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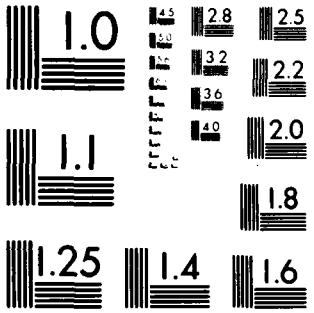

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by

B. Stanley Pons

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SIMULATION OF ELECTROCHEMICAL PROCESSES BY ORTHOGONAL COLLOCATION. SPHERICAL ELECTRODE GEOMETRY

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This paper is dedicated to Professor W.E. Harris on the occasion of his retirement from the University of Alberta.

ABSTRACT

Discretization formulas for the digital simulation of the diffusional processes associated with a variety of electrochemical processes at a spherical electrode are given. The formulas are based on orthogonal collocation techniques. Several mechanisms are represented, and the technique is demonstrated for chronoamperometry, chronopotentiometry, and cyclic voltammetry.

Orthogonal collocation techniques for the simulation of second order partial differential equations have been demonstrated for a variety of problems in electrochemistry [1-7], chemical engineering [8-11], differential scanning calorimetry [12], and other fields [13]. The advantages over other methods have been described, but noteworthy is generally increased accuracy for decreased computational effort [1-7].

In electrochemical diffusion problems, the algorithms needed to compute concentration profiles, chronopotentiograms, chronoamperometric responses, spectrophotometric responses of individual species, cyclic voltammograms, and chronocoulometric responses, all to planar electrode configurations, have been given. This paper deals with some of the same experiments applied to a common configuration, the static spherical electrode (Figure 1).

The programs for solving the equations described herein have been given [7]. Basically, the orthogonal collocation technique is implemented by the following steps:

1. Make the Fick's laws equations suitably dimensionless.
2. Discretize the resulting equations at the roots (zeros) of an orthogonal polynomial of suitable symmetry. The resulting set of equations are now first order ordinary differential equations.
3. Integrate the set of simultaneous differential equations to obtain the set of concentration profiles with respect to distance from the electrode surface and with time.
4. Use these concentrations in the suitably discretized equations to obtain the desired electrochemical parameter (current, absorbance, etc.).

Chronoamperometry

We will only consider diffusion on the solution side of the electrode-solution interface. For a chronoamperometric experiment on the simple charge transfer mechanism at a spherical electrode

$$A \underset{}{\overset{ne^-}{\rightleftharpoons}} B \tag{1}$$

we have the following imposed conditions:

$$[A]_{R,0} = [A]_{\infty,T} = [A^\circ]$$

$$[A]_{r_0,T} = [B]_{\infty,T} = [B]_{R,0} = 0 \tag{2}$$

$$\left(\frac{\delta[A]}{\delta R}\right)_{R=r_0} = -\left(\frac{\delta[B]}{\delta R}\right)_{R=r_0}$$

where R is the distance parameter (radial) from the center of the spherical electrode and r_0 = the radius of the electrode. Since interpolation methods using orthogonal polynomials are simpler to use in a [0,1] interval, we will define M as some distance in the R direction such that no diffusion effects are experienced there during the time frame of the experiment. The differential equation for the A species is:

$$\frac{\delta[A]}{\delta T} = \frac{D_A \delta^2[A]}{\delta R^2} + \frac{2D_A}{R}\frac{\delta[A]}{\delta R} \tag{3}$$

For dimensionless variables, we choose

$$c_A = \frac{[A]}{[A^\circ]} \qquad t = \frac{DT}{(M-r_0)^2} \qquad r = \frac{R-r_0}{M-r_0} \tag{4}$$

