Theory for double potential step chronoamperometry for any potential values at spherical electrodes
Simultaneous determination of the diffusion coefficients of the electroactive species

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A B S T R A C T
We present a general and explicit analytical solution for double potential step chronoamperometry with any applied potential values (E 1, E 2) corresponding to a reversible charge transfer process at spherical electrode. This solution is essential to analyze double pulse electrochemical techniques such as RPV and DPV. We consider unequal diffusion coefficients, initial presence of both electroactive species and that the reaction product can dissolve in the electrolytic solution or in the electrode.

From the analytical equation obtained it is possible to deduce interesting simplified expressions for some particular cases: both species soluble in the electrolytic solution with equal diffusion coefficients (CR = 1), planar electrodes (r 0 → ∞), ultramicroelectrodes (r 0 → 0) when both species are soluble in the electrolytic solution, and double potential step chronoamperometry with limit current potentials (E 1 − E ′ → −∞, E 2 − E ′ → +∞). In this last case, when reaction product is not initially present it is pointed that planar electrodes and ultramicroelectrodes cannot be used for determining both diffusion coefficients. This interesting practical consequence can be demonstrated by means of the analytical expression deduced here, which represents a notable advantage in front of numerical results.

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1. Introduction

In a previous paper [1], we presented a general analytical solution for double potential step chronoamperometry applied to a reversible charge transfer process considering unequal diffusion coefficients and that the reaction product can be soluble in the electrolytic solution or in the electrode. We showed the importance of the proposed mathematical procedure [1,2] against those existing in the literature [3–6] that lead to partial solutions with more complex forms and even to physically meaningless results. Moreover, the mathematical method proposed permits to easily consider that both species are initially present in the system.

In this paper, we extend the mathematical method to obtain the analytical solution for the current response at spherical electrodes of any size for double potential step experiments, giving the details of the mathematical procedure in Appendix B.

The general equation deduced simplifies in some interesting cases: both species soluble in the electrolytic solution with equal diffusion coefficients (γ = 1), planar electrodes (r 0 → ∞), ultramicroelectrodes (r 0 → 0) when both species are soluble in the electrolytic solution, and double potential step chronoamperometry with limiting potentials of E 1 − E ′ → −∞ and E 2 − E ′ → +∞ [1]. In addition, given that the analytical equation is valid for any values of the applied potentials, fundamental expressions for double pulse electrochemical techniques (Reverse Pulse Voltammetry, Differential Pulse Voltammetry, ...) can be derived, which will be tackled in future papers.

Double potential step chronoamperometry, just as other double step techniques, are commonly used for studying the behaviour of the reaction product of the electrode reaction and for determining its diffusion coefficient, and they have been particularly studied in the literature at microdisk electrodes [7–10]. In this state of affairs, the fundamental purpose of this work is the analysis of the chronoamperometric response at spherical electrodes of any size when a double potential pulse is applied, considering different values of E 1 and E 2, in order to establish the most appropriate
conditions for the determination of the diffusion coefficients of both electroactive species when reaction product is initially present or not. Thus, we have deduced that, in initial absence of reaction product, neither planar electrodes nor ultramicroelectrodes can be used in double potential step chronamperometry of limit currents for determining both diffusion coefficients. This interesting result can be demonstrated from the analytical expression obtained in this paper, which represents a notable advantage in front of numerical calculations.

Finally, we have analyzed the influence of a soluble electrode product and of the initial presence of the reaction product on the chronamperometric responses for \(E_1\) and \(E_2\) values based on reverse pulse techniques and differential pulse techniques.

2. Theory

Let us consider a reversible charge transfer reaction:

\[ O + ne^- \rightarrow R \quad (1) \]

when a double potential pulse is applied at a stationary spherical electrode, taking into account that the reduced species is soluble in the electrolytic solution or in the electrode (electrolyte drop electrodes, amalgamation), and that the diffusion coefficients of the electroactive species may be different.

