Reverse pulse voltammetry and polarography: a general analytical solution

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A rigorous analytical solution to reverse pulse techniques for a plane electrode expanding with an arbitrary power of time is presented. Our results include the plane approximation for SMDE as well as the expanding plane electrode model for DME. In the case of SMDE, our results have been contrasted with those obtained by numerical solution of the problem, obtaining identical results. Finally, we have compared our treatment with previous solutions in literature.


On presente une solution analytique rigoureuse pour renverser les techniques de pulsation d’une electrode plane en expansion avec une puissance arbritaire du temps. Nos résultats incluent l’approximation plane de la SMDE ainsi que le modèle de l’électrode plane en expansion de la SME. Dans le cas de la SMDE, on a comparé nos résultats avec ceux obtenus par la solution numérique du problème et les résultats obtenus sont les mêmes. Enfin, on a comparé notre traitement avec les solutions proposées antérieurement dans la littérature.

[Traduit par la rédaction]

Introduction

Many authors have studied the problem of the i–t Faradaic response of a slow charge transfer reaction to a second potential pulse for several electrode models (1–8). Their solutions can be used in Reverse Pulse (RP) techniques: Reverse Pulse Voltammetry (RPV, stationary plane electrode) or Reverse Pulse Polarography (RPP, expanding plane electrode). This application has been explicitly carried out in certain papers (1, 8), while in others the obtained solutions were used only in Differential Pulse (DP) techniques (2–7).

Among double pulse techniques, RP is the least complex and, without doubt, the most powerful in kinetic applications. Up-to-date RP has been applied to the analysis of limiting currents (9–11) yielding qualitative information on the degree of reversibility of the electrode process; this information is similar to that obtained from cyclic voltammetry (12). However, the complexity in the resulting analytical solutions and, more importantly, the controversy over the rigor of these solutions, have limited their kinetic applications in practice.

As far as we know, only the equations derived by Matsuda (1); Aoki et al. (3) (expanding plane electrode), and Lovric and Osteryoung (2) and Aoki and Osteryoung (4) (stationary plane electrode) are mathematically rigorous for a slow charge transfer reaction; however, the analytical response deduced by these authors is given by complex integral equations which should be solved numerically in each particular case. The authors of other papers claim to have obtained a rigorous analytical solution to the problem; however, in most of these papers some kind of approximation was used (5–8). These approximations are, in general, very interesting but sometimes not explicitly assumed in the paper. One of the more frequently used approximations is the analytical expression of surface concentrations and concentration gradient of the first pulse remain unaltered during the second pulse, that is to say, the bases of the superposition principle have been applied under conditions in which this principle is not applicable. The applicability of the superposition principle to yield rigorous results is restricted to reversible systems, it depends on electrode geometry and on the values of diffusion coefficients of the electroactive couple (2, 13–17).

This paper is to present a rigorous and closed analytical solution to a plane electrode expanding with an arbitrary power of time under conditions relevant to RP techniques, i.e., when the boundary conditions selected for the application of the second pulse correspond to a first step controlled by diffusion. Our results, which used plane approximation for SMDE and expanding plane electrode model for DME, are in excellent agreement with the results obtained by numerical solutions (18, 19). In certain cases, we have also reproduced our solutions using Laplace Transforms.

Theory

Let us consider the following charge-transfer reaction

\[ A + ne^- \xrightarrow{t_0} B \]

and assume that the area of the plane electrode \( q(t) = q_0 t^z \), increases with any power of time \( t \geq 0 \) for a DME and \( z = 0 \) for the planar approximation of a SMDE. Operator \( \hat{D}_i \) is given by (20)

\[ \hat{D}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2} - \frac{zx}{i} \frac{\partial}{\partial x} \]

We shall denote by \( E_1, E_2, \) and \( t_1, t_2, \) the potential and...
time durations of each pulse, respectively. Likewise, we shall assume these potentials to be superimposed to a linear ramp of potential, which is only effective in successive drops of lifetime \(t_2\) (see Fig. 1). In the RP technique \(E_1\) is always constant and corresponds to a potential at which the reduction process is controlled by diffusion, whereas \(E_2\) shifts to anodic potentials. However, these potential conditions will be applied later. The corresponding currents for each pulse will be called \(i_1\) and \(i_2\), respectively. The signal used in the RP technique is given by \(i_2 = i_{RP}\).