We note then that

$$dT = \frac{(M-r_0)^2}{D_A}\,dt, \text{ and}$$

$$dR = (M-r_0)\,dr \tag{5}$$

Substitution of the new variables (4) into (3) gives

$$\frac{D_A[A^\circ]\delta c_A}{(M-r_0)^2\delta t} = \frac{D_A[A^\circ]\delta^2 c_A}{(M-r_0)^2\delta r^2} + \left(\frac{2D_A}{(M-r_0)r+r_0}\right)\frac{[A^\circ]\delta c_A}{(M-r_0)\delta r} \tag{6}$$

which, after simplification, leads to

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta r^2} + \frac{2}{r+\beta}\,\frac{\delta c_A}{\delta r} \tag{7}$$

where

$$\beta = \frac{r_0}{M-r_0}$$

The general spatial derivatives in terms of their polynomial interpolation coefficients [1] are given by

$$\left(\frac{dQ}{dX}\right)_{X=X_i} = \sum_{j=1}^{N+2} A_{i,j}\,Q(X_j,t) \tag{8a}$$

$$\left(\frac{d^2Q}{dX^2}\right)_{X=X_i} = \sum_{j=1}^{N+2} B_{i,j}\,Q(X_j,t) \tag{8b}$$

where N is the order of the approximation polynomial chosen, the X_i represents the roots of that polynomial collocation points, and the A_{ij} and B_{ij} are given by [10]

$$[A_{ij}] = \begin{bmatrix} dX_1^0/dX & dX_1^1/dX & \text{------} & dX_1^{N+2}/dX \\ dX_2^0/dX & & & \\ dX_{N+2}^0/dX & & \text{------} & dX_{N+2}^{N+2}/dX \end{bmatrix} \begin{bmatrix} S \end{bmatrix}^{-1} \tag{9}$$

and

$$[B_{ij}] = \begin{bmatrix} d^2X_1^0/dX^2 & d^2X_1^1/dX^2 & \text{------} & d^2X_1^{N+2}/dX \\ d^2X_2^0/dX^2 & & & \\ d^2X_{N+2}^0/dX^2 & & \text{------} & d^2X_{N+2}^{N+2}/dX \end{bmatrix} \begin{bmatrix} S \end{bmatrix}^{-1} \tag{10}$$

The matrix [S] is given by

$$[S] = \begin{bmatrix} X_0^0 & X_0^1 & \text{----} & X_0^{N+2} \\ X_1^0 & \text{----} & & \\ X_{N+2}^0 & & \text{----} & X_{N+2}^{N+2} \end{bmatrix} \tag{11}$$

The algorithms for finding the roots of any orthogonal polynomial and the corresponding $[A_{ij}]$ and $[B_{ij}]$ matrices have been given previously [9]. The N+2 terms arise because X=0 and X=1 are included as roots to the orthogonal polynomial. The concentration profile will be evaluated at the collocation point, i.e. at coencentric spheres surrounding the spherical electrode. Each sphere has radius $r=X_1$, X_2, X_3, etc., i.e. at the collocation points.

Equation (7) is thus written in terms of (8a) and (8b) at the discrete points X_i:

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = \sum_{j=1}^{N+2} B_{ij} c_A(r_j,t) + \frac{2}{r_i+\beta} \sum_{j=1}^{N+2} A_{ij} c_A(r_j,t) \tag{12}$$

Thus we have N+2 simultaneous first order differential equations to solve for the N+2 $c_A(r_j, t)$ unknowns. Any one of several methods may be used for solving this system of equations [1,4,9].

Inserting the boundary conditions (2) further defines the electrochemical method used, and reduces the number of equations from N+2 to N. This is done by first expanding equation (12) partially, exposing the boundary points at $r_1=X_1=0$ and $r_{N+2}=X_{N+2}=1$:

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = B_{i,1}c_A(0,t) + B_{i,N+2}c_A(1,t) + \sum_{j=2}^{N+1} B_{ij}c_A(r_j,t) + \frac{2}{r_i+\beta}\left[A_{i,1}c_A(0,t) + A_{i,N+2}c_A(1,t) + \sum_{j=2}^{N+1} A_{ij}c_A(r_j,t)\right] \tag{13}$$

We have from the original boundary conditions (2) that $c_A(0,t) = 0$ and $c_A(1,t) = 1$, so that (14) becomes

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij}c_A(r_j,t) + \frac{2}{r_i+\beta}\left[A_{i,N+2} + \sum_{j=2}^{N+1} A_{ij}c_A(r_j,t)\right] \tag{14}$$

So we have one equation to solve at each of the N interior collocation points X_i, i = 2, ...N+1 for the N unknown $c_A(r_j, t)$.