The applied potential is set at a value \(E_1\) in the interval \(0 \leq t \leq t_1\) and stepped from \(E_1\) to \(E_2\) at the time \(t = t_1 + t_2\); \(0 \leq t_2 \leq t_2\). During this second period \((0 \leq t_2 \leq t_2)\) the mass transport of the species \(O\) and \(R\) is described by the following differential equation system:

\[
\delta_0 c_0^{(2)}(r, t) = \delta_R c_R^{(2)}(r, t) = 0 \quad (2)
\]

with:

\[
\delta_k = \frac{\partial}{\partial r} - D_k \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right), \quad k = O, R \quad (3)
\]

The boundary value problem is given by the following:

Solution soluble product

\[
\begin{align*}
\tau_0 & \geq 0, \quad r \rightarrow \infty \\
\tau_2 &= 0, \quad r \geq r_0
\end{align*} \quad (4)
\]

Electrode soluble product

\[
\begin{align*}
\tau_2 & \geq 0, \quad r \rightarrow \infty \\
\tau_0 &= 0, \quad r \geq r_0
\end{align*} \quad (5)
\]

\[
\begin{align*}
\tau_2 & \geq 0, \quad r \rightarrow \infty \\
\tau_2 &= 0, \quad r \leq r_0
\end{align*} \quad (6)
\]

\[
\begin{align*}
\tau_0 & \geq 0, \quad r = r_0 \\
\tau_2 &= 0
\end{align*} \quad (7)
\]

The current response for the second potential pulse is given by:

\[
\frac{I_2}{nFA} = D_0 \left( \frac{\partial c_0^{(2)}(r, t)}{\partial r} \right)_{t=r_0} = \mp D_R \left( \frac{\partial c_R^{(2)}(r, t)}{\partial r} \right)_{t=r_0} \quad (9)
\]

We have solved this problem by following a procedure which lies in a modification of Koutecky’s dimensionless parameters method presented in previous papers [1,2], obtaining the following expression for the current in a double potential pulse technique whatever the values of both pulses \((E_1, E_2)\);

\[
I_2 = I_1(t_1 + t_2) + I_{d_2}(t_2) \cdot Z_{1,2} \left[ 1 + \left( 1 + \gamma \cdot \Omega_2 \cdot \xi_2 \right) \right] + \left[ G(\alpha) - 1 \right] + \gamma \cdot \xi_2 \cdot Y_{1,2} \cdot S^{\text{even}}(\alpha, \xi_1) + \gamma \cdot \xi_2 \cdot S^{\text{odd}}(\alpha, \xi_1)
\]

The mathematical method used to obtain this equation is given in Appendix B while the different variables and functions are defined in Appendix A.

2.1. Particular cases

Simplified expressions for the current are easily deduced from Eq. (10) in the following cases:

(a) Both species are soluble in the electrolytic solution and \(D_0 = D_R = D (\gamma = 1)\). Considering the case of equal diffusion coefficients, Eq. (10) becomes:

\[
\frac{I_2}{nFA} = D_0 \left( \frac{1 - (c_k^0/c_k^1)K_2}{1 + K_2} \right)
\]

(b) Ultramicroelectrodes \((r_0 \rightarrow 0)\) when both species are soluble in the electrolytic solution and \(c_k^0\) and \(c_k^1\) values are comparable. In this case it is fulfilled that:

\[
I_{2, \text{micro}} \approx \frac{nFAc_k^0D_0}{r_0} \left( \frac{1 - (c_k^0/c_k^1)K_2}{1 + \gamma K_2} \right) \quad (12)
\]

This response is similar to that corresponding to a single potential pulse under steady state conditions since when reaction product is soluble in the electrolytic solution and a small size electrode is used, steady state is close, so that the second pulse practically does not depend on the first one. Reaching the steady state response requires very small electrodes; for example, for \(E_1 - E_{\text{red}} < -\infty\) and for any value of \(E_2\), the error derived from the use of Eq. (12) is lower than 2% for \(\xi_2 > 90\).

