Voltammetry of Electrochemically Reversible Systems at Electrodes of Any Geometry: A General, Explicit Analytical Characterization

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ABSTRACT: A general, explicit analytical solution for voltammetry using any multipotential waveform for an electrochemically reversible system at an electrode of any geometry is derived. This expression has special physical relevance in the case of electrodes and microelectrodes which possess nonuniform current densities such as disks and bands, where analytical descriptions of voltammetry are confined to predictions of limiting currents. We have applied our analytical expressions to normal pulse voltammetry, staircase cyclic voltammetry, and cyclic voltammetry for disks, spheres, bands, and cylinders. The results have been validated against those obtained by using numerical simulation with the agreement found to be excellent.

1. INTRODUCTION

A general, explicit analytical solution for any multipotential waveform, including normal pulse voltammetry (NPV), valid for an electrochemically reversible system at an electrode of any geometry is presented. This equation is applicable when either or both electroactive species in a redox couple are initially present and regardless of whether the electrode surface is uniformly accessible to the electroactive species.

This is a problem of great interest in electrochemistry, which has been previously treated in the literature by Aoki et al.1 and Cope et al.2 These authors reported a solution based on integral equations in any other situation.1,2,8

Despite the difficulties encountered in the analysis of the influence of different parameters on the response, the derivation of interesting limiting behaviors, and the establishment of simple methodologies for the characterization of the system.

This general solution has been deduced by using the superposition principle, whose foundations and main applications were given in previous papers.3,4,16–22 In this paper we show that it can be applied to any voltammetric electrochemical technique, any electrode geometry, and also when both species are initially present. The following constraints apply: the system studied.

We have applied our analytical expressions to NPV, staircase cyclic voltammetry (SCV), and cyclic voltammetry (CV) for disk, spheres, bands, and cylinders, and limiting cases have been deduced from them. All these results have been checked with those obtained by using numerical simulation in the case of disk and band electrodes by following the procedure discussed in refs 23–29. In all cases, the agreement has been excellent (with errors below 1%).

For the NPV technique, we show that the \((I/I_{lim}) - (E - E^0)\) curve is unique, independent of the geometry considered, even under transient conditions. Moreover, the evolution from SCV to CV is analyzed and the influence of the electrode size, scan rate, and the presence of the reaction product studied.

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2. THEORY

2.1. Application of a Constant Potential $E_0$. Consider the following simple charge transfer reaction

$$O + e^- \rightleftharpoons R$$

(1)

taking place at an electrode of an arbitrary geometry. The diffusional mass transport to the electrode is given by the following system of differential equations

$$\hat{\delta}_i \partial \partial t = \hat{\delta}_i D_i \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \right)$$

(2)

spherical electrode

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right)$$

(3)

band electrode

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

(4)

cylindrical electrode

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right)$$

(5)

with $D_i$ being the diffusion coefficient of species $i$.

If we assume that the charge transfer process (1) is reversible, both species are soluble in the solution, and their diffusion coefficients species are equal, i.e., $D_{O} = D_{R} = D$, the following boundary value problem is fulfilled

$$t = 0, \ q \geq q_{\text{surface}}$$

$$t > 0, \ q \rightarrow \infty$$

$$\begin{cases} c_{O}(q, t) = c_{O}^{*}, \ c_{R}(q, t) = c_{R}^{*} \\ c_{O}(q_{\text{surface}}, t) + c_{R}(q_{\text{surface}}, t) = c_{O}^{*} + c_{R}^{*} \\ c_{O}(q_{\text{surface}}, t) = K c_{R}(q_{\text{surface}}, t) \end{cases}$$

(6)

$$t > 0, \ q = q_{\text{surface}}; \ c_{O}(q_{\text{surface}}, t) + c_{R}(q_{\text{surface}}, t) = c_{O}^{*} + c_{R}^{*}$$

$$c_{O}(q_{\text{surface}}, t) = K c_{R}(q_{\text{surface}}, t)$$

(7)

(8)

with $c_{O}$ and $c_{R}$ being the initial concentrations of O and R species. Symbol $q$ denotes the coordinate normal to the electrode surface ($r$ in the case of spheres and cylinders, $y$ in the case of bands, and $z$ in the case of disks). Moreover

$$K = \exp \left( \frac{F}{RT} (E - E^{0}) \right)$$

(9)

with $E$ and $E^{0}$ being the applied potential and the formal potential of the O/R couple, respectively.

