Electrode “edge effects” analyzed by the Green function method

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Abstract

An exact method based on Green’s equation is used to find the diffusion-controlled faradaic current for certain electrode geometries that incorporate edges and vertices. Thereby the magnitudes of the time-independent current density associated with angled electrode/electrode and electrode/insulator junctions are calculated. As well, the square-root-of-time-dependent currents associated with vertices, receive attention. These terms extend to longer times, the Cottrell formulation appropriate for short times. Though most of the problems solved here have been tackled previously, the novel Green function approach is shown to be straightforward and intuitive.

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1. Introduction

Only a select few electrode geometries, such as the sessile hemisphere, exhibit uniform accessibility towards diffusing solutes. Most electrodes, including all of the ones that are easily constructed, are impaired by an “edge effect” of some sort. The inlaid disk electrode provides an example. It is often regarded as being comprised of an interior region, supporting planar diffusion, together with an edge effect at the perimeter, where diffusion is enhanced. This is a fiction. An enhanced current actually flows over the entire disk and the actual contribution of the perimeter itself is negligible. Nevertheless it is a useful fiction, because the plane-plus-perimeter model accurately predicts the short-time current response of the disk electrode to potential signals.

The plane-plus-perimeter model may be extended to encompass other geometric features, such as curved surfaces, junctions and vertices. The goal is to (falsely) attribute the short-time current to discrete geometric features of the electrode. Studies of this sort were a major preoccupation of this laboratory in prior decades [1–12] and this article represents a resumption of that effort. Whereas variable separation and Laplace transformation were the prime tools used previously, the Green function approach [13] will be employed here. There are rather few new results in this contribution, the main thrust being to expose the Green method.

The archetypal voltammetric process is the “potential leap” experiment in which the potential of an electrode, previously open-circuited, is suddenly brought to a value at which an electrode reaction can proceed under complete diffusion control. The potential-leap experiment is the only electrochemical process that will be considered here, but extensions to more interesting voltammetric experiments are possible via developments similar to those made by Cope and Tallman [14,15]. Attention will be confined to the ways in which the response to the sudden change in potential depends on the geometry of the electrode/solution interface.

2. The Green function approach

There have been only a few uses [16,17] in electrochemistry of the powerful method pioneered by Green.

The distribution of electroactive solute in space and time during the potential-leap experiment is described by the following set of equations:
\[
\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} = \frac{1}{D} \frac{\partial c}{\partial t},
\]
\( t \geq 0 \) all \( x, y, z \) points in the electrolyte solution,

(2.1)

c = C, \ t = 0 \ all \ x, y, z \ points \ in \ the \ electrolyte \ solution,

(2.2)

c = 0, \ t > 0 \ all \ x, y, z \ points \ on \ the \ electrode \ surface,

(2.3)

\[ \frac{\partial c}{\partial n} = 0, \ t \geq 0 \ all \ x, y, z \ points \ on \ any \ insulating \ surfaces. \]

(2.4)

Here \( c \), generally a function of \( x, y, z \) and \( t \), is the concentration of the solute and \( n \) is the normal to a bounding surface at the point in question. \( D \) is the diffusivity (diffusion coefficient) of the electroactive species and \( C \) is its initially uniform concentration. If, as we assume, the electrolyte solution is of sufficient extent, then \( C \) remains the concentration in solution at locations remote from the electrode. It is of interest to determine the surface concentration gradient of the electroactive species

\[ \frac{\partial c}{\partial n}, \ t \geq 0 \ all \ x, y, z \ points \ on \ the \ electrode \ surface, \]

(2.5)

because the local current density is proportional to this quantity.