(c) Planar electrodes \((r_0 \rightarrow \infty)\).

Taking into account that \(\xi_1 \rightarrow 0\) if \((\xi_1 \rightarrow 1)\) and \(\xi_2 \rightarrow 0\), the expression for the current is given by:

\[
\frac{I_{2, \text{plane}}}{D_0} = \frac{\sqrt{r_2}}{r_1 + r_2} \left( \frac{1 - (c_k^0/c_k^1)K_2}{1 + \gamma K_2} \right) \quad (13)
\]
The above expression is valid regardless of whether that species R dissolves in the electrolytic solution or in the electrode. So, it can be concluded that response with planar diffusion is the same regardless of whether species R diffuses in the electrolytic solution or in the electrode [11,12].

(d) Double potential step chronoamperometry with limit current potentials \(E_1 - E' \to -\infty, E_2 - E' \to +\infty\).

Under these conditions, response is given by Eq. (7) of Ref. [1]:

\[
I_2 = I_{l,c} - I_{d,2}(\tau_2) \left[1 + \left(\frac{c'_R}{\nu c'_O}\right) (1 \pm \xi_2) - (\gamma \mp 1)I_{d,2}(\tau_2)\right] \\
\times \left\{\xi_2 \pm 1\right\} \left[1 - F(\xi_1) \pm \frac{\xi_1}{\sqrt{\pi}} G(\alpha - 1) + \frac{\xi_2}{2\sqrt{\pi}} S(\xi_1, \alpha)\right\}
\]

where \(I_{l,c} = I_{d,1}(t_1 + \tau_2) \left[1 + \sqrt{\frac{\pi D_0(t_1 + \tau_2)}{r_0}}\right]\)

\[
S(\xi_1, \alpha) = \sum_{f = 1}^{\infty} \sum_{j = 0}^{\infty} \left[\frac{(-1)^{f + i} \cdot (\xi_1)^f \cdot \alpha^{2i+1} \cdot p_i}{(i + 1) \cdot (2j + 1) \cdot 2^i \cdot (j + 1)! \cdot \prod_{l = 1}^{j} p_l}\right]
\]

3. Results and discussion

3.1. Simultaneous determination of both diffusion coefficients at different electrode radii

In Fig. 1a we study the electrode size influence on current density–time curves for different \(\gamma\) values when both species are soluble in the electrolytic solution, being only species O initially present, and when the applied potential is stepped from \(E_1 - E' \to -\infty\) up to \(E_2 - E' \to +\infty\). As can be observed, the electrode radius has a great influence on the current density corresponding to the first potential pulse, increasing its value when the electrode size decreases (as is well known).

It is interesting to highlight the case in which \(D_0 = D_R\) (i.e., \(\gamma = 1\)) since, surprisingly, in this situation the current density corresponding to the second potential pulse remains unaltered when the electrode radius varies from \(r_0 \to \infty\) (planar electrode) up to \(r_0 \to 0\) (ultramicroelectrodes). This fact can be easily demonstrated from the analytical results, since from Eq. (14) it is deduced that the current density corresponding to the second pulse for any \(r_0\) value when \(\gamma = 1\) is given by:

\[
I_2(\gamma = 1) = \frac{nF c'_O \sqrt{D}}{\sqrt{\pi t_2}} \left[\alpha - 1 - \left(\frac{c'_R}{c'_O}\right) \left(1 + \sqrt{\frac{\pi D t_2}{r_0}}\right)\right]
\]

so that second pulse current density becomes independent of electrode radius when the reaction product is not initially present (\(c'_R = 0\)):

\[
I_2(\gamma = 1) = \frac{nF c'_O \sqrt{D}}{\sqrt{\pi t_2}} (\alpha - 1)
\]

When \(D_0 \neq D_R\) (\(\gamma \neq 1\)) the current density corresponding to the second potential pulse is scarcely affected by the electrode size.

