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Digital Simulation of Diffusion Limited Chronoamperometry at Disk Electrodes without Neumann Boundary Conditions on the axis or at the insulating plane

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It is proposed that in the digital simulation of a disk (or band) electrode flush with an insulating plane, the customary Neumann boundary conditions can be dispensed with on the axis and at the insulating plane, and diffusion can be applied in the relevant regions instead. It is suggested that the application of Neumann boundary conditions in these cases in fact corresponds to the neglect of information. Results show that the application of diffusion conditions leads to practical the same results, but not that results are better.

Keywords: Boundary Conditions; Computational Electrochemistry; Digital Simulation

1. INTRODUCTION

Saito was the first to consider mass transport at a disk electrode embedded in an insulating plane [1], and introduced Neumann boundary conditions (**NBCs**) at the insulating plane. In contrast with Dirichlet boundary conditions (specifying certain values), NBCs specify (in this case, spatial) derivatives. Fig. 1 shows a diagram of the cross-section of a disk electrode, with its dimensions normalised to the disk radius a, so that the disk radius is now unity. Saito's NBC was that $\partial C/\partial Z=0$ at the insulating plane region, $Z=0$, $R>1$ in our dimensionless case. Later workers often refer to another "boundary" condition, at the system's axis, $R=0$, where one can assume that $\partial C/\partial R=0$. This is sometimes stated but not in fact used, see for example Crank & Furzeland (1977) [2]. Their paper has a figure showing both NBCs, but their treatment then uses the diffusion equation on the axis, approximating a certain term by using the Maclaurin expansion (see below). Heinze was the first to simulate the disk electrode [3,4], using the NBC at the insulating plane, but not the one on the axis; Gavaghan and coworkers applied both NBCs [5-7]. All this refers to the disk electrode in cylindrical

coordinates (*R*,*Z*). Because of the problems associated with the singularity at the disk edge, it became evident that coordinate transformation is desirable, and several were suggested, among them that by Michael et al [8] and by Verbrugge and Baker [9] which transformed (*R*,*Z*) space into elliptic (θ,Γ) coordinates, eliminating the singularity, and leading to greatly improved simulation efficiency. In this paper, we will consider the representative Verbrugge and Baker transformation (see below). In these transformed systems, the axial and insulating plane regions are represented as well (see later), and again, NBCs can be invoked and usually are, for example, in the works of Michael et al [8], and our own work [10]. The related simulation area of the Scanning Electrochemical Microscope (SECM), which often is a disk electrode in a special environment, again most workers invoke NBCs. The works cited above are only a small representative section of the total possible citations. It will be argued in this paper that NBCs are not necessary, and may even be undesirable. For further details on the theory of the disk electrode and simulations of electrochemistry at it, see [11]. In that work, the subject of this paper is briefly mentioned but not detailed.

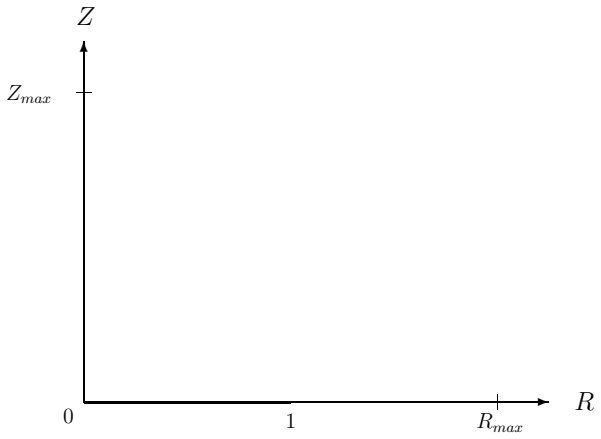

Figure 1. Diagram of the cross section of a disk electrode flush with an insulating plane

2. THEORY

In cylindrical coordinates, the transport equation for the disk electrode, in dimensionless form, is

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} \qquad (1)$$

where *C* denotes concentration, *R* and *Z* the axial and normal coordinates, and *T* dimensionless time, normalised by

$$T = \frac{4Dt}{a^2} \tag{2}$$

in which a is the electrode radius and D the diffusion coefficient. The common (Dirichlet) boundary condition for the diffusion-limited chronoamperometric experiment is

$$T > 0,\ 0 \le R \le 1,\ Z = 0: \quad C(0,R) = 0. \tag{3}$$

All workers cited above use the Neumann boundary condition

$$R > 1,\ Z = 0: \quad \partial C / \partial Z = 0 \tag{4}$$

and some also use

$$R = 0: \quad \partial C / \partial R = 0. \tag{5}$$

Discretisation of these NBCs are described in the next section.