Green’s method, as applied to the diffusion of a solute dissolved in a liquid, keeps track of concentration changes by imagining each element of the solution to be a source, continuously transmitting solute to every other location in the solution. In an infinite three-dimensional spatial domain, the concentration change at point \( x, y, z \) at time \( t \) arising from a source of concentration \( c' \) at point \( x', y', z' \) at some previous time \( t = 0 \) is

\[
d^3c = \frac{c'}{(4\pi Dt)^{3/2}} \times \exp\left\{\frac{-((x-x')^2-(y-y')^2-(z-z')^2)}{4Dt}\right\} dx' dy' dz',
\]

(2.6)

in cartesian coordinates. This increment of concentration at \( x, y, z \) is that arriving from the rectangular parallelepiped element of volume bounded by the planes \( x = x', x = x' + dx', y = y', y = y' + dy', z = z' \) and \( z = z' + dz' \).

Recognize that Eq. (2.6), as it stands, is a solution to Eq. (2.1) that is applicable only to a three-dimensional space, \(-\infty < x < \infty, -\infty < y < \infty, -\infty < z < \infty\), wholly filled with solution. It can sometimes, however, be adapted to apply to bounded spaces by designing a fictitious system that, in the region of interest, mimics the real electrochemical situation in its diffusional behaviour.

The strategy that will be adopted throughout this article is to evade the need to meet condition (2.3) explicitly by modifying the geometry so that each surface, be it electrode or insulating, is replaced by a junction between two solutions, so contrived that the concentration at the junction, or its gradient there, is zero. With neither conducting nor insulating surfaces present, diffusion can occur in a three-dimensional spatial continuum, validating Eq. (2.6).

3. Cottrell conditions

The classic equation \[18\]

\[
\frac{\partial c}{\partial n} = \frac{c}{\sqrt{\pi Dt}}, \ t > 0 \ all \ x, y \ points \ on \ the \ electrode \ surface
\]

(3.1)

is the solution to the equation set (2.1)–(2.3) when the electrode is the infinite plane \( z = 0 \) and the electrolyte solution occupies the half-space \( z > 0 \). To set the stage for what is to follow, we shall derive Eq. (3.1) by an unusual route, via the Green function approach.

The half-space \( 0 < z < \infty \) is occupied initially by solution containing an electroactive solute at a uniform concentration \( C \). Now discard the electrode and, instead, as in Fig. 1(b), imagine the complementary half-space \(-\infty < z < 0\) to be filled with a solution of initial concentration \(-C\), notwithstanding the unusual concept of a negative concentration. The purposes of this fictitious construct are to create a condition of mirror symmetry across the plane \( z = 0 \), thereby enforcing condition (2.3), and to replace the bounded geometry by

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Cottrell geometry. The \( x \)-axis lies perpendicular to the plane of the paper. (a) The real geometry, with solution occupying the region above the electrode, shown hatched, the surface of which occupies the \( z = 0 \) plane. (b) The fictitious model, in which the electrode has been removed and a solution of negative concentration occupies the region \( z < 0 \).}
\end{figure}
an unbounded one, so that Eq. (2.6) becomes applicable. The concentration at any point \(x, y, z\) in the half-space \(z > 0\) can now be found by integration of Eq. (2.6) over all space:

\[
c = \frac{C}{(4\pi Dt)^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left\{\frac{-(x-x')^2-(y-y')^2-(z-z')^2}{4Dt}\right\} dx' dy' dz' + \frac{(-C)}{(4\pi Dt)^{3/2}}
\]

\[
\times \int_{-\infty}^{0} \int_{-\infty}^{\infty} \exp\left\{\frac{-(x-x')^2-(y-y')^2-(z-z')^2}{4Dt}\right\} dx' dy' dz'.
\]

(3.2)

The triple integrals split neatly into products of single integrals, each of which is readily evaluated:

\[
\int_{-\infty}^{\infty} \exp\left\{\frac{-(y-y')^2}{4Dt}\right\} dy' = \sqrt{4\pi Dt}
\]

(3.3)

with a similar result for the \(x\)-integration, and

\[
\left(\int_{0}^{\infty} - \int_{-\infty}^{0}\right) \exp\left\{\frac{-(z-z')^2}{4Dt}\right\} dz' = \sqrt{4\pi Dt} \text{erf}\left\{\frac{z}{\sqrt{4Dt}}\right\}.
\]

