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Orthogonal Collocation Simulation of the Rotating Disc Electrode

By

Bernd Speiser, Stanley Pons and Jerome McAleer

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University of Alberta
Department of Chemistry
Edmonton, Alberta, Canada
T6G 2G2

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The theory of orthogonal collocation as applied to rotating disc systems is presented and its advantages are described. The technique is extremely fast and application of chemical reactions is easily implemented.

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ORTHOGONAL COLLOCATION SIMULATION OF THE ROTATING DISK ELECTRODE

Stanley Pons*, Bernd Speiser, and Jerome F. McAleer

Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada
T6G 2G2

ABSTRACT

The hydrodynamic problem of the rotating disc electrode is approximated using the weighted residual technique of orthogonal collocation. Results are given for a potential step applied to the electrode where simple reversible charge transfer to a single species takes place.

Analytical solutions for the current at rotating disc electrides (RDE) (Figure 1) are known for only the simplest electrochemical reaction mechanisms or electrical perturbations. Orthogonal collocation solution techniques, like finite difference approaches, give a single mathematical method for approximating virtually all electrochemical responses and mechanisms. The RDE is described by a partial differential equation containing square distance terms. It is shown that such non-linearity presents no special problems in the approximation technique. The results for the RDE are available from changing only 2 program steps in the general program solving a simple electron transfer mechanism at a stationary planar electrode.

DIMENSIONAL ANALYSIS

The general differential equation describing mass transport to a rotating disc electrode is given by

$$V_r \frac{\delta c_i}{\delta r} + \frac{V_\theta}{r} \frac{\delta c_i}{\delta \theta} + V_z \frac{\delta c_i}{\delta z} \qquad [1]$$

where the c_i are the concentrations of electroactive species, t is the time, z is the distance coordinate normal to the electrode surface, D_i are the diffusion coefficient, r is the distance coordinate parallel to the electrode surface, the V_i are velocity components of the fluid, and θ is the rotation coordinate about the z axis.

In the assumption of an ideal hydrodynamic model, there is no change in concentration in the θ direction. Also, we assume that V_z is independent of r, which implies a uniform flow. We can thus approximate $\delta c/\delta r = 0$ over the whole electrode when the radius of the electrode is small with respect to the sheath.

The assumptions reduce the differential equation to the form:

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta z^2} - V_z \frac{\delta c}{\delta z} \qquad [2]$$

The velocity term V_z has been given by Levitch (1) and is a function of the kinematic viscosity v and the rotation velocity w:

$$V_z = -0.51\, w^{3/2} v^{-1/2} z^2 = Kz^2 \qquad [3]$$

Thus

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta z^2} - Kz^2 \frac{\delta c}{\delta z} \qquad [4]$$

We require to have the equation in dimensionless form. We choose as the distance coordinate

$$Z = z/L \qquad [5]$$

where L is a distance along the z axis where, during the time

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frame of the experiment, no diffusion effects are present. We choose the time coordinate as

$$\tau = \frac{Dt}{L^2} \qquad [6]$$

and a dimensionless constant

$$\beta = \frac{KL^3}{D} \qquad [7]$$

Concentration is made dimensionless by dividing by the bulk concentration c^b:

$$c^* = \frac{c}{c^b} \qquad [8]$$

Substitution of [5], [6], and [8] into the differential equation [2] yields:

$$\frac{Dc^b}{L^2}\frac{\partial c^*}{\partial \tau} = \frac{Dc^b}{L^2}\frac{\partial^2 c}{\partial z^2} - \frac{KL^2 z^2 c^b}{L}\frac{\partial c^*}{\partial z} \qquad [9]$$

or

$$\frac{\partial c^*}{\partial \tau} = \frac{\partial^2 c^*}{\partial z^2} - \frac{KL^3}{D} z^2 \frac{\partial c^*}{\partial z} \qquad [10]$$

$$\frac{\partial c^*}{\partial \tau} = \frac{\partial^2 c^*}{\partial z^2} - \beta z^2 \frac{\partial c^*}{\partial z} \qquad [11]$$

We consider the transient current at the rotating electrode

when a potential step is applied which drives the surface concentration of the electroactive species to zero.

$$c^*(0,\tau) = 0 \qquad c(1,\tau) = 0$$
$$c(z,0) = 1 \qquad [12]$$

It has been shown that the weighted residual method of orthogonal collocation can furnish accurate solutions to differential equations (2-4) at certain distance points in solution. The points correspond to the roots or zeros (collocation points) of orthogonal shifted Jacobi polynomials.

DISCRETIZATION OF THE DIFFERENTIAL EQUATION

The z differentials are discretized in terms of collocation coefficients (3):

$$\left.\frac{dc^*}{dz}\right|_{z_i} = \sum_{j=1}^{N+2} A_{ij}\, c^*(z_j,\tau) \qquad [13]$$

and

$$\left.\frac{d^2c^*}{dz^2}\right|_{z_i} = \sum_{j=1}^{N+2} B_{ij}\, c^*(z_j,\tau) \qquad [14]$$

where z_i are the roots of the Jacobi polynomial of order N chosen, and the A_{ij} and B_{ij} are elements of matrices given in terms of the z_i only:

$$\bar{X} = \left|\frac{dz_j}{dz_i}\right| \cdot \bar{D}^{-1} \qquad [15]$$

$$\bar{B} = \left|\frac{d^2 z_j}{dz^2_i}\right| \cdot \bar{O}^{-1} \qquad [16]$$

$$\bar{O} = |z_i^j| \qquad [17]$$

The values of each of these matrix elements are easily calculated by matrix multiplication and inverse matrix routines (such as those based on Gauss-Jordan elimination) (4).