The concentration profile for the B species is derived similarly, and leads to identically the same result as equation (12):

$$\left.\frac{dc_B}{dt}\right|_{r_i=X_i} = \sum_{j=1}^{N+2} B_{ij}c_B(r_j,t) + \frac{2}{r_i+\beta}\sum_{j=1}^{N+2} A_{ij}c_B(r_j,t) \tag{15}$$

Partial expansion leads again to equation (13) with $c_B(r_j, t)$ substituted for the $c_A(r_j, t)$. However, even though it is true that one boundary

condition, $c_B(i,t) = 1$ may be immediately substituted, the other boundary condition $c_B(0,t)$ is not known explicitly. This problem is easily resolved in collocation methods. We observe that the flux relation

$$D_A \left.\frac{dc_A}{dr}\right|_{r_1=X_1=0} = -D_B \left.\frac{dc_A}{dr}\right|_{r_1=X_1=0} \tag{16}$$

We will let $D_A=D_B$ here for convenience even though it presents no problem in setting up the equations if we do not [1,4]. The flux relation is replaced by equation (8a) on each side:

$$\sum_{i=1}^{N+2} A_{1,j}c_A(r_j,t) = -\sum_{i=1}^{N+2} A_{1,j}c_B(r_j,t) \tag{17}$$

Partially expanding so that known conditions may be inserted, we have

$$A_{1,1}c_A(0,t)+A_{1,N+2}c_A(1,t)+\sum_{i=2}^{N+1} A_{1,j}c_A(r_j,t) =$$

$$-[A_{1,1}c_B(r_j,t)+A_{1,N+2}c_B(1,t)+\sum_{i=2}^{N+1} A_{1,j}c_B(r_j,t)] \tag{18}$$

Inserting known quantities, we deduce

$$A_{1,N+2}+\sum_{i=1}^{N+1} A_{1,j}c_A(r_j,t) = -[A_{1,1}c_B(0,t)+\sum_{i=2}^{N+1} A_{1,j}c_B(r_j,t)] \tag{19}$$

Solving for our unknown boundary condition,

$$c_B(0,t) = U + \sum_{i=2}^{N+1} C_{1,j}(c_A(r_j,t) + c_B(r_j,t)) \tag{20}$$

where

$$U = \frac{A_{1,N+2}}{A_{1,1}} \quad , \quad \text{and}$$

$$C_{1,j} = \frac{A_{1,j}}{A_{1,1}}$$

We can now substitute this explicit value for $c_B(0,t)$ in equation (15), along with $c_B(1,t) = 0$ to obtain the equation necessary to represent the concentration profiles for B:

$$\left.\frac{dc_B}{dt}\right|_{r_j=X_i} = V_i + \sum_{j=2}^{N+1} D_{ij}c_A(r_j,t) + \sum_{j=2}^{N+1} E_{ij}c_B(r_j,t) \tag{21}$$

where

$$V_i = B_{i,1}T + \frac{2A_{i,1}U}{r_i+\beta}$$

$$D_{ij} = C_{i,j}\left[B_{i,1} + \frac{2A_{i,1}}{r_i+\beta}\right]$$

$$E_{ij} = B_{ij} + C_{i,j}\left[G_{i,1} + \frac{2A_{i,1}}{r_i+\beta}\right] + \frac{2A_{ij}}{r_i+\beta}$$

Again we have N equations in the N unknown $c_B(r_j,t)$ to solve simultaneously.

Table 1 compares results obtained for the current obtained by equation (33) and the analytic solution for this case, which is

$$i = \frac{nFAD_A^{1/2}[A^\circ]}{\pi^{1/2}T^{1/2}} + \frac{nFAD_A[A^\circ]}{r_0} \tag{22}$$

We use, by example, $D_A = 1. \times 10^{-5}$ cm^2s^{-1}, $[A^\circ] = 10^{-6}$ moles cm^{-3}, $A = \pi r_0^2$, $r_0 = 0.1$ cm, and $n = 1$. β for the example was 10^4.