(3.4)

Accordingly, putting these results together:

\[
c = C \text{erf}\left\{\frac{z}{\sqrt{4Dt}}\right\},
\]

(3.5)

which leads directly to the Cottrell result, Eq. (3.1). The areal current density \(i\) (A m\(^{-2}\)) follows in the standard way:

\[
i = NF \frac{\partial c}{\partial n} = NF \frac{\partial c}{\partial z} = D \frac{\partial c}{\partial n} = D \frac{\partial c}{\partial z} = C \sqrt{\frac{D}{\pi t}} \approx \frac{i_{\text{cot}}}{NF},
\]

(3.6)

where \(N\) is the electron number (positive for an oxidation) and \(F\) is Faraday’s constant. Applied to Eq. (3.5), this procedure establishes the formula for the cottrellian current density. The final item in (3.6) establishes the symbol \(i_{\text{cot}}\) as a representation of the cottrellian current density.

4. Right-angled groove-shaped electrode

Next, consider an electrode consisting of the two half-planes, \((z = 0, x > 0, -\infty < y < \infty)\) and \((x = 0, z > 0, -\infty < y < \infty)\), as illustrated in Fig. 2(a). Under potential-leap conditions, both these planar surfaces are equiconcentration surfaces at which \(c = 0\). We expect the current density in this case to be cottrellian at locations far from the junction line \(x = z = 0\), but to be curtailed close to this line.

Zero concentration on the two half-planes can be ensured by a procedure similar to that employed in the previous section. Remove the electrode and replace the three solution-free quadrants in Fig. 2(a) by fictitious solution-filled regions, as shown in Fig. 2(b). Two of these regions are of negative concentration, initially having the uniform value \(-C\). However, the third quadrant – that diametrically opposite the real solution region – holds a fictitious solution of positive solute concentration, initially \(+C\). This symmetrical arrangement of alternating zones of positive and negative concentration ensures that concentration on both the \(z = 0\) and \(x = 0\) half-planes remains permanently zero, as required by the potential-leap experiment.

Starting at \(t = 0\) with uniform solute concentrations of \(\pm C\), the ensuing changes can be predicted by suitably integrating Eq. (2.6)

\[
c = \frac{C}{(4\pi Dt)^{3/2}} \left[\int_{0}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho^2}{4Dt}\right\} dx' dy' dz' + \frac{(-C)}{(4\pi Dt)^{3/2}} \left[\int_{-\infty}^{0} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho^2}{4Dt}\right\} dx' dy' dz' + \int_{0}^{\infty} \int_{-\infty}^{0} \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho^2}{4Dt}\right\} dx' dy' dz'\right]
\]

\[
+ \int_{-\infty}^{\infty} \int_{-\infty}^{0} \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho^2}{4Dt}\right\} dx' dy' dz' + \frac{(-C)}{(4\pi Dt)^{3/2}} \left[\int_{-\infty}^{0} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho^2}{4Dt}\right\} dx' dy' dz' + \int_{0}^{\infty} \int_{-\infty}^{0} \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho^2}{4Dt}\right\} dx' dy' dz'\right]
\]

(4.1)

where \((x-x')^2 + (y-y')^2 + (z-z')^2\) has been abbreviated to \(\rho^2\). The integrations follow a route similar to those in Eqs. (3.3) and (3.4), the formula

\[
c = C \text{erf}\left\{\frac{x}{\sqrt{4Dt}}\right\} \text{erf}\left\{\frac{z}{\sqrt{4Dt}}\right\}
\]

(4.2)

being the well-known [19] result.