From this figure we can conclude that when double potential step chronoamperometry at the diffusion limits is used, \(I_2 \approx I_1\) for planar electrodes and the ratio \(I_2/I_1\) decreases when \(r_0\) decreases until \(I_2/I_1 \to 0\) for ultramicroelectrodes.

Regarding the \(\gamma\) value, it is observed that current density–time curves corresponding to the first potential pulse are independent of \(D_R\) value, since cathodic limit conditions are imposed. On the contrary, \(\gamma\) value has a meaningful effect on the curves corresponding to the second potential pulse at spherical electrodes, so that the lower current density, the greater \(D_R\) value. This effect is more noticeable when the electrode radius decreases. However, a practical limit appears as consequence of the decrease of the ratio \(I_2/I_1\) at small electrodes, which makes difficult the determination, in the same experiment, of a small current density \(I_2\) after a big current density \(I_1\). By studying the behaviour of the ratio \(I_2/I_1\), it is concluded that values of \(\sqrt{D_0 \cdot t_1/r_0}\) in the range \(0.5 < \sqrt{D_0 \cdot t_1/r_0} < 1.25\) are optimum for this purpose since the ratio \(I_2/I_1\) is adequate, and \(I_2\) is sensitive to \(D_R\); for example, for \(D_0 = 10^{-5}\) cm²/s and \(t_1 = 1\) s the optimum electrode radius are 25–65 μm. At planar electrodes the second potential current density–time curve is not sensitive to species R diffusion coefficient under these conditions \((c'_R = 0, E_1 - E' \to -\infty\) and \(E_2 - E' \to +\infty\)), as can be deduced from Eq. (13):

\[
\frac{I_{2,\text{plane}}}{A} = \frac{nF c'_O \sqrt{D_0}}{\sqrt{\pi t_2}} (\alpha - 1)
\]

![Fig. 1. Current density–time curves when both species are soluble in the electrolytic solution and only species O is initially present. Three electrode sizes are considered: planar electrode (—), spherical electrode with \(r_0 = 10^{-3}\) cm (—), and ultramicroelectrode with \(r_0 = 10^{-5}\) cm (—), and three \(\gamma\) values: \(\gamma = 0.5\) (green curves), \(\gamma = 1.0\) (black curves) and \(\gamma = 2.0\) (red curves). The applied potential sequences are: \(E_1 - E' \to -\infty, E_2 - E' \to +\infty\) (Fig. 1a) and \(E_1 - E' = -12.5\) mV, \(E_2 - E' = -12.5\) mV (Fig. 1b).](image-url)
which coincides with the current density at a spherical electrode when both diffusion coefficients are equal (see Fig. 1a).

So, we can conclude that, when reaction product is not initially present, double potential step chronoamperometry of limit currents can only be used for determining both diffusion coefficients when spherical electrodes are used. The use of planar electrodes or ultramicroelectrodes for calculating \( D_R \) needs that species R be initially present.

When the applied potentials are close to the formal potential (Fig. 1b), the current density increases when the electrode size decreases in a similar way for both potential step curves, contrarily to the above case. The \( \gamma \) effect on the chronoamperometric curves is very noticeable and also increases when the electrode radius decreases.

### 3.2. Influence of soluble electrode product

As has been indicated above, when the product is soluble in the electrode, we have assumed Koutecky’s approximation (Eq. (6)) which does not take into account the electrode finite volume. This widely used approximation makes possible the analytical resolution of the problem but limits the applicability of the solutions obtained.

We have studied the validity of the analytical solution presented in this work by comparing with numerical results calculated considering the rigorous condition of null net flux at the electrode centre \( (\frac{\partial c}{\partial r})_{r=0} = 0 \) [2]. Analytical and numerical results are coincident for \( \xi_1 < 1 \) with a relative difference \( \leq 1.7\% \). For higher \( \xi_1 \) values (i.e., higher \( D_R \), longer electrolysis time and/or smaller electrode radius) the error resulting from neglecting the electrode finite volume increases and the numerical solution should be used.