The experimental time may be divided into two periods. In the first period \((0 \leq t \leq t_1)\) the potential is maintained at value \(E_1\). Under these conditions the concentration profiles \(C_A(x, t)\) and \(C_B(x, t)\) and the current–time response are given by (21)

\[
\frac{C_A(x, t)}{C_A^*} = \frac{C_A((s1A, \chi))}{C_A^*} + \frac{1}{1 + \gamma K_i} \sum_{j=1}^{\infty} \frac{(-1)^j \psi_j(s1A) \chi^j}{\prod_{k=1}^{j} p_k(z)}
\]

\[
\frac{C_B(x, t)}{C_A^*} = \frac{C_B((s1B, \chi))}{C_A^*} = \frac{1}{1 + \gamma K_i} = \sum_{j=1}^{\infty} \frac{(-1)^j \psi_j(s1B) \chi^j}{\prod_{k=1}^{j} p_k(z)}
\]

\[
i_1(t) = nFqD^\ast i \sqrt{\frac{(2z + 1)D_A}{n^i} \frac{F_i(\chi)}{1 + \gamma K_i}} C_A^*
\]

\[
i_2(t) = \frac{i_2}{nFq(t)} = k_i K_i^\alpha \frac{C_A(x = 0, t) - K_c^2 C_B(x = 0, t)}
\]

As differential equations [10] are linear (see eq. [2] or [9]), any linear combination of solutions is also a solution. Thus, we will suppose that \(C_A(x, t)\) and \(C_B(x, t)\) have the form

\[
C_A(x, t) = C^i_A(x, t) + \hat{C}_A(x, t)
\]

\[
C_B(x, t) = C^i_B(x, t) + \hat{C}_B(x, t)
\]

where the superscripts of \(C_A^i\) and \(C_B^i\) \((i = 1 \text{ or } 2)\) refer to first and second pulse, respectively.

The new unknown functions \(\hat{C}_A(x, t)\) and \(\hat{C}_B(x, t)\) have the advantage that they are solutions for the problem with null initial conditions (see eq. [11]).

When using dimensionless parameters, it is appropriate to assume that \(\hat{C}_A(x, t)\) and \(\hat{C}_B(x, t)\) have the form (22, 23)

\[
\begin{align*}
\hat{C}_A(x, t) &= \sum_{j,m} \phi_{jm}(s2A) B^{1/2 \gamma m} \\
\hat{C}_B(x, t) &= \sum_{j,m} \delta_{jm}(s2B) B^{1/2 \gamma m}
\end{align*}
\]

with

\[
s_{2i} = \frac{x}{2 \sqrt{D_i \tau_2}}
\]

\[
\beta = \frac{t_2}{t_1 + t_2}
\]

\[
y = \sqrt{\frac{4 \tau_2 K_i}{D_A K_i^\alpha}} \frac{1 + \gamma K_i}{K_i^\alpha}
\]

Inserting eqs. [15]–[18] in [10], we obtain

\[
\phi_{jm}(s2A) + 2s_{2A} \phi_{jm}(s2A) - 2(j + m) \phi_{jm}(s2A) = -4s_{2A} \phi_{j-2m}(s2A) - 2(j - 2) \phi_{j-2m}(s2A)
\]
\( \phi_{j,m}(s) = \phi_{j,m}(s_2) = 0 \) for \( s_2 \to \infty \).

\( \gamma \phi_{j,m}(s) = -\delta_{j,m}(s) \) from eq. [12], with eqs. [27] and [28], it is clear that

and from eqs. [13], [21], [22], [25]–[27] we obtain

\[ \sum_{j,m} \phi_{j,m}(s_2) = 0 \]
Results and discussion

Previous to this study, we performed a careful analysis of the properties of the $H_{2}(\beta, y)$ function (see appendix A). A 3D plot of $H_{0}(\beta, y)$ is shown in Fig. 2. For $\beta \to 0$, $H_{0}(0, y) = G_{2}(0, y) = F_{0}(y)$. As $\beta$ increases and approaches unity, the absolute value of the $H_{0}$-function decreases, showing a maximum for $y$ values close to 5.