The current density flowing to the \(z = 0\) half-plane is calculated in the usual way

\[
i = D \frac{\partial c}{\partial n} = C \sqrt{\frac{D}{\pi t}} \text{erf}\left\{\frac{x}{\sqrt{4Dt}}\right\}.
\]

(4.3)
The excess current density, over and above that expected on the basis of cottrellian behaviour, can be found by subtracting Eq. (3.6). On integration of the difference, one obtains

$$\frac{1}{NF} \int_0^\infty (i - i_{\text{cot}}) \, dx = C \sqrt{D} \int_0^\infty \left[ \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) - 1 \right] \, dx = -\frac{2CD}{\pi} = \frac{i_{\text{excess}}}{NF}. \quad (4.4)$$

This current “enhancement” is negative, as expected, because accessibility to the electrode is hindered by the presence of the groove. The left-hand integral in (4.4) has dimensions corresponding to the A m\(^{-1}\) unit, and may be considered as a lineal current density, to which we give the symbol \(i\) (iota), as in the definition incorporated as the final item in (4.4). Thus, a time-independent lineal density given by

$$\frac{i}{NF} = 2 \frac{i_{\text{excess}}}{NF} = -\frac{4CD}{\pi},$$

for a 90° electrode/electrode junction \( (4.5) \)

may be associated with the right-angled groove. The factor of “2” arises from the current flowing to the other half-plane, \( x = 0 \). This result is already in the literature, having been derived there by a totally different approach.

The actual response of the grooved electrode is described by Eq. (4.3), for the \( z = 0 \) half-plane, together with a similar equation describing the current density on the \( x = 0 \) half-plane. Alternatively, the response may be considered to be cottrellian everywhere on the electrode surface, plus an additional, time-independent current of lineal density \(-4CD/\pi\) associated with the line of junction between the two halves of the electrode.

### 5. Triply right-angled corner

An obvious extension of the procedure in the previous section is to an electrolyte solution bounded by an electrode consisting of three quarter-planes, all mutually perpendicular. The Green function method of solving this problem juxtaposes this real solution-filled octant with seven fictitious octants, four holding solution of negative concentration, initially \(-C\), while three are occupied by solution that initially has a concentration of \(+C\). The analogue of Eq. (4.1) now has eight triple integral terms. The solution turns out to be

$$c = C \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \text{erf} \left( \frac{y}{\sqrt{4Dt}} \right) \text{erf} \left( \frac{z}{\sqrt{4Dt}} \right). \quad (5.1)$$

which is not surprising in the light of Eqs. (3.5) and (4.2).

The current density flowing to the \( z = 0 \) quarter-plane can be found by differentiation and specialization to the surface:

$$i_{z=0} = D \frac{c}{\partial n} = C \sqrt{D} \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \text{erf} \left( \frac{y}{\sqrt{4Dt}} \right). \quad (5.2)$$

Integration of this over the plane provides an expression for the (infinite) current flowing to this quadrant

$$I_{z=0} = \frac{C}{\sqrt{D}} \int_0^\infty \int_0^\infty \text{erf} \left( \frac{y}{\sqrt{4Dt}} \right) \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \, dx \, dy. \quad (5.3)$$

We can identify four contributions to the current given in Eq. (5.3): current associated with the vertex, current associated with the junction line between the \( z = 0 \) and \( x = 0 \) quarter-planes, current associated with the \( z = y = 0 \) junction line, and cottrellian current associated with the \( z = 0 \) quarter-plane itself. By recourse to Eqs. (4.4) and (3.6), the last three effects may be subtracted away, leaving

$$I_{z=0} = \frac{C}{\sqrt{D}} \int_0^\infty \int_0^\infty \text{erf} \left( \frac{y}{\sqrt{4Dt}} \right) \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \, dx \, dy - \frac{2CD}{\pi} \left[ \int_0^\infty dx + \int_0^\infty dy \right] = 4C \sqrt{\frac{D}{\pi}} = \frac{I_{\text{residual}}}{NF}. \quad (5.4)$$

Thus the current associated with the vertex is given by

$$\frac{I}{NF} = 3 \frac{I_{\text{residual}}}{NF} = 12C \sqrt{\frac{D}{\pi}},$$

for a 90° - 90° - 90° electrode/electrode /electrode vertex \( (5.5) \)

the factor of 3 having arisen from the fact that three quarter-planes contribute to the vertex. Note that this verticular current is positive and increases with time. The divergent integrals multiplying \(2CD/\pi\) in Eq. (5.4) represent the infinite lengths of the \( x \) and \( y \) axes.