The assumption of equal diffusion coefficients or both electroactive species is fulfilled for a great variety of experimental systems of interest. Also, small deviations from this equality lead to deviations with no practical significance in many cases.

The expression for the current in the four geometries considered above can be written in the following general way (see refs 3 and 4 and Appendix)

$$I_{NPV} = FA_{G} \sqrt[\frac{D}{\pi} (c_{O}(\text{surface}) - c_{O}^{*}) C_{G}f_{G}(t)}$$

$$= FA_{G} \sqrt[\frac{D}{\pi} (c_{O}^{*} - Kc_{R}^{*}) C_{G}f_{G}(t)}$$

(10)

where $A_{G}$ denotes the electrode area (see Table 1). The subindex $G$ refers to the geometry considered ($G = d$ for disks, $G = s$ for spheres, $G = b$ for bands, and $G = c$ for cylinders).

In eq 10 $C_{G}$ is a geometrical factor given in Table 1. Function $f_{G}$ depends on time and electrode geometry (i.e., size of the disk, sphere, band, or cylinder), in the way shown in Table 1.

It is important to highlight that in all cases the current (eq 10) is given as a product of a function only dependent on the potential (which is identical in all cases: $c_{O}(\text{surface}) - c_{O}^{*} = (c_{O}^{*} - Kc_{R}^{*})/(1 + K)$) and another dependent on the electrode geometry and of time ($f_{G}(t)$, see Table 1). This fact is a consequence of the temporal independence of the surface concentrations.

Equation 10 corresponds to the cathodic–anodic voltammetric wave (both oxidized and reduced species are initially present), and from it, we can deduce the cathodic and anodic limiting currents for any geometry:

For $K \rightarrow 0$ (cathodic limit)

$$I_{\text{lim},c}^{\text{an}} = FA_{G} \sqrt[\frac{D}{\pi} c_{O}^{*} C_{G}f_{G}(t)}$$

(11)

For $K \rightarrow \infty$ (anodic limit)

$$I_{\text{lim},a}^{\text{an}} = -FA_{G} \sqrt[\frac{D}{\pi} c_{R}^{*} C_{G}f_{G}(t)}$$

(12)

Equations 11 and 12 coincide with those previously obtained by Shoup and Szabo for disk electrodes, by McGillivray et al and Rius et al for spherical electrodes, by Szabo et al for band electrodes, and by Aoki et al and Szabo et al for cylinder electrodes.

It is important to highlight that these equations are valid for electrodes which present uniform accessibility (such as spheres and cylinders) and also for those which are not uniformly accessible (i.e., discs and bands).

For the case of disk and bands electrodes of any radius, eq 10 has not been previously reported in the literature. This expression has the following simpler forms

$$I_{NPV}^{d} = FA_{G} \sqrt[\frac{D}{\pi} (c_{O}^{*} - Kc_{R}^{*}) \frac{4}{1 + K} f_{d}(t)}$$

$$I_{NPV}^{b} = FA_{G} \sqrt[\frac{D}{\pi} (c_{O}^{*} - Kc_{R}^{*}) \frac{1}{1 + K} f_{b}(t)}$$

(13)

where $f_{d}(t)$ and $f_{b}(t)$ are given in Table 1.
Table 1. Expressions for the Electrode Areas \((A_e)\), Geometrical Factors \((C_G)\), and Function \(f_G(t)\) for the Four Electrode Geometries Considered

<table>
<thead>
<tr>
<th>electrode</th>
<th>area ((A_e))</th>
<th>geometrical factor ((C_G))</th>
<th>function (f_G(t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>disk (radius (r_d))</td>
<td>(\pi r_d^2)</td>
<td>((4/\pi)(\pi D)^{1/2}/r_d)</td>
<td>(0.7854 + 0.44315 \frac{r_d}{\sqrt{D}t} + 0.2146 \exp \left(-0.39115 \frac{r_d}{\sqrt{D}t}\right))</td>
</tr>
<tr>
<td>sphere (radius (r_s))</td>
<td>(4\pi r_s^2)</td>
<td>1</td>
<td>(\frac{\sqrt{\pi D}}{r_s} + \frac{1}{\sqrt{t}})</td>
</tr>
<tr>
<td>band (height (w), length (l))</td>
<td>(wl)</td>
<td>((\pi D)^{1/3}/w)</td>
<td>(1 + \frac{w}{\sqrt{D}t} ) if (Dt/w^2 &lt; 0.4)</td>
</tr>
<tr>
<td>cylinder (radius (r_c), length (l))</td>
<td>(2\pi r_c l)</td>
<td>((\pi D)^{1/2}/r_c)</td>
<td>(\frac{r_c}{\sqrt{\pi D}} e^{-\frac{0.5(Dt/Dc)^{1/3}}{t}} + \frac{1}{\ln \left(5.2945 + 1.4986 \frac{\sqrt{D}t}{r_c}\right)})</td>
</tr>
</tbody>
</table>