An analogous plot for $H_{2/3}(\beta, y)$ (Fig. 3) shows a shape similar to Fig. 2. In order to guarantee high accuracy, only the values of $H_{2/3}$ corresponding to $\beta \leq 0.5$ have been presented in Fig. 3. The function $H_{2/3}$ has been evaluated with only five terms of the sum in $\beta$, since the general term of this series could not be obtained because of its mathematical complexity (see comments in appendix A). As can be observed, these curves are less dependent on $\beta$ than those in Fig. 2.

The behavior of eq. [36] has been exhaustively studied and has been compared with the solution given in ref. 8, as well as with the numerical solution obtained in Appendix B (see eqs. [B13]–[B15]). In Fig. 4 the plot of $i_{RP}/i_{DC}$ vs. $E_{2} - E^{0}$ ($i_{DC} = nFq_{0}^{2}/(\Delta S/2\pi Z_{2})C_{\alpha}$) is shown for $k_{s} = 10^{-4}$ cm s$^{-1}$, $t_{1} = s$, $t_{2} = 0.4$ s, $n = 1$, $\alpha = 0.5$, $D_{A} = 10^{-5}$ cm$^{2}$ s$^{-1}$, $\gamma = 1$, and $z = 0$. Solid line corresponds to the predictions of eq. [36]. Triangle correspond to the solution given in ref. 8. Circles correspond to the numerical solution given in Appendix B (eq. [B13] with $r = 160$).

The three analyzed solutions are numerically indistinguishable, even for relatively high values of $\beta$ in a typical experimental record such as that in Fig. 4 ($\beta = 0.4/1.4 = 0.285$). For $z = 2/3$ the behavior (not shown) is similar.

For larger values of $\beta$ some deviations are observed in the solution given in ref. 8 with respect to that obtained from eq. [36] and [B15]. In Fig. 5 we have plotted $i_{RP}/i_{DC}$ vs. $E_{2} - E^{0}$ for $k_{s} = 10^{-5}$ cm/s, $\beta = 2/3$, and $z = 0$. The results obtained from eq. [36] and from the numerical solution of Appendix B are in total agreement. This concordance is maintained for all of our calculations indicating the rigorous character of our treatment (eq. [36]). In Fig. 5, one can also observe how the variation of $i_{RP}$ obtained from the solution given in ref. 8 (dashed line) is different. This discrepancy is only evident in
the extreme conditions under which Fig. 5 has been obtained. The deviations are more prominent at the potential region near the peak, where the error amounts to 18%. To appreciate the magnitude of the deviations at this potential, we have plotted as Fig. 6 a theoretical i-t curve for the same conditions as those of Fig. 5, for \( E_2 - E^0 = 300 \text{ mV} \). Part I of Fig. 6 represents the current \( (i_1) \) due to the application of first pulse \( (t \leq t_1 = 1 \text{ s and } E_1 - E^0 \rightarrow -\infty, \text{ eq. [24]} \), while part II corresponds to the current \( (i_2 - i_{bg}) \) during the application of second pulse \( (t > t_1, t_2 = 10 \text{ s and } E_2 - E^0 = 300 \text{ mV}) \). Again, a total concordance between numerical solution and eq. [36] is observed, while the results obtained from the solution given in ref. 8 only agree for small values of \( t \). For \( t - t_1 > 0.5 \text{ s} \), some deviations are observed. For \( t_2 = 5 \text{ s} \) the error amounts to 30%.

The solutions from ref. 8 lead to a reasonable agreement with the rigorous solution for \( i_{bg} \) (eq. [36]), provided \( \beta \) is small. In general, \( \beta = 0.33 \) may be considered a limit for the correct use of the solution in ref. 8, as the error is always less than 10%.

Experimentally, deviations from the rigorous solution can be observed in careful experiments similar to those described in Figs. 5 and 6.

There is no mention in the literature about the problems inherent to the solution in ref. 8 analyzed in this paper. The reason being experimentally, the RP technique has so far been used for \( \beta \leq 0.1 \), and therefore the wrong behavior of the solution in ref. 8 cannot be observed.

The final analysis of the three solutions compares the time dependence of surface concentration of reactant, \( C_A^*(0,t) \). For this purpose, we have used eq. [A5], corresponding to the prediction made in this paper, eq. [A7] corresponding to the solution given in ref. 8 and eq. [B16], corresponding to the numerical solution to the problem.