It should be emphasized that there are no approximations in our derivation. The current flowing to the \( z = 0 \) plane is given exactly by

$$I_{z=0} = C \sqrt{\frac{D}{\pi}} \int_0^\infty \int_0^\infty \, dx \, dz = \frac{2CD}{\pi} \int_0^\infty \, dx - \frac{2CD}{\pi} \int_0^\infty \, dy + 4C \sqrt{\frac{D}{\pi}}. \quad (5.6)$$

The questionable step in the present treatment lies only in associating each of the four right-hand terms in Eq. (5.6) with a specific geometric feature. The advantage of this association is that the current response is thereby temporally resolved into terms that decrease with the square-root of time, are time-independent, or increase with the square-root of time. Notice also that Eq. (5.6) may be factored as follows:
\[
\frac{I_{z=0}}{NF} = C \sqrt{\frac{D}{\pi}} \left[ \int_0^\infty dx - \sqrt{\frac{4Dt}{\pi}} \right] \left[ \int_0^\infty dy - \sqrt{\frac{4Dt}{\pi}} \right].
\]

(5.7)

This elegant result can be interpreted as follows: Initially the current flowing to the \(z = 0\) quarter-plane is proportional to its area—that is, to the product of the lengths of two adjacent sides. As time progresses, the effect of the proximity of the two other quarter-planes is to decrease the lengths of those two sides by the expanding distance \(\sqrt{4Dt}/\pi\).

6. Acute-angled grooves

Consider the situation portrayed in Fig. 3(a) which electrolyte solution occupies the space between two intersecting half-planes, one (shown hatched in the diagram) of which is an electrode, the other surface being an inert insulator (shown stippled). The electrode has been aligned with the positive moiety of the \(z = 0\) plane, and the angle between the two planes is \(\theta\) (30° in the figure). Eq. (2.4) applies at the insulator surface, but we shall make no explicit use of this property. Instead, we shall argue from a consideration of symmetry, that the current crossing the \(z = 0\) half-plane in Fig. 3(a) must be identical to that crossing the corresponding half-plane in Fig. 3(b), if the electrical and chemical properties of the two systems are the same and if the angle between the two electrode planes in (b) is twice the angle \(\theta\) in (a). Mostly, we shall dwell on the two-electrode configuration, bearing in mind that the solution for geometry 3(b) is directly transferable to geometry 3(a).

Of course, an earlier section dealt with a system having the geometry of Fig. 3(b) when \(2\theta = 90^\circ\). Treatment of an electrode composed of two intersecting planes is especially simple when the dihedral angle is 90° because of helpful registration with cartesian coordinates, but the situation is less facile with other angles.

Let the interplanar dihedral angle \(2\theta\) be \(\pi/M\) where \(M\) is an integer. For example, Fig. 3(b) illustrates the \(M = 3\) case. There are \(2M\) sectors (6 in Fig. 3(b), where \(\theta = 30^\circ\)), which will be numbered 0, 1, \ldots, \((2M - 1)\), where Sector 0 is the one that holds the original real solution, the other sectors—the fictitious ones—being numbered counterclockwise. As before, the sectors are filled alternately with solutions that were originally of concentration +C or −C, to enforce, by symmetry, zero concentration on the lines that separate the sectors. Recall Eq. (2.6). Our tactic in integrating it will be to consider separately the instances in which \(\phi\) is even or odd. It is bounded by the half-planes \((x = z \cot(2(m + 1)\theta)), -\infty < \phi < \infty, z > 0\) and \((x = z \cot(2m\theta)), -\infty < \phi < \infty, z > 0\). The appropriate version of Eq. (2.6) is therefore

\[
c(\text{Sector } m) = \frac{(-)^m C}{(4\pi Dt)^{1/2}} \int_0^\infty \int_0^{\infty} \exp \left\{ -\frac{(x-x')^2}{4Dt} - \frac{(y-y')^2}{4Dt} - \frac{(z-z')^2}{4Dt} \right\} dy'dx'dz'.
\]