For the mechanism,

$$A \rightleftharpoons B \xrightarrow{k} C$$

the profile for the A species is the same as equation (14). The B species has a different profile due to loss of material through the chemical reaction, i.e.

$$\frac{\delta[B]}{\delta t} = D_B \frac{\delta^2[B]}{\delta R^2} + \frac{2D_B}{R}\frac{\delta[B]}{\delta R} - k[B] \tag{23}$$

After discretization to the collocation points and insertion of the dimensionless variables (4), we have

$$\left.\frac{dc_B}{dt}\right|_{r_i=X_i} = \sum_{j=1}^{N+2} B_{i,j}c_B(r_j,t) + \frac{2}{r_i+\beta}\sum_{j=1}^{N+2} A_{i,j}c_B(r_j,t) - \alpha c_B(r_i,t) \tag{24}$$

where

$$\alpha = \frac{k(M-r_0)^2}{D_B}$$

Continuing precisely as for the simple electron transfer case, except with the addition of this last chemical kinetic term, we find that

$$\left.\frac{dc_B}{dt}\right|_{r_i=X_i} = V_i + \sum_{j=2}^{N+1} D_{ij}c_A(r_j,t) + \sum_{j=2}^{N+1} E_{ij}c_B(r_j,t) - \alpha c_B(r_j,t) \tag{25}$$

For the catalytic mechanism

$$A \rightleftharpoons B \xrightarrow{k} C + A \tag{26}$$

both the A and B profiles are modified by the presence of the chemical reaction. The differential equations are

$$\frac{\delta[A]}{\delta t} = D_A \frac{\delta^2[A]}{\delta R^2} + \frac{2D_A}{R}\frac{\delta[A]}{\delta R} + k[B] \tag{27}$$

$$\frac{\delta[B]}{\delta t} = D_B \frac{\delta^2[B]}{\delta R^2} + \frac{2D_A}{R}\frac{\delta[B]}{\delta R} - k[B]$$

The boundary conditions are exactly as the previous cases, so that discretization is the same. We find that

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij}c_A(r_j,t) + \frac{2}{r_i+\beta}[A_{i,N+2} + \sum_{j=2}^{N+1} A_{ij}c_A(r_j,t)] + \alpha c_B(r_j,t) \tag{28}$$

$$\left.\frac{dc_B}{dt}\right|_{r_i=X} + \sum_{j=2}^{N+1} D_{ij}c_A(r_j,t) + \sum_{j=2}^{N+1} E_{ij}c_B(r_j,t) - \alpha c_B(r_j,t) \tag{29}$$

again letting $D_A = D_B$.

To calculate the current at any time for the mechanisms listed above under the chronoamperometric experiment, we note the following:

$$i = nFAD_A\left(\frac{d[A]}{dR}\right)_{R=0} \tag{30}$$

where A is the electrode surface area and F is the Faraday constant. The flux term is converted to dimensionless terms by insertion of the newly defined variables (4).

$$i = \frac{nFAD[A^\circ]}{M-r_0}\left(\frac{dc_A}{dr}\right)_{r_1=X_1=0} \tag{31}$$

The flux term may then be discretized to

$$i = \frac{nFAD[A^\circ]}{M-r_0}\,[A_{1,1}c_A(0,t) + A_{1,N+2}c_A(1,t) + \sum_{j=2}^{N+1} A_{1,j}c_A(r_j,t)] \tag{32}$$

or

$$i = \frac{nFAD[A^\circ]}{M-r_0}\,[A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}c_A(r_j,t)] \tag{33}$$

after insertion of the known values of $c_A(0,t)$ and $c_A(1,t)$.

So the current i may be calculated at any time $T = \frac{(M-r_0)^2 t}{D}$ by insertion of the calculated concentrations from

equations (14) or (28) into equation (33). If there are additional electroactive species in the mechanism, their contribution is simply added into equation (33), since generally,

$$i = \frac{nFAD[A^\circ]}{M-r_0} \sum_{n=1}^{m} \left(\frac{dc_n}{dr}\right)_{r=X_1=0} \tag{34}$$

where m is the total number of electroactive species.