Figures 7 and 8 show theoretical curves of \( C_A^*(0,t) \) vs. \( t \) for \( t_1 = 1 \text{ s and } t_2 = 10 \text{ s for } \varepsilon = 0 \) (Fig. 7) and for \( \varepsilon = 2/3 \) (Fig. 8). When \( t < t_1 \) the surface concentration of reactant is zero as a consequence of the large negative potential applied \( (E_1 - E^0 \rightarrow -\infty) \). When \( t > t_1 \) a total agreement between our treatment (eq. [A5]) and our numerical solution (eq. [B16]) is observed, while the values of \( C_A^*(0,t) \) obtained from eq. [A7] differ notably from the others. The conditions imposed in Figs. 7 and 8 correspond to a limiting reduction process, selected to guarantee that there is no anodic or cathodic current so that \( i_{bg} \rightarrow 0 \). Moreover, under these conditions \( \mu_{el} \gg Z \) (eqs. [37], [38]). Physically, the situation is such that, as a consequence of the absence of any Faradaic current, the surface concentration of species A must return to its initial value: \( C_A^*(0,t_2 \rightarrow \infty) \rightarrow C_A^* \).

If the conditions of Fig. 7 (\( \varepsilon \ll 1 \)) are applied to eq. [A5], the following expression is obtained

\[
\frac{C_A^*(0,t)}{C_A^*} = \frac{2}{\pi} \sqrt{2z + 1} \beta h_d(\beta)
\]

where

\[
h_d(\beta) = 1 + \sum_{k=1}^{\infty} \frac{(2k - 1)!\beta^k}{2^{2k-1}k!(k - 1)!(2k + 1)}
\]

\[
h_{2/3}(\beta) = 1 + \frac{\beta}{2^5} - \frac{7\beta^2}{1080} - \frac{461\beta^4}{93312} + \cdots
\]
We have also solved this problem using Laplace Transform on eq. [B11], and found a solution identical to eq. [40], but in a more compact general form:

\[ C_A^2(0, t) \over C_A^2 = \frac{2}{\pi} \arctan \sqrt{\frac{1}{(1 - \beta)^{2z+1}} - 1} \]

where

\[ \sqrt{(2z+1)\beta} h_2(\beta) = \arctan \sqrt{\frac{1}{(1 - \beta)^{2z+1}} - 1} \]

The condition \( t_2 \to \infty \) is equivalent to \( \beta \to 1 \), and therefore, \( C_A^2(0, t)/C_A^2 = 1 \), for any value of \( z \), which is in accordance with the previous reasoning; the process is very slow, but takes places at infinitely large time. However, the application of the same conditions to eq. [A7] leads to the following result

\[ C_A^2(0, t) \over C_A^2 = \frac{2}{\pi} \sqrt{(2z+1)g_0(\beta)} \]

\[ g_0(\beta) = 1 \]

\[ g_{2/3}(\beta) = 1 - \frac{1}{9} \beta - \frac{11}{270} \beta^2 - \frac{10}{567} \beta^3 - \frac{3087}{367416} \beta^4 \ldots \]

If \( \beta = 1 \), the prediction of eq. [45] is \( C_A^2(0, t)/C_A^2 = 2/\pi = 0.6366 \) (for \( z = 0 \)) and \( C_A^2(0, t)/C_A^2 = 0.7995 \) (for \( z = 2/3 \)), that is to say, eq. [45] is unable to predict the return to initial conditions in the pulse sequence applied in the ideal experiment of Figs. 7 and 8.

It may be surprising that the method applied at ref. 8 allows us to calculate \( i_{RP} \) very close to the correct values (even for moderately large \( \beta \)) but it is unable to obtain accurate values of the surface concentrations. The reason of this apparent paradox must be sought in the very structure of eqs. [36] and [A5], as well as in the analysis of the conditions under which these equations coincide with that deduced in ref. 8. When the electrode process is reversible \( (k_e \to \infty) \) or diffusion conditions are applied \( (E_2 - E^0 \to \pm \infty) \), the treatment developed in ref. 8 and our own treatment are the same (conditions under which the superposition principle is applicable). In short, the function \( H_s(\beta, y) \) is operative only when the process is not at equilibrium or when \( y \) does not increase towards infinity.