Simulations using direct discretisation in the cylindrical coordinates are inefficient, because of the singularity at the disk edge, for which reason transformations are commonly used. The transformation by Verbrugge and Baker [9] is one of these:

$$\begin{aligned} R &= \cos\theta\ \cosh\Gamma \\ Z &= \sin\theta\ \sinh\Gamma \end{aligned} \tag{6}$$

(writing, for convenience, $\Gamma' \equiv \Gamma/(1-\Gamma)$), resulting in the new coordinates (θ,Γ). The transport equation then transforms to

$$\frac{\partial C}{\partial T} = \frac{1}{\sin^2\theta + \sinh^2\Gamma'}\left(\frac{\partial^2 C}{\partial \theta^2} - \tan\theta\frac{\partial C}{\partial \theta} + (1-\Gamma)^4\frac{\partial^2 C}{\partial \Gamma^2} + \left((1-\Gamma)^2\tanh\Gamma' - 2(1-\Gamma)^3\right)\frac{\partial C}{\partial \Gamma}\right) \tag{7}$$

Condition (3) here becomes

$$T > 0, \Gamma = 0: \quad C(\theta,0) = 0 \tag{8}$$

and the NBCs are

$$\theta = 0: \quad \partial C / \partial \theta = 0 \tag{9}$$

(corresponding to the insulating plane) and

$$\theta = \frac{\pi}{2}: \quad \partial C / \partial \theta = 0 \tag{10}$$

(corresponding to the axis). Discretisations of these too are described below.

However, there is no need to invoke NBCs. Consider the system axis in Fig. 1, and consider that although it is true that there is no concentration gradient normal to the axis (R=0), there is indeed diffusion along the axis, described by the transport equation there. As pointed out by Crank and Furzeland [2], there is, at $R = 0$, the problem of the 1/R term. They invoked the Maclaurin series (a special case of the Taylor series) to approximate the first derivative term in (1), resulting in the axial diffusion equation

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial Z^2} + 2\frac{\partial^2 C}{\partial R^2} \quad . \tag{11}$$

The second derivative in R can be expressed discretely without problems, see below, and this has been done by some, for example Gavaghan [12]. This practice is an example of the NBCs being replaced by a specification of diffusion.

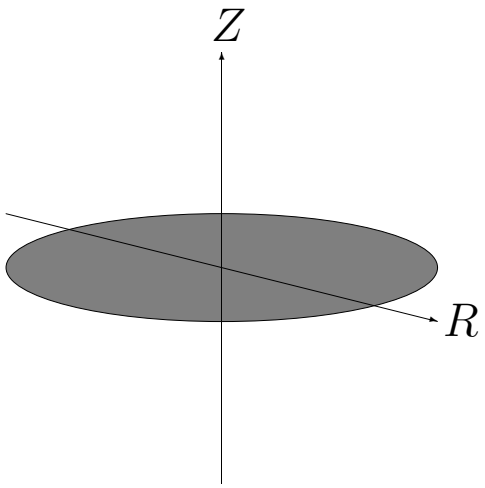

Figure 2. Diagram of an infinitely thin disk floating in space

The same can be done for the insulating plane. Consider Fig. 2, where we consider the disk as an infinitely thin disk suspended in space. Clearly, conditions on the axis are the same as for the disk in an insulating plane (except for the space below the disk, where we now also have diffusion). But where the insulating plane was, conditions are also the same. Symmetry dictates that there is no net flux of substance across the plane where the insulating surface formerly was. However, we now see that we can simply invoke diffusion on this plane in space; there is no boundary there. Going back to the disk in the insulating plane, we do not have points below the plane but we can equate them to points above the plane at equal distances from it. In this manner, we can obtain discrete approximations for the second derivative in Z, see below.

It can be argued that if we invoke NBCs at these two regions, we are throwing away information, which we do not throw away by invoking diffusion there. This is because when we express discrete approximations that correspond to the NBCs, we let the points on the axis and on the plane depend on neighbouring points, without using the information we might obtain from the diffusion equation. This suggests that invoking diffusion, rather than NBCs, should improve simulations. It turns out that it makes almost no difference.

In what follows, we shall distinguish between the two cases of NBCs and what will be called diffusion here, that is, dispensing with NBCs and invoking diffusion instead.

Similar arguments can be invoked for the band electrode flush with an insulating plane, where there is a vertical plane instead of an axis, and no problem with a $1/R$ term.

Note that this does not apply to simulations involving a Neumann boundary condition at the electrode itself (for example, chronopotentiometry). These must be discretised as such.

3. DISCRETISATIONS

No details of the actual discretisations will be presented here, except for the regions in question; the reader can find details of these in [11]. The method of simulation, too, is not detailed here; there is a variety of choices, also described there. We shall here focus on the discretisations at the axis and insulating plane only, in both the cases of NBCs and diffusion.