We will study the case of the application of a fixed first potential and a second potential, \( E_2 \), varying from cathodic limit values towards anodic limit values. Specifically, we consider that first potential pulse corresponds to cathodic limit current conditions \( (E_1 - E^\circ \to \infty) \), which of great interest since these conditions match Reverse Pulse Voltammetry technique (RPV). The analytical solution for this case is given by

\[
\hat{I} = I_{\text{RPV}} = I_{1C} + I_{2C}(t_2) \cdot Z_2 \left[ 1 + \left( \frac{E_R^\circ}{\gamma - E_R^\circ} \right) \right]
\]

\[
\times (1 + \gamma \cdot \Omega_2 \cdot \xi_2) \pm (\gamma = 1) \cdot I_{2C}(t_2) \cdot Z_2
\]

\[
\times \left\{ (1 + \gamma \cdot \Omega_2 \cdot \xi_2)[1 - F(\xi_1)] + \frac{\xi_1}{\sqrt{\gamma}} [G(\alpha) - 1]
\right.
\]

\[
\left. + \gamma \cdot \xi_2 \cdot Y_2 \cdot S_{\text{even}}(\alpha, \xi_1) + \frac{\gamma \cdot \xi_2}{\sqrt{\gamma}} \cdot S_{\text{odd}}(\alpha, \xi_1) \right\} \tag{20}
\]

where \( I_{1C} \) is given by Eq. (15) and:

\[
Z_2 = \frac{-\gamma K}{1 + \gamma K} \tag{21}
\]

\[
Y_2 = \frac{K_2(\gamma + 1)}{(1 + \gamma K)^2} \tag{22}
\]

and considering in \( \xi_1 \), \( S_{\text{even}}(\alpha, \xi_1) \) and \( S_{\text{odd}}(\alpha, \xi_1) \) that:

\[
f_1 = \pm 1 \tag{23}
\]

In Fig. 2 we have plotted \( I-t \) curves at a spherical electrode for three \( E_2 \) values and two values of species R diffusion coefficient, when both species are soluble in the electrolytic solution (solid lines) and when reaction product is soluble in the electrode (dotted lines). As was expected, whereas the first pulse \( I_1 \) – \( t \) curves corresponding to different \( D_R \) values coincide, second pulse \( I_2 \) – \( t \) curves depend on species R diffusion coefficient and on the behaviour of the reaction product (soluble in the electrolytic solution or in the electrode), so that when this dissolves in the electrode more negative current values are obtained.

Fig. 3 shows the comparison between double pulse \( I-t \) curves at a spherical electrode, when both species are soluble in the

Fig. 3. Current–time curves at a spherical electrode ($r_0 = 10^{-2}$ cm) when both species are soluble in the electrolytic solution (solid lines) and when reaction product dissolves in the electrode (dotted lines). Three first and second potential values are considered (shown on the curves). $D_R = 5 \times 10^{-6}$ cm$^2$/s. Other conditions as in Fig. 1.

electrolytic solution (solid lines) and when the reaction product is soluble in the electrode (dotted lines), by using two successive potential pulses in a similar way to the potential sequence used in the differential double pulse techniques: Differential Pulse Voltammetry (DPV) and Differential Normal Pulse Voltammetry (DNPV). Three potential regions have been considered: near anodic limit (Fig. 3a), near the formal potential (Fig. 3b) and near cathodic limit (Fig. 3c), being in the three cases the difference between both pulse potentials $\Delta E = E_2 - E_1 = -25$ mV. As can be observed, first and second pulse currents are affected by species R amalgamation, being this effect more meaningful when applied potential values are near the formal potential value (Fig. 3b) and leading to lower current values.