If we analyze the expression for the current \( i_{RP} \) (eq. [36]), one sees that as the value of \( y \) decreases, the importance of the product \( \mu_0 H_s(\beta, y) \), i.e., of \( H_s(\beta, y)/y \) (see eq. [38]) increases while the current \( i_{RP} \) simultaneously decreases. For this reason, the difference between eq. [36] and eq. [32] in ref. 8 is not very great in absolute value. Moreover, it should be added that the functions \( H_s(\beta, y) \) and \( G_2(\beta, y) \) are more similar as \( y \) becomes smaller.

The expressions for surface concentration depend on the product \( \mu_0 H_s(\beta, y)/y = H_s(\beta, y)/y^2 \), which also increases as \( y \) decreases but \( C_A^2(0, 1)_{y \leq 1} \neq 0 \). For example, while \( C_A^2(0, 1) \) is strongly dependent on \( H_s(\beta, y) \), \( i_{RP} \) can be represented approximately by eq. [32] in ref. 8. However, this does not mean the method in ref. 8 can be used indiscriminately. For example, these results should not be used to obtain the current-time response corresponding to posterior pulses, as in the technique called Reverse Differential Normal Pulse (16, 23, 24), or in the Double Differential Pulse Voltammetry technique (25). In these cases the current is obtained from surface concentrations and surface concentration gradients deduced for second pulse, and the use of eq. [A7] leads to inadequate results.

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Appendix A

\( F_c(\chi) \) is the Koutecky Function. For \( \varepsilon = 0 \) (planar approximation of SMDE) and for \( \varepsilon = 2/3 \) (planar approximation of DME)

\[ F_c(\chi) = \sum_{j=0}^{\infty} \frac{(-1)^j \chi^{j+1}}{j! \prod_{k=0}^{j} p_k(z)} \]

\( G_c(\chi) \) is the Galvez Function (8, 26)

\[ G_c(\beta, \chi) = \sum_{j=0}^{\infty} \frac{(-1)^j \chi^{j+1}}{j! \prod_{k=0}^{j} p_k(z)} \left\{ 1 - \frac{j \beta}{3(j+2)} - \frac{j(2j+9)}{18(j+2)(j+4)} \cdot \beta^2 \cdot \ldots \right\} \]

\[ p_k(z) = p_{k(2z+1)} = \frac{2\Gamma\left(1 + \frac{k}{4z+2}\right)}{\Gamma\left(\frac{1}{2} + \frac{k}{4z+2}\right)} \]

\[ p_{k-1} = 2k \]

The surface concentrations of species A and B for \( \tau_2 > 0 \) are given by

\[ C_A^2(0, t) \]

\[ C_A^2(0, t) = Z \left( \frac{2}{\sqrt{\pi}} \frac{C_c(\beta, y)}{y} - 1 \right) \right) \frac{H_c(\beta, y)}{y} - 1 \]

\[ C_A^2(0, t) = \gamma \left( 1 - \frac{C_A^2(0, t)}{C_A^2} \right) \]

However, from eq. [16] in ref. 8 with \( E_1 \rightarrow -\infty \), we deduce

\[ \left( \frac{C_A^2(0, t)}{C_A^2} \right) \text{ref. 8} = (Z + \mu_d) \left( \frac{2}{\sqrt{\pi}} \frac{G_c(\beta, y)}{y} - 1 \right) \]

\[ H_c \text{ function which appears in eq. [35] is given for } y < 10 \text{ by } (\varepsilon = 0) \)

\[ H_0(\beta, y) = \sum_{m=0}^{\infty} \frac{(-1)^m y^{m+1}}{\prod_{i=0}^{m} p_i(0)} \left\{ 1 + \sum_{k=1}^{\infty} \frac{(2k-1)!m!\beta^k}{2^{2k-1}k!(k-1)!(m+2k)} \right\} = \sum_{m=0}^{\infty} \frac{(-1)^m y^{m+1}}{\prod_{i=0}^{m} p_i(0)} \gamma_{2Fi}[1/2, m/2, 1 + m/2, \beta] \]

\[ \gamma_{2Fi}[a, b, c, \beta] \text{ is the hypergeometric function } z_{2Fi}(a, b, c, z) \text{ and for } y > 10 \]

\[ H_0(\beta, y) = \sqrt{1 - \beta} + \sqrt{\pi} \sum_{k=1}^{\infty} \frac{(-1)^{k-1} (2k-1)!\beta^k}{(k-1)!(k-2)!} + \sum_{m=1}^{\infty} \frac{(-1)^m 2(2m-1)!}{m!(m-1)!} \gamma_{2Fi}[1/2, -\beta/2, 1 - m/2, \beta] \]

The function \( H_0(\beta, y) \) is defined for \( 0 \leq \beta \leq 1 \), and can be obtained with the desired precision in this interval. The value \( \beta = 1 \) corresponds to two extreme situations, as are \( t_1 = 0 \), that is to say, the first pulse does not exists (this situation is physically meaningless, since \( H \) is only obtained if the departure point is a perturbed system) or \( t_2 \rightarrow \infty \).