Note that eq 13, which has been deduced by using eqs 6–8 and results of refs 3, 4, and 30 is valid for any value of the applied potential \(E_p\) with function \(f_G(t)\) (with \(G = d\) or \(b\)) being identical to that which appears in the expression for limiting current \(I_{NPV}\) (see Appendix). This fact is also related to the temporal independence of the surface concentrations of the electroactive species, and thus the following is fulfilled for any geometry

\[
I_{NPV} = \frac{1}{\pi n v c} = \frac{1 - K(c^*_b/c^*_d)}{1 + K} \tag{14}
\]

2.2. Application of a General Multipulse Potential Sequence. Consider a series of successive potential steps \(E_{1p}, E_{2p}, \ldots, E_{nP}\) of amplitude \(\Delta E\) and duration \(\tau\). Since the operators of Fick’s second law are linear, the expressions for the concentrations of species \(O\) and \(R\) corresponding to any potential pulse \(E_p\) of the perturbation sequence can be written as

\[
d_{p}^{\tau}(q, t) = c_{p}^{\tau-1}(q, t) + d_{p}^{\tau}(q, t) \quad i = O, R \tag{15}
\]

where

\[
d_{p}^{\tau-1} = c_{p}^{\tau-1}(q, t) + \sum_{m=2}^{p-1} c_{p}^{m}(q, t) \quad i = O, R \tag{16}
\]

In the above equations \(d_{p}^{\tau}(q, t)\), with \(p = 2, 3, \ldots\), are unknown functions of coordinates and time to be determined.

By using eqs 7 and 8 and 15 and 16, it is possible to express the boundary value problem for any potential \(p\) of the applied sequence in terms of the unknown functions \(d_{p}^{\tau}(q, t)\), in the following general way

\[
\hat{d}_{p}^{\tau} c_{O} = \hat{d}_{p}^{\tau} c_{R} = 0 \tag{17}
\]

\[
t_p = 0, q \geq q_{surface}
\]

\[
t_p > 0, q \rightarrow \infty \]

\[
\hat{d}_{p}^{\tau} c_{O}(q, t) = \hat{d}_{p}^{\tau} c_{R}(q, t) = 0 \tag{18}
\]

Equations 17–20 show that the boundary value problem has the same general form for any pulse potential \(p\) (with \(p \geq 1\)) and is independent of the geometry of the electrode. This generalization demonstrates that the superposition principle can be rigorously applied whatever the electrode geometry, in such a way that, taking into account eq 10, the current corresponding to any potential pulse \(p\), is given by the general following expression

\[
I_p = \frac{FAc_{O}^{*} \sqrt{D}}{\pi C_{G}} \left\{ \begin{array}{l}
f_G(\tau) \mu_p \frac{1}{1 + K_p} + \sum_{m=0}^{p-1} \left[ f_G((p-m)\tau) \mu_m - f_G((p-m)\tau) \mu_{m+1} \right] \frac{1}{1 + K_m} \end{array} \right\} \tag{22}
\]

where

\[
\mu_p = \begin{cases} 1 - K(p/c^*_b/c^*_d) & p = 1 \\ 1 + (c^*_b/c^*_d) & p > 1 \end{cases} \tag{23}
\]

and \(f_G\) and \(K_p\) being given by Table 1 and eq 9, respectively.
For the case of disk or band electrodes, eq 22 becomes

\[
\frac{I_p^b}{I_p^c} = \frac{FADc_0^s}{\pi r_d} \left\{ \frac{m}{1 + K_p} \left[ \sum_{m=1}^{\infty} \left( \begin{array}{c} \frac{f_d((p - m + 1)\tau)}{1 + K_m} \\ \frac{f_b((p - m + 1)\tau)}{1 + K_m} \end{array} \right) \right] \right\}
\]

Equation 22 can be applied to any multipotential pulse technique including cyclic voltammetry as a limiting case (see below).