(6.1)

The \(y'\) integration is readily accomplished via Eq. (3.3), leading to

\[
c(\text{Sector } m) = \frac{(-)^m C}{4\sqrt{\pi Dt}} \int_0^\infty \int_0^{\infty} \exp \left\{ -\frac{(x-x')^2}{4Dt} - \frac{(z-z')^2}{4Dt} \right\} dx'dz'.
\]

(6.2)

Splitting the exponential function and a change of variable to \((x-x')/\sqrt{4Dt}\) next permit the \(x'\) integration to be accomplished, yielding

\[
c(\text{Sector } m) = \frac{(-)^m C}{4\sqrt{\pi Dt}} \int_0^\infty \exp \left\{ -\frac{(z-z')^2}{4Dt} \right\} \sqrt{4Dt} \left\{ \text{erf} \left\{ x - z' \cot(2(m + 1)\theta) \right\} \right. \\
- \left. \text{erf} \left\{ x - z' \cot(2m\theta) \right\} \right\} dz'.
\]

(6.3)
The remaining integral resists analytical evaluation. Note that when $m = 0$, the second cotangent in Eq. (6.3) equals $+\infty$ and the error function to whose argument it contributes therefore becomes equal to $-1$. Conversely, when $m = M - 1$, the first cotangent becomes $\cot(\pi)$, which is to be interpreted as $-\infty$, so that the corresponding error function equals $+1$.

Now transfer attention to Sector $2M - m - 1$, which is the mirror image of Sector $m$ across the plane $z = 0$. The analogue of Eq. (6.1) is

$$
c(Sector \ 2M - m - 1) = \frac{(-)^{m-1}C}{4\sqrt{\pi Dt^3}} \int_{0}^{\infty} \exp \left( -\frac{(z - z')^2}{4Dt} \right) \times \left[ \text{erf} \left( \frac{x + z' \cot(2(m + 1)\theta)}{\sqrt{4Dt}} \right) - \text{erf} \left( \frac{x + z' \cot(2m\theta)}{\sqrt{4Dt}} \right) \right] dz'.
$$

(6.4)

Two integrations proceed as in the previous paragraph, leading to

$$
c(Sector \ 2M - m - 1) = \frac{(-)^{m-1}C}{4\sqrt{\pi Dt^3}} \int_{0}^{\infty} \exp \left( -\frac{(z - z')^2}{4Dt} \right) \times \left[ \text{erf} \left( \frac{x + z' \cot(2(m + 1)\theta)}{\sqrt{4Dt}} \right) - \text{erf} \left( \frac{x + z' \cot(2m\theta)}{\sqrt{4Dt}} \right) \right] dz'.
$$

(6.5)

In this equation, $z'$ plays the role of an integration variable and, on changing its sign, we obtain an expression that is identical with Eq. (6.3), apart from a few signs. The two can therefore be combined into the following formula:

$$
c(Sectors \ m \ and \ 2M - m - 1) = \sum_{\text{sign}} \frac{(-)^{m}C}{4\sqrt{\pi Dt^3}} \int_{0}^{\infty} \exp \left( -\frac{(z - sz')^2}{4Dt} \right) \times \left[ \text{erf} \left( \frac{x - sz' \cot(2(m + 1)\theta)}{\sqrt{4Dt}} \right) - \text{erf} \left( \frac{x - sz' \cot(2m\theta)}{\sqrt{4Dt}} \right) \right] dz'.
$$

(6.6)