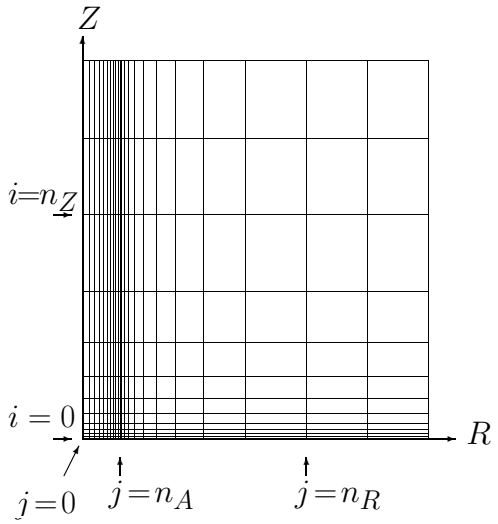

Figure 3. Discrete grid representing the cylindrical disk system

Fig. 3 shows a grid in (*R*,*Z*) space, divided into unequal intervals, as described, for example, in [11,12], using exponentially expanding intervals as described by Feldberg [13] (preceded by Pao and Dougherty [14], albeit in a non-electrochemical context), expanding up the *Z*-axis and away from the

disk edge in both directions. Let the index of grid positions be *i* in the *Z* direction and *j* in the *R* direction, so that we have points on the grid, with values $C_{i,j}$.

Applying NBCs now on the axis, we simply express the first derivative in *R* as a discrete approximation and set it equal to zero. For example, a four-point approximation might be chosen, using the positions (-1, 0, 1 and 2) along *j*, where the point at $j=-1$ is the same as that at $j=1$ by symmetry, giving

$$(\beta_1+\beta_3)C_{i,1}+\beta_2 C_{i,0}+\beta_4 C_{i,2}=0\,. \tag{12}$$

This, effectively using the point on the other side of the axis, might be a better approximation than the one-sided one,

$$\beta_1 C_{i,0}+\beta_2 C_{i,1}+\beta_3 C_{i,2}+\beta_4 C_{i,3}=0\,. \tag{13}$$

In these expressions, the β coefficients are those for the first derivative on arbitrarily spaced points, for which a routine has been described [15], but an algorithm due to Fornsberg [16] is in fact preferable (a Fortran subroutine based on this, yielding interpolation values or first- or second-order derivatives at any point within a group of arbitrarily spaced points can be obtained from the author).

On the insulating plane, similar discretisation formulae can be used, in the *Z* direction, again using a chosen set of points, for example the four-point approximation

$$(\beta_1+\beta_3)C_{1,j}+\beta_2 C_{0,j}+\beta_4 C_{2,j}=0\,. \tag{14}$$

The two-dimensional system to be solved is thus cast into a large banded linear system including the above expressions, and can be solved by a sparse matrix technique. The present author favours the package MA28 [17], available from the Harwell site [18] or the package YM12 [19], available from netlib [20]. There are other methods of solving the system, but they will all in some manner use the above formulae.

On the axis, using (11), the second derivative term in *R* is readily discretised as a three-point approximation, but due to symmetry this reduces to

$$\frac{\partial^2 C}{\partial R^2}\approx\frac{1}{\delta R^2}\left(-2C_{i,0}+2C_{i,1}\right) \tag{15}$$

With $\delta R=R_1$, the other term, in *Z*, being straight-forward.

On the insulating plane there is no problem with (1), and again using symmetry, we get

$$\frac{\partial^2 C}{\partial R^2}+\frac{1}{R_j}\frac{\partial C}{\partial R} \approx \alpha_1 C_{0,j-1}+\alpha_2 C_{0,j}+\alpha_3 C_{0,j+1}+\alpha_4 C_{0,j+2} + \frac{1}{R_j}(\beta_1 C_{0,j-1}+\beta_2 C_{0,j}+\beta_3 C_{0,j+1}+\beta_4 C_{0,j+2}) \tag{16}$$

again using coefficients for the four-point approximations, and

$$\frac{\partial^2 C}{\partial Z^2} \approx (\alpha_1+\alpha_3)C_{1,j}+\alpha_2 C_{0,j}+\alpha_4 C_{2,j} \tag{17}$$

where the coefficients are now those for the Z direction, again using symmetry.

Simulation using discretisation directly in (*R*,*Z*) is however not an efficient procedure, and transformation greatly improves the matter. The transformation by Verbrugge and Baker (6), yielding the new transport equation (7) is used preferentially by the present author, and Fig. 4 shows an evenly divided grid in (θ,Γ) space and its equivalent in (*R*,*Z*). The two regions where NBCs usually are applied are the left-hand edge, corresponding to the insulating plane, and the right-hand edge, corresponding to the axis. The base line corresponds to the electrode.

