variety of non-steady state experiments will be given elsewhere.

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Table 1.

The coefficients d_j (Equation [38]) expressed as a function of the coefficients c_j (Equation [26]) for different lengths of the Fourier series.

Series Length	d_0	d_1	d_2	d_3	d_4
n=0	$2D(C^{\infty}-C^{s})/\pi$				
n=1	c_0	c_1			
n=2	c_0-c_2	c_1	$2c_2$		
n=3	c_0-c_2	c_1-3c_3	$2c_2$	$4c_3$	
n=4	$c_0-c_2+c_4$	c_1-3_3	$2c_2-8c_4$	$4c_3$	$8c_4$
n=5	$c_0-c_2+c_4$	$c_1-3_3+5c_5$	$2c_2-8c_4$	$4c_3-20c_5$	$8c_4$
n=6	$c_0-c_2+c_4-c_6$	$c_1-3_3+5c_5$	$2c_2-8c_4+18c_6$	$4c_3-20c_5$	$8c_4-48c_6$
n=7	$c_0-c_2+c_4-c_6$	$c_1-3_3+5c_5-7c_7$	$2c_2-8c_4+18c_6$	$4c_3-20c_5+56c_7$	$8c_4-48c_6$
n=8	$c_0-c_2+c_4-c_6+c_8$	$c_1-3_3+5c_5-7c_7$	$2c_2-8c_4+18c_6-32c_8$	$4c_3-20c_5+56c_7$	$8c_4-48c_6+160c_8$
n=9	$c_0-c_2+c_4-c_6+c_8$	$c_1-3_3+5c_5-7c_7+9c_9$	$2c_2-8c_4+18c_6-32c_8$	$4c_3-20c_5+56c_7-120c_9$	$8c_4-48c_6+160c_8$
n=10	$c_0-c_2+c_4-c_6+c_8-c_{10}$	$c_1-3_3+5c_5-7c_7+9c_9$	$2c_2-8c_4+18c_6-32c_8+50c_{10}$	$4c_3-20c_5+56c_7-120c_9$	$8c_4-48c_6+160c_8-400c_{10}$

Table 1. (Continued)

d_5	d_6	d_7	d_8	d_9	d_{10}
$16c_5$					
$16c_5$	$32c_6$				
$16c_5-112c_7$	$32c_6$	$64c_7$			
$16c_5-112c_7$	$32c_6-256c_8$	$64c_7$	$128c_8$		
$16c_5-112c_7+432c$	$32c_6-256c_8$	$64c_7-576c_9$	$128c_8$	$256c_9$	
$16c_5-112c_7+432c_9$	$32c_6-256c_8+1120c_{10}$	$64c_7-576c_9$	$128c_8-1280c_{10}$	$256c_9$	$512c_{10}$

Table 2

The coefficients e_j (Equation [41]) and the function $f_j\left(\frac{r}{a}\right)$ (Equation [44] as a function of j.

Value of j	e_j	$f_j\left(\frac{r}{a}\right)$
0	$(\pi/2)^{1/2}$	$\frac{\pi^{1/2}}{2^{1/2} a}\ {}_2F_1\left\{\frac{1}{2},\ 0;\ 1;\ \frac{r^2}{a^2}\right\}$
1	1	$\frac{1}{a}\ {}_2F_1\left\{\frac{1}{2}, -\frac{1}{2};\ 1;\ \frac{r^2}{a^2}\right\}$
2	$(\pi/2)^{1/2}$	$\frac{\pi^{1/2}}{2^{3/2} a}\ {}_2F_1\left\{\frac{1}{2}, -1;\ 1;\ \frac{r^2}{a^2}\right\}$
3	2	$\frac{1}{3a}\ {}_2F_1\left\{\frac{1}{2}, -\frac{3}{2};\ 1;\ \frac{r^2}{a^2}\right\}$
4	$3(\pi/2)^{1/2}$	$\frac{\pi^{1/2}}{2^{7/2} a}\ {}_2F_1\left\{\frac{1}{2}, -2;\ \frac{1}{2};\ \frac{r^2}{a^2}\right\}$
5	8	$\frac{1}{15a}\ {}_2F_1\left\{\frac{1}{2}, -\frac{5}{2};\ 1;\ \frac{r^2}{a^2}\right\}$
6	$15(\pi/2)^{1/2}$	$\frac{\pi^{1/2}}{3 \cdot 2^{9/2} a}\ {}_2F_1\left\{\frac{1}{2}, -3;\ 1;\ \frac{r^2}{a^2}\right\}$
7	48	$\frac{1}{105a}\ {}_2F_1\left\{\frac{1}{2}, -\frac{7}{2};\ 1;\ \frac{r^2}{a^2}\right\}$
8	$105(\pi/2)^{1/2}$	$\frac{\pi^{1/2}}{12 \cdot 2^{11/2} a}\ {}_2F_1\left\{\frac{1}{2}, -4;\ 1;\ \frac{r^2}{a^2}\right\}$

Table 2 (continued)

Value of j	e_j	$f_j\left(\frac{r}{a}\right)$
9	384	$\frac{1}{945a} \; {}_2F_1\left\{\frac{1}{2}, -\frac{9}{2}; \; 1; \; \frac{r^2}{a^2}\right\}$
10	$945(\pi/2)^{1/2}$	$\frac{\pi^{1/2}}{60 \cdot 2^{13/2} a} \; {}_2F_1\left\{\frac{1}{2}, -5; \; 1; \; \frac{r^2}{a^2}\right\}$

Glossary of Symbols Used

a	Radius of disk, cm
b_i	Weighting function series coefficients
c_i	Fourier coefficients, mols $(\mathrm{cm\ s})^{-1}$
d_i	Fourier coefficients, mols $(\mathrm{cm\ s})^{-1}$
e_i	Fourier constant terms
f_i	Fourier series integral terms, cm^{-1}
C	Concentration, mols cm^{-3}
C^{∞}	Bulk concentration, mols cm^{-3}
C_{Av}	Average concentration, mols cm^{-3}
C^{s}	Surface concentration, mols cm^{-3}
D	Diffusion coefficient, $\mathrm{cm}^{2}\mathrm{s}^{-1}$
F	Faraday constant, 96485 C $\mathrm{equivalent}^{-1}$
i_0	Exchange current density, A cm^{-2}
i	Current, A
I	Current density, A cm^{-2}
J_i	Bessel functions
k	Heterogeneous rate constant, cm s^{-1}
k_0	Heterogeneous standard rate constant, cm s^{-1}
$\left(k_m\right)_C$	Mass transport coefficient, cm s^{-1}
$\left(k_m\right)_Q$	Mass transport Coefficient, cm s^{-1}
Q	Flux, mols $\mathrm{cm}^{-2}\mathrm{s}^{-1}$
R	Gas constant, 8.314 J $\mathrm{mols}^{-1}\mathrm{K}^{-1}$
r	Radial coordinate, cm
s	Laplace transform variable

T	Temperature, K
z	Coordinate normal to plane of disk, cm
z	Charge of an ion
α	Transfer coefficient (when in exponent)
α	Continuous dummy integration variable.
ϕ	Solution potential, V
ρ	a sin(θ), cm
κ	Solution Conductivity, ohms^{-1}cm^{-1}
η	Overpotential, V

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