It remains to sum Eq. (6.6) over $0 \leq m \leq M - 1$. On carrying out this operation, one finds conveniently that each error function term occurs twice. The final formula is

$$
c = \frac{C}{2\sqrt{\pi Dt^3}} \sum_{\text{sign}} \frac{(-)^{m}C}{4\sqrt{\pi}} \int_{0}^{\infty} \exp \left( -\frac{(z - sz')^2}{4Dt} \right) \times \left[ \frac{1 - (-1)^{m}}{2} - \sum_{m=1}^{M-1} (-)^{m} \text{erf} \left( \frac{x - z' \cot(2m\theta)}{\sqrt{4Dt}} \right) \right] dz'.
$$

(6.7)

The $z'$ integration will not be performed just yet. Formula (6.7) provides an expression for the concentration of the electroactive solute at any point $x, y, z$ within a groove of the dihedral angle $2\theta = \pi/M$ at a time $t$ after imposition of a potential leap. The next step is to apply Eq. (6.6) and thereby calculate the following formula for the current density at each point on the $z = 0$ half-plane

$$
i_{z=0}^{\prime} = \frac{C}{2\sqrt{\pi Dt^3}} \int_{0}^{\infty} z' \exp \left( -\frac{(z')^2}{4Dt} \right) \times \left[ 1 + \sum_{m=1}^{M-1} (-)^{m} \text{erfc} \left( \frac{x - z' \cot(2m\theta)}{\sqrt{4Dt}} \right) \right] dz'.
$$

(6.8)

In carrying out this step, the square-bracketed term has remained intact but its form has been changed by replacing each error function by its complement. At this juncture, it will help to define $\zeta = z'/\sqrt{4Dt}$. Because the Cottrell current density is the $M = 1$ version of this equation, subtraction of the Cottrell current density devolves into simply subtracting unity within the square-bracketed term, whence

$$
i_{\text{excess}}^{\prime} = \frac{C}{\sqrt{\pi}} \int_{0}^{\infty} \zeta \exp \left( -\zeta^2 \right) \times \sum_{m=1}^{M-1} (-)^{m} \text{erfc} \left( \frac{x}{\sqrt{4Dt}} - \zeta \cot \left( \frac{m\pi}{M} \right) \right) d\zeta.
$$

(6.9)

The final step is to integrate over the $x = 0$ half-plane, so as to find the excess linear current density associated with the junction. This produces an expression involving the integrated error function complement:

$$
i_{\text{excess}}^{\prime} = \frac{C}{\sqrt{\pi}} \int_{0}^{\infty} \int_{0}^{\infty} \zeta \exp \left( -\zeta^2 \right) \times \sum_{m=1}^{M-1} (-)^{m} \text{erfc} \left( -\zeta \cot \left( \frac{m\pi}{M} \right) \right) d\zeta.
$$

(6.10)

Because it is based on diffusion to a single electrode half-plane, the lineal current density in this equation is that appropriate to an insulator/electrode junction of the type portrayed in Fig. 3(a).

On doubling expression (6.10) to take account of both half-planes and hence give applicability to the Fig. 3(b) geometry, the conclusion is reached that the lineal current density associated with a groove of angle $2\theta = \pi/M$ is given by

$$
i^{\prime} = CD \sum_{m=1}^{M-1} (-)^{m} \frac{8}{\sqrt{\pi}} \int_{0}^{\infty} \zeta \exp \left( -\zeta^2 \right) \text{erfc} \left( -\zeta \cot \left( \frac{m\pi}{M} \right) \right) d\zeta.
$$

(6.11)
The abscissa calculated, and formulas (6.13), which provided the data for the points. Values, calculated via formulas (6.13), of the dimensionless lineal current density at a grooved electrode, when the dihedral angle is $2\theta$.