### 2.3. Limiting Cases

Equation 22 can be simplified in the following limiting cases:

(a) Spherical electrodes

In the case of spherical electrodes, eq 22 can be rewritten in the following simplified form (see Table 1)

\[
\frac{I_p^s}{I_p^c} = \frac{FAc_0^s}{\sqrt{\pi D}} \left\{ \frac{m}{1 + K_m} \left[ \sum_{m=1}^{\infty} \left( \begin{array}{c} \frac{\mu_m}{\sqrt{(p - m + 1)}} \\ \frac{\mu_m}{\sqrt{(p - m + 1)}} \end{array} \right) \right] \right\}
\]

(b) Ultramicroelectrodes

In this case, eq 22 becomes

\[
\frac{I_p^{micro}}{I_p^{micro}} = \frac{FAc_0^s}{\sqrt{\pi D}} \left\{ \sum_{m=1}^{\infty} \left( \begin{array}{c} \frac{\mu_m}{\sqrt{(p - m + 1)}} \\ \frac{\mu_m}{\sqrt{(p - m + 1)}} \end{array} \right) \right\}
\]

(c) Planar electrodes

Under these conditions, \(r_0 >> (\pi D)^{1/2}\) for disks, cylinders, bands, or spheres (with \(r_0\) being equal to \(r_d \) or \(r_0 = \mu_0 \)), and the following expression for the current \(I_p^{planar}\) is deduced

\[
I_p^{planar} = \frac{FAc_0^s}{\sqrt{\pi D}} \left\{ \sum_{m=1}^{\infty} \left( \begin{array}{c} \frac{\mu_m}{\sqrt{(p - m + 1)}} \\ \frac{\mu_m}{\sqrt{(p - m + 1)}} \end{array} \right) \right\}
\]

### 3. RESULTS AND DISCUSSION

All the results obtained from eqs 10 and 22 shown in this section have been compared with those obtained with numerical calculation by following the procedure discussed in refs 26–28 and the agreement found was excellent (errors below 1%).

#### 3.1. Normal Pulse Voltammetry at Electrodes of Arbitrary Geometry When Both Electroactive Species Are Present in the Solution

In this section we apply eq 10 to normal pulse voltammetry (NPV) at the four electrode geometries considered.

In Figure 1 we have plotted the \((I_{NPV}/I_{lim,c}) - (E - E^0)\) curves for disks, spheres, bands, and cylinders calculated from eqs 10 and 11 when both species are initially present in the solution, in order to show that this ratio is independent of discs, spheres, bands and cylinders.
the size and geometry of the electrode considered, and independently of the transient or stationary character of the response.

Figure 2 shows the \( I_{NPV}/(nFA_c^0c^0(D/\pi)^{1/2}) \) curves calculated in NPV for disks (solid line), spheres (dashed line), bands (dashed-dotted line), and cylinders (dotted line) by considering \( c^*_R/c^*_O = 1 \) and three values of \( r_0 (r_d = r_s = (w/2) = r_c) \) (shown in the figure). \( \tau = 50 \) ms, \( D = 10^{-5} \) cm\(^2\) s\(^{-1}\), \( n = 1 \).

Figure 3. Application of eqs 33 to the study of the influence of \( \Delta E \) (with \( \Delta E \geq 0.01 \) mV) on the \( \Psi_{disk} - E \) curves with \( r_d = 0.01 \) cm (\( v = 100 \) mV s\(^{-1}\)), where only the oxidized species (a) or both species (b and 3c) are initially present in the electrolyte solution. The values of \( \Delta E \) appear on the curves. \( E_{initial} \) (in V) = 0.3 (a, b) and -0.3 (c). Other conditions as in Figure 2.

3.2. Cyclic Staircase (CSCV) and Cyclic Voltammetry (CV) at Disk and Band Electrodes. Comparison with Cylinders and Spheres. In this section we apply eq 22 to cyclic staircase different NPV curves begin to separate until they reach a steady state (disk, sphere) or quasi-steady state (band, cylinder) behavior (Figure 2c). Under these conditions, the ratio between the NPV currents at disks and spheres is in agreement with eqs 26 and 27. Note that in all the cases the potential of zero current does not depend in the geometry considered and it coincides with the equilibrium potential \( E_{eq} = E^0 + (RT/F) \ln(c^*_R/c^*_O) = 0 \) for \( c^*_O = c^*_O \) and \( E^0 = 0 \).
voltammetry (CSCV) and cyclic voltammetry (CV). In all cases, we have compared analytical results with the numerical ones obtained from refs 26–28. We also compare the results obtained with disk and band electrodes with those corresponding to spheres and cylinders.