3.3. Influence of the initial presence of the reaction product

The analytical solution obtained also permits to study current density–time response when both species are initially present ($c_O^* = c_R^*$). In Fig. 4 we analyze this case at a spherical electrode with $r_0 = 10^{-3}$ cm both when the applied potential is stepped from $E_1 - E_t' \to -\infty$ up to $E_2 - E_t' \to +\infty$ (Fig. 4a) and when both potentials are close to the formal potential (Fig. 4b). In the first case, the great influence of different values of diffusion coefficients (through $\gamma$) on the second pulse current density–time curves is shown. Moreover, this influence is inverted with regard to the case at which only species O is initially present (see Fig. 1a), that is, the higher current density, the greater $D_R$ value. In Fig. 4b two potential slightly greater and lower than the equilibrium potential (which coincides with the formal potential since $c_O^* = c_R^*$) are used, in a similar way to Fig. 1b.

Fig. 4. Current density–time curves at a spherical electrode ($r_0 = 10^{-3}$ cm) when both species are soluble in the electrolytic solution and initially present. Three $\gamma$ values are considered: $\gamma = 0.5$ (---), $\gamma = 1.0$ (– -) and $\gamma = 2.0$ (– – –). The applied potential sequences are: $E_1 - E_t' \to -\infty$, $E_2 - E_t' \to +\infty$ (a) and $E_1 - E_t' = -12.5$ mV, $E_2 - E_t' = -12.5$ mV (b). $c_O^* = c_R^* = 1$ mM. Other conditions as in Fig. 1.
We can observe how the first pulse potential gives rise to anodic current and how the influence of the diffusion coefficients is very meaningful in both chronoamperograms.

4. Conclusions

- In this paper we have deduced a general analytical solution for spherical electrodes. This solution considers unequal diffusion coefficients for both electroactive species, the initial presence of reaction product and also that the reaction product may diffuse in the electrolytic solution or in the electrode. Moreover, from this general equation the limit situations corresponding to planar electrodes and ultramicroelectrodes can be deduced.

- When only species O is initially present, simultaneous determination of both diffusion coefficients can only be carried out by means of this technique with limit currents if conventional spherical electrodes are used (this determination is not possible at planar electrodes or ultramicroelectrodes). In these last two cases, for evaluating both diffusion coefficients a second pulse close to the formal potential should be used.

- The validity of the solution presented for any value of applied potentials will permit its application to any double pulse electrochemical technique, such as DPV or RPV.

- From the chronoamperograms corresponding to double pulse sequence as that used in DPV we have verified that the nearer to formal potential both applied potentials are, the higher effect of amalgamation.

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Appendix A. Symbols and definitions

\[ s_{k,2} = \frac{r - r_0}{2\sqrt{D_k \cdot \tau_2}} \quad k = O, R \]

\[ F(\xi_1) = e^{\xi_1/2} \cdot \text{erfc}(\xi_1/2) \]

\[ \xi_1 = \frac{2\sqrt{D_k (t_1 + \tau_2)}}{r_0 \cdot i_1} \]

\[ \xi_2 = \frac{\sqrt{\pi \cdot D_R \cdot \tau_2}}{r_0} \]

\[ I_{d,1}(t_1 + \tau_2) = \frac{nFAc_O \sqrt{D_O}}{\sqrt{\pi (t_1 + \tau_2)}} \]

\[ I_{d,2}(\tau_2) = \frac{nFAc_O \sqrt{D_O}}{\sqrt{\pi \tau_2}} \]

\[ \gamma = \left( \frac{D_O}{D_R} \right)^{1/2} \]

\[ \eta_m = \frac{nE_{RT}}{E_m - E^{*}} \quad m = 1, 2 \]

\[ K_m = \exp(\eta_m) \quad m = 1, 2 \]

\[ \Omega_m = \frac{1 \pm K_m}{1 + \gamma K_m} \quad m = 1, 2 \]