The general term of the sum in \( \beta \) in the above equations has been obtained taking into account the relationship between the coefficients of the series depending on \( \beta \) in the \( H_0 \) function and the following expression

\[ (1 - \beta)^{-1/2} = 1 + \sum_{k=1}^{\infty} \frac{(2k-1)!\beta^k}{2^{k-1}k!(k-1)!} \]
For $z = 2/3$ and for $y < 10$ we find

\[ H_{2/3}(\beta, y) = \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{\prod_{i=0}^{m-1} p_i} \left( 1 + \frac{m}{6(m+2)} \beta^2 + \frac{m(7m-6)}{72(m+2)(m+4)} \beta^4 + \frac{m(13m-34)}{1296(m+2)(m+4)m+6) \beta^6 + \cdots \right) \]

and for $y > 10$

\[ H_{2/3}(\beta, y) = \sum_{m=1}^{\infty} \frac{(-1)^{m+1}y^{-m+1}}{p^{-m}} \left( 1 + \frac{m}{6(m-2)} \beta^2 + \frac{m(7m+6)}{72(m-2)(m-4)} \beta^4 + \frac{m(13m+34)}{1296(m-2)(m-6)} \beta^6 + \cdots \right) \]

\[ + \frac{m(1729m^3 + 9828m^2 - 23284m + 133488)}{31104(m-2)(m-4)(m-6)(m-8)} \beta^4 + \cdots \]

\[ = 1 - \frac{1}{6} \beta^2 + \frac{13}{216} \beta^4 + \frac{329}{6480} \beta^6 + \frac{2269}{72576} \beta^8 + \cdots \]

\[ + \ldots + \frac{1}{3} \beta \left( 1 - \frac{5}{6} \beta^2 - \frac{35}{72} \beta^4 - \frac{20}{81} \beta^6 - \cdots \right) y^{-1} \]

\[ = 2 + \beta - \frac{9}{4} \beta^2 - \frac{511}{648} \beta^4 - \frac{7289}{25920} \beta^6 + \cdots \]

\[ - \frac{\beta^2}{3} \left( \frac{34}{9} - \frac{65}{324} \beta^2 - \cdots \right) y^{-3} + 2 \left( \frac{12}{3} \beta - \frac{205}{18} \beta^2 - \frac{385}{36} \beta^3 - \frac{20845}{3888} \beta^4 - \cdots \right) y^{-2} \]

Equation [A11] suggests us the grouping of $\beta$ into the expression

\[ (1 - \beta)^{-1/6} = 1 + \frac{\beta}{6} + \frac{7\beta^2}{72} + \frac{91\beta^3}{1296} + \frac{1729\beta^4}{31104} + \cdots \]

However, because of its complexity, we can not find a general expression for [A11].

We have also used the relationship

\[ \lim_{k \to m} (m-k) = \pm \frac{p^{-1}}{p_1} \]

in which the upper sign relates to direct treatment and the lower sign to the asymptotic one.

Appendix B

For a stationary plane electrode ($z = 0$), the Faradaic current corresponding to process [1], can be expressed by a Volterra integral of the form (1)

\[ \phi = k - \frac{\lambda}{\sqrt{\pi}} \int_{0}^{t} \frac{\phi du}{\sqrt{t-u}} \]

where

\[ k = k_{c}K^{-\alpha} \]

\[ \lambda = \frac{k(1 + \gamma K)}{\sqrt{D_{\lambda}}} \]

\[ \phi = \frac{i}{nFq_{0}C_{\lambda}} \]