The charge or spectroelectrochemical absorbance can be calculated by use of Gaussian quadrature weights [4,9,10] for the integration of the current in time or the concentration profiles in time.

Cyclic Voltammetric Response

Several modifications have to be made to the method of Speiser and Rieker [6] to develop the cyclic voltammetric responses for the spherical electrode. We define new dimensionless time and distance variables

$$t = \frac{DTa}{(M-r_0)^2}$$

and (35)

$$r = \frac{(R-r_0)a^{1/2}}{M-r_0}$$

where

$$a = nFv/R'T'$$

with v = the potential sweep rate in volts s^{-1}, R' the gas constant, and T' the temperature. Thus,

$$dT = \frac{(M-r_0)^2 dt}{aD}$$

and

$$dR = \frac{(M-r_0)dr}{a^{1/2}} \tag{36}$$

For the simple electron transfer reaction (1), the differential equation (6) becomes

$$\frac{aD[A^\circ]\delta c_A}{(M-r_0)^2\delta t} = \frac{aD[A^\circ]\delta^2 c_A}{(M-r_0)^2\delta r^2} + \frac{2D[A^\circ]}{((M-r_0)r+r_0)(M-r_0)}\frac{\delta c_A}{\delta r} \tag{37}$$

which simplifies to

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta r^2} + \frac{2a^{1/2}}{r+\beta}\frac{\delta c_A}{\delta r} \tag{38}$$

The derivation now proceeds as described by Speiser and Rieker [6].

The cyclic voltammetric boundary conditions are

$$\begin{aligned} &[A]_{R;0} = [A]_{\infty,t} = [A^\circ] \\ &[B]_{R;0} = [B]_{\infty,t} = 0 \\ &\frac{\delta[A]}{\delta R}_{R=0} = -\frac{\delta[A]}{\delta R}_{R=0} \\ &\frac{[A]_{0,T}}{[B]_{0,T}} = \exp[nF/R'T'(E^{\ominus}_{A/B} - E)] = \theta_{A/B}S_\lambda(t) \end{aligned} \tag{39}$$

Inserting the potential sweep rate (14) v, we have

$$\theta_{A/B} = \exp[nF/R'T'(E^{\ominus}_{A/B} - E_{START})]$$

$$S_\lambda(T) = \begin{cases} \exp(-nFvT/R'T') = \exp(-aT) & \text{for } T \leq T_\lambda \\ \exp(at - 2aT_\lambda) & \text{for } T_\lambda \leq T \leq 2T \end{cases} \tag{40}$$

where T is the time when the forward potential sweep is reversed.

We convert equations (39) to dimensionless form normalized to t and M:

$$c_A(r,0) = c_A(1,t) = 1$$

$$c_B(r,0) = c_B(1,t) = 0$$

$$\left(\frac{\delta c_A}{\delta r}\right)_{r=0} = \left(\frac{-\delta c_B}{\delta r}\right)_{r=0} \tag{41}$$

$$\frac{c_A(0,t)}{c_B(0,t)} = \theta_{A/B} S_\lambda(t)$$

Discretizing using equations (8a) and (8b) on (38), we have

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = \sum_{j=1}^{N+2} B_{ij} c_A(r_j,t) + \frac{2a^{1/2}}{r_i+\beta} \sum_{j=1}^{N+2} A_{ij} c_A(r_j,t) \tag{42}$$

or after partial expansion

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = B_{i,1} c_A(0,t) + B_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} B_{ij} c_A(r_j,t) +$$

$$\frac{2a^{1/2}}{r_i+\beta} [A_{i,1} c_A(0,t) + A_{i,N+2} c_A(1,t) + \sum_{j=2}^{N+1} A_{ij} c_A(r_j,t)] \tag{43}$$