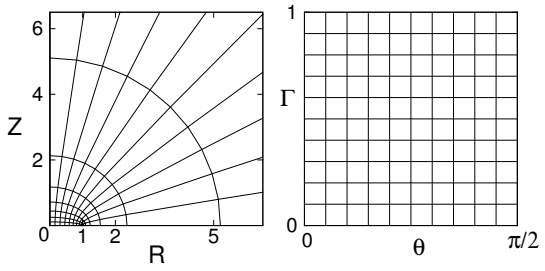

Figure 4. Discrete grid in transformed coordinates on the right with equal intervals, and the equivalent grid in cylindrical coordinates on the left (some grid lines are outside the picture in (R,Z))

NBCs are expressed very simply here; we have equal intervals, and three-point approximations yield second-order approximations. Again using *i* as the vertical, and *j* as the horizontal index, we have, for example, on the insulating plane, the one-sided three-point expression (at $\theta = 0$)

$$\frac{\partial C}{\partial \theta} \approx \frac{-3C_{i,0}+4C_{i,1}-C_{i,2}}{2\delta\theta} \tag{18}$$

with $\delta\theta$ being the intervals in θ, and for the axis ($\theta = \frac{\pi}{2}$)

$$\frac{\partial C}{\partial \theta} \approx \frac{C_{i,N_\theta-2} - 4C_{i,N_\theta-1} + 3C_{i,N_\theta}}{2\delta\theta}. \tag{19}$$

The coefficients are tabled in [11, p. 281].

Upon invoking diffusion in this space, we use (7), setting the first derivatives with respect to θ to zero but retaining the second derivatives. These can be approximated by mirroring points on the other side of the respective edge, so that the three-point approximation at the left-hand edge ($\theta = 0$) becomes, similar to (15)

$$\frac{\partial^2 C}{\partial \theta^2} \approx \frac{1}{\delta\theta^2}\left(-2C_{i,0} + 2C_{i,1}\right) \tag{20}$$

and at the right-hand edge ($\theta = \frac{\pi}{2}$)

$$\frac{\partial^2 C}{\partial \theta^2} \approx \frac{1}{\delta\theta^2}\left(2C_{i,N_\theta-1} - 2C_{i,N_\theta}\right). \tag{21}$$

As before, these approximations will join those for the bulk of the points making a large banded linear system to be solved.

4. COMPUTATIONAL

All the above cases have been implemented using Intel Fortran 90/95, running on a PC under Suse Open Linux, always specifying a precision of at least 14 decimals. For the simulations, the algorithm used was a single backwards implicit step followed by three-point BDF, see [11] for details. The particular algorithm employed is not important, however.

5. RESULTS AND DISCUSSION

For the grid in (*R*,*Z*), it was possible to go up to a grid of 160 x 220, and choosing a smallest interval in *R* and *Z* as 10^{-6}, which means expansion factors γ [11, p. 108] of 1.088 along *Z*, and respectively 1.072 and 1.276 along *R*, going left and right away from the disk edge, all reasonable values. Computed currents were compared with the recent formula of Mahon and Oldham [21], found to be very accurate [10]. Time intervals of 0.01 were used, 100 steps to $T = 1$.

For the simulations in (*R*,*Z*) using NBCs, the final error in the flux at *T*=1 was -0.06%, while for the diffusion discretisation, it was 0.08%. This is an insignificant difference and is partly explained by the restricted diffusion space allowed (8 units in *Z* and 9 units in *R*). When this is extended, the

errors become smaller and more equal. In (θ,Γ) space, using a 100 x 100 grid and the same step size in time, the error at T=1 was -0.01% in both cases.

The same boundary conditions (or lack thereof) can be invoked for the steady state, setting the left-hand side of (1) or (7) to zero and solving. Since the current was normalised to the steady state value (Saito, [1]), this should be equal to unity. This was tried only in (θ,Γ) space, and in both NBCs and diffusion discretisations, the steady state flux came to 1.000, with an error of -0.004% in both cases.

6. CONCLUSIONS

It is seen that it is possible to replace Neumann boundary conditions with diffusion equations, suitably adapted to the various cases R=0, using, in (R,Z) space, approximations derived from Maclaurin expansion, and symmetry consideration for points on the insulating plane. Results of simulations are almost the same with or without Neumann boundary conditions. It can be argued nevertheless that it is better to use diffusion-based expressions, as these use more information on points in the grid than when invoking Neumann conditions. The same argument applies to other electrodes, such as the band electrode flush with an insulating plane, and the disk in a SECM cell.

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