Table 1

<table>
<thead>
<tr>
<th>$M$</th>
<th>$\theta$</th>
<th>$k(\theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\frac{\pi}{4}$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{\pi}{8}$</td>
<td>$\frac{\pi}{4}$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{\pi}{4}$</td>
<td>$-2 - \frac{\pi}{4}$</td>
</tr>
<tr>
<td>4</td>
<td>$\frac{\pi}{8}$</td>
<td>$4 \left[ \sqrt{1 - \frac{\pi}{4}} - \sqrt{1 + \frac{\pi}{4}} \right]$</td>
</tr>
<tr>
<td>5</td>
<td>$\frac{\pi}{4}$</td>
<td>$\frac{20}{3\sqrt{3} - \frac{\pi}{4}}$</td>
</tr>
<tr>
<td>6</td>
<td>$\frac{\pi}{8}$</td>
<td>$-6.02916593$</td>
</tr>
<tr>
<td>7</td>
<td>$\frac{\pi}{4}$</td>
<td>$-4\sqrt{2} - \frac{\pi}{4}$</td>
</tr>
</tbody>
</table>

Recognize that the quantity that multiplies $CD$ in Eq. (6.11) is dimensionless and is a function only of the angle $\theta$. The notation

$$ t_{\text{groove}} = \frac{k(\theta)CD}{NF} $$

where $k(\theta) = \frac{8}{\sqrt{\pi}} \int_0^\infty \varphi \exp \left\{-\frac{\varphi^2}{2}\right\} \times \sum_{m=1}^{\frac{\theta}{2\pi}} (-)^m \text{erfc}\left\{-\varphi\cot(2m\theta)\right\} d\varphi$ (6.12)

is therefore appropriate, with the understanding that the groove in question has the dihedral angle $2\theta$ in the case of an electrode/electrode geometry resembling Fig. 3(b). The equation then gives the lineal current density associated with such an electrode junction. For application to the electrode/insulator interface, as in Fig. 3(a), the dihedral angle is represented by $\theta$, not $2\theta$, and the magnitude given by Eq. (6.12) should be halved.

Though with no little difficulty [20] when $M$ is even, the integral in (6.12) can be evaluated, to give the twin results

$$ k(\theta) = \begin{cases} \frac{4 \sum_{m=1}^{(M-1)/2} (-)^m \cot \left( \frac{\pi m}{M} \right)}{\pi \sum_{m=1}^{(M/2)-1} [1 - \frac{2m}{M}] \cot \left( \frac{\pi m}{M} \right)} , & \text{when } M \text{ equal to } \frac{4 \pi}{\theta} \text{ is odd,} \\ \frac{\pi}{4} + 4 \sum_{m=1}^{(M/2)-1} [1 - \frac{2m}{M}] (-)^m \cot \left( \frac{\pi m}{M} \right) , & \text{when } M \text{ is even.} \end{cases} $$ (6.13)

These formulas are believed to be novel. Some values calculated by their help are included in Table 1.

The calculation of the lineal current density at a grooved electrode has been addressed before [3]. That study produced the following formula involving hyperbolic Bessel functions

$$ k(\theta) = \sqrt{\frac{8}{\pi}} \int_0^\infty \left[ \frac{\pi \exp\left\{-\frac{\varphi^2}{2}\right\}}{\theta} \sum_{m=1,3}^{\infty} I_p\left(\frac{\varphi^2}{2}\right) + I_q\left(\frac{\varphi^2}{2}\right) \right] -2 \varphi d\varphi , $$ (6.14)

and where, as in the present research, $k(\theta) = t_{\text{groove}}/NFCD$. Though it is a good deal more complicated than (6.13). Eq. (6.14) has the advantage of applying to angles $\theta$ that are not necessarily submultiples of $\pi$. Moreover, (6.14) can be applied to cases in which $\theta$ exceeds $\pi$, this is when the geometry is that of a wedge, rather than a groove. As do numerical experiments, Fig. 4 illustrates the identity of the values from formulas (6.14) and (6.13).

7. Commentary

For the limited number of geometries to which it is applicable, Green’s method provides a relatively simple method of solving problems arising in diffusion-controlled voltammetry. In this article, we have restricted attention to the potential-leap experiment and have emphasized the assignment of the faradaic current to geometric features of the electrode. Such an assignment may be valuable at short times, but the virtue of the Green function approach is not conditional on this particular usage of the results. Thus, for example, Eq. (5.7) is valuable in its own right in describing the response of an inlaid rectangular electrode of sufficiently large size.

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References