Inserting the explicit boundary conditions, we have

$$\left.\frac{dc_A}{dt}\right|_{r_j=X_j} = B_{i,1} c_A(0,t) + B_{i,N+2} + \sum_{j-2}^{N+1} B_{ij} c_A(r_j,t) + \frac{2a^{1/2}}{r_i+\beta} [A_{i,1} c_A(0,t)$$

$$+ A_{i,N+2} + \sum_{j=2}^{N+1} A_{ij} c_A(r_j,t)] \tag{44}$$

Identical treatment for the B species yields

$$\left.\frac{dc_B}{dt}\right|_{r_i=X_i} = B_{i,1}c_B(0,t) + \sum_{j=2}^{N+1} B_{ij}c_B(r_j,t) + \frac{2a^{1/2}}{r_i+\beta}\left[A_{i,1}c_B(0,t) + \sum_{j=2}^{N+1} A_{ij}c_B(r_j,t)\right] \tag{45}$$

We discretize the flux relation in (41) to get an equation relating $c_A(0,t)$ and $c_B(0,t)$, presently implicit boundary conditions.

$$\sum_{j=1}^{N+2} A_{k,j}c_A(r_j,t) = -\sum_{j=1}^{N+2} A_{j,j}c_B(r_j,t) \tag{46}$$

Rieker and Speiser [6] showed that after expansion of equation (46), one may then substitute in equation (44) and arrive at the following result giving the time (potential) dependence of $c_A(0,t)$ and $c_B(0,t)$:

$$c_A(0,t) = -\frac{\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left[A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}(c_A(r_j,t)+c_B(r_j,t))\right]$$

$$c_B(0,t) = -\frac{1}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left[A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}(c_A(r_j,t)+c_B(r_j,t))\right] \tag{47}$$

Inserting these time dependent boundary conditions into the discretized equations (44) and (45) yield the 2N simultaneous first order differential equations necessary to solve for the concentration profiles in time:

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = W_i + \sum_{j=2}^{N+1} F_{ij}c_A(r_j,t) + \sum_{j=2}^{N+1} G_{ij}c_B(r_j,t)$$

$$\left.\frac{dc_B}{dt}\right|_{r_i=X_i} = X_i + \sum_{j=2}^{N+1} H_{ij}c_A(r_{j,t}) + \sum_{j=2}^{N+1} I_{ij}c_B(r_{j,t}) \tag{48}$$

with

$$W_i = = \frac{\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}[B_{i,1}A_{1,N+2}+\frac{2a^{1/2}}{r_i+\beta} A_{i,1}A_{1,N+2}] +$$

$$B_{i,N+2}+\frac{2a^{1/2}}{r_i+\beta} A_{i,N+2}$$

$$F_{ij} = B_{ij}+\frac{2a^{1/2}}{r_i+\beta} A_{ij} - \frac{2a^{1/2}A_{i,1}A_{1,j}\theta_{A/B}S_\lambda(t)}{(r_i+\beta)A_{1,1}[1+\theta_{A/B}S_\lambda(t)]} -$$

$$\frac{B_{i,1}A_{1,j}\theta_{A/B}S_\lambda(t)}{A_{1,1}[1-\theta_{A/B}S_\lambda(t)]}$$

$$G_{ij} = = \frac{\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}[B_{i,1}A_{1,j}+\frac{2a^{1/2}A_{i,1}A_{1,j}}{(r_i+\beta)}]$$

$$W_i = - \frac{1}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}[B_{i,1}A_{1,N+2}+\frac{2a^{1/2}}{r_i+\beta} A_{i,1}A_{1,N+2}]$$

$$H_{ij} = - \frac{1}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}[B_{i,1}A_{1,j} - \frac{2a^{1/2}A_{i,1}A_{1,j}}{r_i+\beta}]$$

$$I_{ij} = B_{ij} + \frac{2a^{1/2}}{r_i+\beta} A_{ij} - \frac{2a^{1/2}A_{i,1}A_{1,j}}{(r_i+\beta)A_{1,1}[1+\theta_{A/B}S_\lambda(t)]} -$$

$$\frac{B_{i,1}A_{1,j}}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}$$

The 2N equations (48) are solved simultaneously as before to find the $c_A(r_j,t)$ and $c_B(r_j,t)$.