\[ J_m = \frac{1 + \gamma K_m}{\gamma^2 K_m \pm 1} \quad m = 1, 2 \]

\[ Z_{1,2} = \frac{\gamma(K_1 - K_2)}{(1 + \gamma K_1)(1 + \gamma K_2)} \]

\[ Y_{1,2} = \frac{K_2(\gamma + 1)(\gamma J_2 - 1)J_1^2}{(1 + \gamma K_2)J_2^2} \]

\[ P_1 = \frac{(\gamma - / + 1)\left(1 - (c_O^* / c_R^*)K_1\right)}{(\gamma^2 K_1 \pm 1)} \]

\[ \alpha = \sqrt{\frac{\tau_2}{t_1 + \tau_2}} \]

\[ G(\alpha) = \alpha \cdot \text{arcsin}(\alpha) + \sqrt{1 - \alpha^2} \]

\[ I_1(t_1 + \tau_2) = I_{d,1}(t_1 + \tau_2) \cdot \left( \frac{1 - (c_O^* / c_R^*)K_1}{1 + \gamma K_1} \right) \]

\[ \times \left\{ 1 + \sqrt{\pi D_0 (t_1 + \tau_2)} \left[ \frac{1 + \gamma K_1}{1 + \gamma^2 K_1} \right] \right\} \left( \frac{1}{\gamma^2 K_1 \pm 1}(1 + \gamma K_1) \right) \]
Appendix B

In order to solve the differential equation system (Eq. (2)) it is convenient to introduce the following variable change:

$$u_k(r, t) = \frac{c_k(r, t) \cdot r}{c_0 \cdot r_0} \quad (k = O, R)$$

Taking into account the new variable $u_k(r, t)$ and that the operator $\bar{\delta}_k$ given by Eq. (3) is linear, solutions corresponding to the second potential step can be written as:

$$u_k^{(2)}(r, t) = u_k^{(1)}(r, t) + \bar{u}_k^{(2)}(r, t) \quad (k = O, R)$$

being $u_k^{(1)}(r, t)$ the solutions of the first potential pulse [2], and $\bar{u}_k^{(2)}(r, t)$ the new unknown partial solutions with null initial conditions ($t_2 = 0$).

The differential equation system becomes,

$$\begin{align*}
\frac{\partial \bar{u}_k^{(2)}(r, t_2)}{\partial t_2} &= D_O \frac{\partial^2 \bar{u}_k^{(2)}(r, t_2)}{\partial r^2} \\
\frac{\partial^2 \bar{u}_k^{(2)}(r, t_2)}{\partial r^2} &= D_R \frac{\partial^2 \bar{u}_k^{(2)}(r, t_2)}{\partial r^4}
\end{align*}$$

and the boundary value problem is given by:

Solution soluble product

$$\begin{align*}
t_2 &\geq 0, \quad r \to \infty & \bar{u}_k^{(2)} = 0 \\
t_2 &\geq 0, \quad r \geq r_0 & \bar{u}_k^{(2)} = 0
\end{align*}$$

Electrode soluble product

$$\begin{align*}
t_2 &\geq 0, \quad r \to \infty & \bar{u}_k^{(2)} = 0 \\
t_2 &\geq 0, \quad r \to -\infty & \bar{u}_k^{(2)} = 0 \\
&\quad r = r_0 & \bar{u}_k^{(2)} = 0 \\
&\quad r > r_0
\end{align*}$$

and:

$$\begin{align*}
&\quad i \text{ even : } A = 0 \\
&\quad i \text{ odd : } A = \prod_{l=1}^{j-1} (i-2l)! & \frac{1}{2^j (j)!} \sum_{l=0}^{\frac{j}{2}} \left( \frac{J_1}{J_2} \right)^{2l} \frac{(j-1)!}{(j-1)!}
\end{align*}$$