In double pulse conditions eq. [B1] can written as (1)

\[ \phi_{2} = k_{2} - \frac{\lambda_{2}}{\sqrt{\pi}} \left( \int_{0}^{t_{1}} \frac{\phi_{1} du}{\sqrt{t_{1}+t_{2}-u}} + \int_{t_{1}}^{t_{1}+t_{2}} \frac{\phi_{2} du}{\sqrt{t_{1}+t_{2}-u}} \right) \]

\[ \phi_{2} = k_{2} - \frac{\lambda_{2}}{\sqrt{\pi}} \left( \int_{0}^{t_{1}} \frac{\phi_{1} du}{\sqrt{t_{1}+t_{2}-u}} + \int_{t_{1}}^{t_{1}+t_{2}} \frac{\phi_{2} du}{\sqrt{t_{1}+t_{2}-u}} \right) \]
where the subscripts 1 and 2 indicate, respectively, the conditions corresponding to first pulse, $E_1$ of length $t_1$ and current $i_1$ and those corresponding to the second pulse $E_2$ of length $t_2$ and current $i_2$.

Taking into account eq. [B1], eq. [B5] can be rearranged as (27)

\[
\phi_2 - \phi_1 = \left( k_2 - k_1 \frac{\lambda_2}{\lambda_1} \right) - \phi_1 \left( \frac{\lambda_2}{\lambda_1} - 1 \right) - \frac{\lambda_2}{\sqrt{\pi}} \int_0^{t_2} \frac{(\phi_2 - \phi_1) du}{\sqrt{t_2 - u}}
\]

Let us define

\[
\psi = \phi_2 - \phi_1
\]

In the conditions of RP, $E_1 - E^0 \to -\infty$, therefore $K_1 \to 0$, $k_1 \to \infty$ and $(k_1/\lambda_1) = (D_A)^{1/2}$, consequently

\[
k_2 - k_1 \frac{\lambda_2}{\lambda_1} \approx -\gamma K_2 k_2 = -\gamma k_2^{(1/\alpha)} = k_2
\]

\[
\frac{\lambda_2}{\lambda_1} - 1 \approx -1
\]

\[
\phi_1(t) = \sqrt{\frac{D_A}{\pi t}}
\]

which allows us to rewrite eq. [B6] as follows

\[
\psi = -k_2 - \sqrt{\frac{D_A}{\pi(t_1 + t_2)}} - \frac{\lambda_2}{\sqrt{\pi}} \int_0^{t_2} \frac{\psi du}{\sqrt{t_2 - u}}
\]

The numerical method that followed to solve this integral equation has been previously described in literature (18, 19). In accordance with this method, the integral in eq. [B11] is substituted by

\[
\int_0^{t_2} \frac{\psi du}{\sqrt{t_2 - u}} \approx 2\sqrt{t_2/r} \left( \psi_r + \sum_{i=1}^{r-1} \psi_i(\sqrt{r + 1 - i} - \sqrt{r - i}) \right)
\]

where $r$ is the number of steps in which $t_2$ is divided, in such a way that $\Delta t = t_2/r$. Thus $\psi_i$'s evaluated from

\[
\psi_i = \frac{-k_2 - \sqrt{\frac{D_A}{\pi(t_1 + i\Delta t)}} - 2\lambda_2 \sqrt{\frac{\Delta t}{\pi}} \sum_{j=1}^{i-1} \psi_j(\sqrt{i + 1 - j} - \sqrt{i - j})}{1 + 2\lambda_2 \sqrt{\frac{\Delta t}{\pi}}}
\]

where

\[
\psi_i = \frac{-k_2 - \sqrt{\frac{D_A}{\pi(t_1 + \Delta t)}}}{1 + 2\lambda_2 \sqrt{\frac{\Delta t}{\pi}}}
\]

The current $i_2 = i_{RP}$ is determined from

\[
\phi_2 = \psi_r + \phi_1 = \psi_r + \sqrt{\frac{D_A}{\pi(t_1 + t_2)}} = \frac{i_{RP}}{nFq_0C_*}
\]

Finally, $C^2_A(0, t)$ can be evaluated from

\[
\frac{C^2_A(0, t)}{C^2_A} = \frac{\phi_2/k_2 + \gamma K_2}{1 + \gamma K_2}
\]

All the calculations have been carried out with $r = 160$. In all cases, the difference observed in $i_{RP}$ or in $C^2_A(0, t)$ with respect to the predictions of eqs. [36] and [A5], respectively, are always less than 1%.