The current response is represented similar to the chronoamperometric case:

$$i = nFAD_A\left(\frac{\delta[A]}{\delta R}\right)_{R=0} \tag{49}$$

or in the dimensionless space

$$i = \frac{nFAD_A[A°]a^{1/2}}{(M-r_0)} \left(\frac{dc_A}{dr}\right)_{r_1=X_1=0} \tag{50}$$

Discretizing the flux and inserting the boundary conditions leads to (6)

$$\left.\frac{dc_A}{dr}\right|_{r_1=X_1} = \frac{1}{1+\theta_{A/B}S_\lambda(t)} \left[A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}c_A(r_j,t) - \theta_{A/B}S_\lambda(t) \sum_{j=2}^{N+1} A_{1,j}c_B(r_j,t)\right] \tag{51}$$

So that

$$i = \frac{nFAD_A[A°]a^{1/2}}{(M-r_0)} \left[\frac{1}{1+\theta_{A/B}S_\lambda(t)}\left[A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}c_A(r_j,t) - \theta_{A/B}S_\lambda(t) \sum_{j=2}^{N+1} A_{1,j}c_B(r_j,t)\right]\right] \tag{52}$$

The concentrations $c_A(r_i,t)$ and $c_B(r_i,t)$ found at each time $T = (M-r_0)^2 t/aD$ are used in equation (52) to determine the current as a function of time and hence potential by the relation

$$E = \begin{cases} E_{START} + \dfrac{(M-r_0)^2 tR'T'}{nFD} & t \le t \\ E_{START} + 2vt_\lambda - \dfrac{(M-r_0)^2 tR'T'}{nFD} & t \le t \le 2t \end{cases} \tag{53}$$

where t is the dimensionless potential sweep reversal time

$$t_\lambda = \frac{aDT_\lambda}{(M-r_0)^2}$$

Chronopotentiometry

The chronopotentiometric case for planar electrodes was described in a previous paper. For a chronopotentiometric response to the simple reversible charge transfer reaction, we must consider the following conditions:

$$[A]_{r,0} = [A]_{\infty,T} = [A^\circ]$$

$$[B]_{r,0} = [B]_{\infty,T} = 0 \tag{54}$$

$$E + E^{\ominus}_{A/B} - \frac{R'T'}{nF} \ln[B]_{r_0}$$

$$\left(\frac{\delta[A]}{\delta R}\right)_{r_0} = -\left(\frac{\delta[B]}{\delta R}\right)_{r_0} \tag{55}$$

$$i = nFAD_A\left(\frac{\delta[A]}{\delta r}\right)_{R=r_0} = \text{Constant}$$

The new dimensionless parameters are

$$t = T/\tau \qquad r = \frac{R-r_0}{M-r_0} \tag{56}$$

with τ the transition time of the experiment. Insertion of these values into the differential equation (3) and simplification yields

$$\frac{\delta c_A}{\delta t} = \alpha \frac{\delta^2 c_A}{\delta r} + \frac{2\alpha}{r+\beta} \frac{\delta c_A}{\delta r} \tag{57}$$

where

$$\alpha = \frac{D\tau}{(M-r_0)^2}$$

The conditions (54-55) in dimensionless form become

$$c_A(r,0) = c_A(1,t) = 1$$

$$c_B(r,0) = c_B(1,t) = 0 \tag{58}$$

$$\left(\frac{\delta c_A}{\delta r}\right)_{r_0} = -\left(\frac{\delta c_B}{\delta r}\right)_{r_0}$$

$$i = \frac{nFAD[A^\circ]}{(M-r_0)}\left(\frac{dc_A}{dr}\right)_{r_0} = \frac{nFAD^{1/2}\alpha^{1/2}}{\tau^{1/2}}\ \frac{nFAD^{1/2}[A^\circ]\alpha^{1/2}}{\tau^{1/2}}\left(\frac{dc_A}{dr}\right)_{r_0} \tag{59}$$