For this purpose we consider the following staircase potential sequence of amplitude $\Delta E$ in which the current is measured at time $t$ (i.e., at the end of each potential step)

$$E_p = \begin{cases} E_{\text{initial}} - p\Delta E; & p = 1, 2, \ldots, (j/2) \\ E_{\text{final}} + p\Delta E; & p = (j/2) + 1, \ldots, j \end{cases}$$

(33)

Figure 4. Influence of the pulse amplitude $\Delta E$ in the values of the peak potential ($E_{\text{peak}} - E^0$) and the peak-to-peak distance ($\Delta E_{\text{peak}}$) of the voltammograms calculated from eq 22 for disks (circles), spheres (squares), bands (hexagons), and cylinders (triangles), for three different values of the scan rate. $r_d = r_s = (w/2) = r_c = 0.01 \text{ cm}$, $c_b/c_0 = 0$. Other conditions as in Figure 2.

For the case of linear sweep voltammetry (LSV) and cyclic voltammetry (CV) the pulse amplitude ($\Delta E$) which appears in eq 33 tends to zero for a fixed scan rate (i.e., $\Delta E < 0.01 \text{ mV}$ in the practice, see refs 3 and 19), so the applied potential waveform given by eq 33 behaves as a continuous function of time of the form

$$E(t) = \begin{cases} E_{\text{initial}} - vt; & t \leq \lambda \\ E_{\text{final}} + vt; & t > \lambda \end{cases}$$

(34)

where $\lambda$ is the time at which the scan is reversed and $v = \Delta E/\tau$. 

The dimensionless current for a disk or microdisc electrode is given by

\[
\Psi^d = \frac{D}{a \pi r_d} \left\{ \sum_{m=1}^{r-1} \left[ f_d((p-m+1)\tau)m_m - f_d((p-m)\tau)m_{m+1} \right] \right\} + \frac{f_d((p+1)\tau)m_p}{1 + K_p}
\]

\[
\Psi^b = \frac{D}{a \omega} \left\{ \sum_{m=1}^{p-1} \left[ f_b((p-m+1)\tau)m_m - f_b((p-m)\tau)m_{m+1} \right] \right\} + \frac{f_b((p+1)\tau)m_p}{1 + K_p}
\]

where

\[
\Psi^G = \frac{r_G^2}{F A C_O^*} \sqrt{aD} (G = d \text{ or } b)
\]

\[
a = \frac{F v}{RT}
\]

Functions \(f_d\) and \(f_b\) are given in Table 1.

Figure 3 shows several examples of application of eqs 35 to the study of the influence of \(\Delta E\) (with \(\Delta E \geq 0.01 \text{ mV}\)) at disk electrodes with \(r_d = 0.01 \text{ cm}\) \((v = 100 \text{ mV s}^{-1})\), where only the oxidized species (Figure 3a) or both species (Figure 3, panels b and c) are initially present in the electrolyte solution. We have verified that the agreement between numerical and analytical results has been excellent in all cases with differences in the cathodic and anodic peak currents below 0.5%.

From these figures we can observe that the forward peak current decreases and is shifted toward more negative potentials as \(\Delta E\) increases, in line with the results reported in ref 36. In order to compare experimental and theoretical data, eq 35 allows to fitting of experimental results to any staircase waveform instead of that corresponding to CV. Panels b and c of Figure 3 show that this effect is similar when both species are initially present. From these figures we can also observe in the cyclic voltammograms an initial anodic (Figure 3b) or cathodic (Figure 3c) current when sweeping toward cathodic or anodic potentials, respectively.

In Figure 4 we apply the general eq 22 for comparing the influence of the pulse amplitude \(\Delta E\) in the values of the peak potential \(E_{\text{peak}}\) and the peak-to-peak distance \(\Delta E_{\text{peak}}\) of the voltammograms calculated at disks (circles), spheres (squares), bands (hexagons), and cylinders (triangles), for three different values of the scan rate.

From these curves it can be seen that in all the cases \(\Delta E_{\text{peak}}\) increases and \(E_{\text{peak}}\) is shifted toward more negative potentials as \(\Delta E\) increases.