Substitution of the discretized differentials into [11] yields:

$$\left.\frac{dc^*}{dT}\right|_{z_i} = \sum_{j=1}^{N+2} B_{ij}\, c^*(z_j,T) - \delta z_i^2 \sum_{j=1}^{N+2} A_{ij}\, c^*(z_j,T) \qquad [18]$$

We have now N+2 equations (Z=0 and Z=1 plus the N central roots) in N+2 unknown $c^*(z_j,T)$. The dimension is reduced by two, and the problem specified to final form by introducing into [18] the known boundary conditions

$$c^*(0,t) = 0$$
$$c^*(1,T) = 1 \qquad [19]$$

which are the first and last terms of each summation:

$$\left.\frac{dc^*}{dT}\right|_{z_i} = B_{i,1}\, c^*(0,T) + B_{i,N+2} c^*(1,T) + \sum_{j=2}^{N+1} B_{ij} c^*(z_j,t) - \delta z_i^2 \left[A_{i,1} c^*(0,T) + A_{i,N+2}(1,T) + \sum_{j=2}^{N+1} A_{ij} c^*(z_j,T)\right] \qquad [20]$$

to yield

$$\left.\frac{dc^*}{dT}\right|_{z_i} = B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij} c^*(z_j,T) - \delta z_i^2 \left[A_{i,N+2}(1,T) + \sum_{j=2}^{N+1} A_{ij} c^*(z_j,T)\right] \qquad [21]$$

Thus the concentration profiles as a function of time are readily and efficiently generated by integrating the N sets of first order differential equation [21]. One may use available subroutines from software libraries such as IMSL or SSP, or more specialized programs taking the stiffness of the differential equations into account (2,4).

As has been shown previously, more complicated mechanisms may be readily incorporated into the equations (3,4) as well as a *variety of electrochemical techniques, electrode geometries* (5-8), and edge effect considerations (9,10).

RDE CURRENT

Current to the RDE is given by the flux at the surface:

$$i = nFAD \left(\frac{\delta c}{\delta Z}\right)_{Z=0} \qquad [22]$$

or in terms of the dimensionless concentration [8] and distance [5],

$$i = \frac{nFADc^b}{L} \left(\frac{\delta c^*}{\delta Z}\right)_{Z=0} \qquad [23]$$

or

$$i = \frac{nFAD^{2/3}c^b\kappa^{1/3}}{\beta^{1/3}} \left(\frac{\delta c^*}{\delta Z}\right)_{Z=0} \qquad [24]$$

which is given immediately during the simulation at each time point by

$$i = nFAD^{2/3}c^b\kappa^{1/3}\beta^{-1/3}\left[A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}c^*(Z_j,T)\right] \qquad [25]$$

since the term in brackets is the dimensionless flux in equation [24] at Z=0 by equation [13].

We can compare our result to a series solution () which states that the time dependent current is proportional to

$$1 + 2\sum_{m=1}^{\infty} \exp\left(\frac{-m^2\pi^2Dt}{\delta_0^2}\right) \qquad [26]$$

where

$$\delta_0 = 1.61\, D^{1/3}\omega^{-1/2}\nu^{1/6} \qquad [27]$$

Introducing the dimensionless time variable [9] into [26] we find the current is proportional to

$$1 + 2\sum_{m=1}^{\infty} \exp(-1.5m^2\,\beta^{2/3}T) \qquad [28]$$

, so that the ratio of the current calculated from equation [25] to the expression [28] should be constant. Results for a given set of parameters are given in Table 1. It is seen that for only six collocation points, the current values are accurate to 0.05%. This value may be further decreased by forcing higher accuracy in the integrations (2) or increasing the number of collocation points, although ten points do not exhibit significant improvement over nine. The maximum relative error decrease using ten instead of nine collocation points is 0.007%.

The results for the rotating ring disc electrode are being optimized, and will be the subject of a forthcoming publication.

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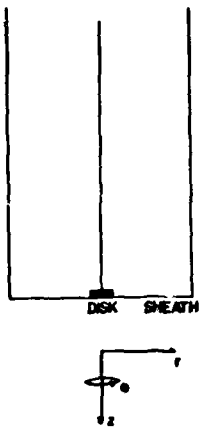
T	Simulated Flux / Eqn. 28
10^{-5}	0.7985
10^{-4}	0.7702
10^{-3}	0.7700
10^{-2}	0.7700
10^{-1}	0.7700
10^{0}	0.7704

Table 1. Ratio of simulated flux to analytical current-time function (Ref. 11) Beta = 10^{-1}. For typical rotation speeds (1000 RPM), viscosities, and diffusion coefficients, the real total time simulated in the table is t = 100 ms.



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