The flux relation at the electrode is given from (8a)

$$\left(\frac{dc_A}{dr}\right)_{r_0} = \sum_{j=1}^{N+2} A_{1,j}c_A(r_j,t)$$

$$\left(\frac{dc_B}{dr}\right)_{r_0} = \sum_{j=1}^{N+2} A_{1,j}c_B(r_j,t) \tag{60}$$

Upon entering the known boundary conditions and expanding, and then substituting these into (59) we have

$$c_A(0,t) = Q - \sum_{j=2}^{N+1} a_j c_A(r_j,t)$$

$$c_B(0,t) = R - \sum_{j=2}^{N+1} a_j c_B(r_j,t) \tag{61}$$

with

$$Q = \frac{1}{A_{1,1}}\left[\frac{i\tau^{1/2}}{nFA[A^\circ]D^{1/2}\alpha^{1/2}} - A_{1,N+2}\right]$$

$$R = \frac{1}{A_{1,1}}\left[\frac{i\tau^{1/2}}{nFA[A^\circ]D^{1/2}\alpha^{1/2}}\right]$$

$$a_j = \frac{A_{1,j}}{A_{1,1}}$$

The discretized equations for A and B are thus

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = \sum_{j=1}^{N+2} B_{ij}c_A(r_j,t) + \frac{2\alpha}{r_i+\beta}\sum_{j=1}^{N+2} A_{ij}c_A(r_j,t)$$

$$\left.\frac{dc_B}{dt}\right|_{r_i=X_i} = \sum_{j=1}^{N+2} B_{ij}c_B(r_j,t) + \frac{2\alpha}{r_i+\beta}\sum_{j=1}^{N+2} A_{ij}c_B(r_j,t) \tag{62}$$

The known boundary conditions from equations (58) and (61) are entered, and we have

$$\left.\frac{dc_A}{dt}\right|_{r_i=X_i} = \alpha Q_i' + \alpha\sum_{j=2}^{N+1} b_{ij}c_A(r_j,t)$$

$$\left.\frac{dc_B}{dt}\right|_{r_i=X_i} = \alpha R_i' + \alpha\sum_{j=2}^{N+1} b_{ij}c_B(r_j,t) \tag{63}$$

where

$$Q_i' = B_{i,1}Q + B_{i,N+2} + \frac{2\alpha}{r_i+\beta}(A_{i,1}Q + A_{i,N+2})$$

$$R_i' = B_{i,1}R + \frac{2A_{i,1}R}{r_i+\beta}$$

$$b_{ij} = -B_{i,1}a_j + B_{ij} = \frac{2}{r_i+}(A_{i,1}a_j - A_{ij})$$

The usual display of the response is given by

$$E = \overset{\ominus}{E}_{A/B} - \frac{R'T'}{nF}\ln\left(\frac{c_B(0,t)}{c_A(0,t)}\right) \tag{64}$$

where the two concentration terms in brackets are found from equation (61). The concentration terms in (61) are found by integration of the simultaneous equation (63) by the methods described [1,4,5,9] previously.

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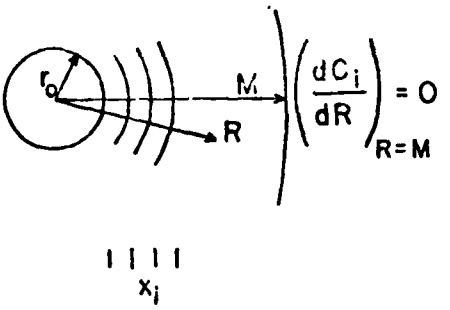
Table 1

Time, sec	i_{exact}, ma	$i_{sinulated}$, ma
1×10^{-5}	1.7104	1.7104
1×10^{-4}	0.5411	0.5412
1×10^{-3}	0.1713	0.1712
1×10^{-2}	0.0054	0.0054
1×10^{-1}	0.0017	0.0017
1×10^{0}	0.0001	0.0001

Comparison of exact and simulated currents for the simple change transfer chronoamperometric experiment. (N = 6 collocation points.) See text for parameters.

FIGURE CAPTION

Figure 1. Spherical electrode geometry.


r_0
M
R
$\left(\frac{dC_i}{dR}\right)_{R=M} = 0$
x_i

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