Concerning the influence of the scan rate, for \(v = 1.0 \text{ V s}^{-1}\) (see Figure 4a), no significative differences are observed between the four geometries. These results point out that for high scan rates.
given by the following expressions

$$
\Psi^{\pm}_{\text{ss}} = \sqrt{\frac{D}{4} \left( 1 - K \left( \frac{c^*_r / c^*_o}{1 + K} \right) \right)}
$$

(Figure 5 shows the influence of the electrode radius on the cyclic voltammograms (Ψ–E curves) obtained for disks, spheres, bands, and cylinders in the more general case in which both species are initially present in the electrolytic solution (c_k)/c_r = 1. In order to analyze the effects of the electrode curvature on the dimensionless voltammetric current, we have chosen disks, spheres, and cylinders with equal radii, and also a band whose semiwidith is identical to the cylinder radius. As can be deduced from these curves, the voltammograms present a shape closer to the sigmoidal one as the electrode size decreases, in such a way that for small enough radius a steady state is reached at disks and spheres and therefore the current is given by the following expressions

$$
\Psi^{\pm}_{\text{ss}} = \frac{I_{NPV}}{I_{\text{lim},c}} = \frac{1 - K \left( c^*_r / c^*_o \right)}{1 + K}
$$

with $K = \exp(\Delta F/(RT)(E(t) - E^0))$.

By comparing eq 38 for the CV steady state currents and eqs 10–14 for NPV under transient conditions, we deduce that the following is fulfilled for disks and spheres

$$
\Psi^{\pm}_{\text{ss}} = \Psi^{\pm}_{\text{lim},c}
$$

where $\Psi^{\pm}_{\text{ss}}$ is the value of $\Psi^{\pm}_{\text{ss}}$ for $E = -\infty$ (or $K \rightarrow 0$).

The above behavior cannot be expected for microcylinders and microbands, for which only quasi-steady-state curves are obtained (see Figure 5, panels c and d).

4. CONCLUSIONS

Analytical explicit expressions applicable to the transient I–E response of a reversible charge transfer reaction when both species are initially present in the solution at microelectrodes of different geometries (spheres, disks, bands, and cylinders) have been deduced.

These results are of special relevance in the case of disk and band electrodes since this is the first time that general analytical solutions are available for these geometries, which have only been tackled numerically except in the simpler case of limiting current. These equations have been applied to the most usual electrochemical techniques such as NPV, SCV, and CV. The independence of the geometry and time of the NPV I/E–E curves has been proved. With regard to the multipulse techniques of SCV and CV, the influence of the scan rate, electrode size, and presence of the reaction product has been analyzed.

All of the above results have been compared with those obtained from numerical simulation, with an excellent concordance being observed.

APPENDIX

According to the results shown in ref 30, the differential equation system for the diffusion mass transport of species O and R is given by

$$
\begin{align*}
\frac{\partial c_O}{\partial t} &= D_O \nabla^2 c_O \\
\frac{\partial c_R}{\partial t} &= D_R \nabla^2 c_R
\end{align*}
$$

(A1)

where $\nabla^2$ is the Laplacian operator. When $D_O = D_R$ and the flux is conserved at the electrode surface, the following solution for the sum of concentrations of species O and R is obtained

$$
c_O(q,t) + c_R(q,t) = c^*_O + c^*_R
$$

(A2)

where q and t refer to any coordinate and time values, respectively, and $c^*_O$ and $c^*_R$ to the initial concentrations of both species.

Equation A2 at the electrode surface (i.e., $q = q_{\text{surface}}$), becomes into eq 7 in section 2.

The combination of eqs 7 and 8 transforms the problem of two variables $c_O$ and $c_R$ (see eqs 2–8) into two problems of only one variable with constant surface conditions in the way

$$
\begin{align*}
\frac{\partial c_O}{\partial t} &= D \nabla^2 c_O \\
\frac{\partial c_R}{\partial t} &= D \nabla^2 c_R
\end{align*}
$$

(A3)

and

$$
\begin{align*}
\frac{\partial c_O}{\partial t} &= D \nabla^2 c_O \\
\frac{\partial c_R}{\partial t} &= D \nabla^2 c_R
\end{align*}
$$

(A4)

Diffusional problems (A3) and (A4) are identical to the limit diffusion problem unless in this last case $c_O(q_{\text{surface}}) = 0$ (limiting cathodic current) or $c_R(q_{\text{surface}}) = 0$ (limiting anodic current). Thus the current obtained for the application of any constant potential only differs from that corresponding to the limit cathodic or anodic current in the constant term $(c^*_O - c^*_O(q_{\text{surface}}))/(1 + K)$ instead of $c^*_O$ or $c^*_R$. This conclusion is confirmed by the numerical results.26–28

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NOTE ADDED AFTER ASAP PUBLICATION

This article was published ASAP on February 18, 2011. Equation 25 has been modified. The correct version was published on February 24, 2011.