where the sum is only effective for $j \geq 2$

$$\begin{align*}
&\quad i \text{ odd : } A = \frac{1}{2^j (j)!} \sum_{l=0}^{\frac{j}{2}} \left( \frac{J_1}{J_2} \right)^{2l} \frac{(j-1)!}{(j-1)!}
\end{align*}$$

and:

$$\begin{align*}
&\quad i \text{ even : } A = 0 \\
&\quad i \text{ odd : } A = \prod_{l=1}^{j-1} (i-2l+1)! & \frac{1}{2 \cdot \gamma \cdot (j+1)!} \sum_{m=0}^{j-1} (-1)^m \cdot 2^m \cdot \left[ \frac{J_1}{J_2} \right]^{2m-1} \prod_{k=0}^{m} \frac{(j-k+1)}{2k-1}
\end{align*}$$

where the sum is only effective for $j \geq 1$

$$\begin{align*}
&\quad i \text{ even : } B = \prod_{l=1}^{j} (i-2l+1)! & \frac{1}{2 \cdot \gamma \cdot (j+1)!} + \frac{Y_{1,2}}{2} \sum_{m=0}^{j-1} (-1)^m \cdot 2^m \cdot \left[ \frac{J_1}{J_2} \right]^{2m-1} \prod_{k=0}^{m} \frac{(j-k+1)}{2k-1}
\end{align*}$$

where the sum is only effective for $j \geq 1$

$$\begin{align*}
&\quad i \text{ odd : } B = 0
\end{align*}$$
\[
\gamma^2 \left[ \left( \frac{\partial u^{(2)}_O(r, \tau_2)}{\partial r} \right)_{r=r_0} - \frac{u^{(2)}_O(r_0, \tau_2)}{r_0} \right] \\
= \mp \left[ \left( \frac{\partial u^{(2)}_R(r, \tau_2)}{\partial r} \right)_{r=r_0} - \frac{u^{(2)}_R(r_0, \tau_2)}{r_0} \right] \\
\]  
(B6)

\[
u^{(2)}_O(r_0, \tau_2) - K_2 \cdot u^{(2)}_R(r_0, \tau_2) = K_2 \cdot u^{(1)}_R(r_0, \tau) - u^{(1)}_O(r_0, \tau) \\
\]  
(B7)

As can be seen the differential equation system (B3) only depends on the new functions \(u^{(2)}_O(r, \tau_2)\), while the surface condition (B7) introduces dependence with the first potential pulse.

We have solved this problem by means of Kouteký’s dimensionless parameters method \([13,14]\). In order to apply it, we suppose that solutions have the form:

\[
u^{(2)}_O(r, \tau_2) = \hat{u}^{(2)}_O(s_{O,2}, \xi_1, \alpha) = \sum_{i,j=0}^{\infty} \sigma^{(-)}_{i,j}(s_{O,2}) \xi_1^i \alpha^j \\
\]  
(B8)

\[
u^{(2)}_R(r, \tau_2) = \hat{u}^{(2)}_R(s_{R,2}, \xi_1, \alpha) = \sum_{i,j=0}^{\infty} \phi^{(\pm)}_{i,j}(s_{R,2}) \xi_1^i \alpha^j \\
\]

Taking into account the dimensionless variables, the differential equation system (B3) becomes:

\[
\begin{align*}
\frac{\partial^2 \hat{u}^{(2)}_O(s_{O,2}, \xi_1, \alpha)}{\partial s_{O,2}^2} + 2s_{O,2} \frac{\partial \hat{u}^{(2)}_O(s_{O,2}, \xi_1, \alpha)}{\partial s_{O,2}} - 2 \alpha^2 \xi_1 \frac{\partial \hat{u}^{(2)}_O(s_{O,2}, \xi_1, \alpha)}{\partial \xi_1} \\
\frac{\partial^2 \hat{u}^{(2)}_R(s_{R,2}, \xi_1, \alpha)}{\partial s_{R,2}^2} + 2s_{R,2} \frac{\partial \hat{u}^{(2)}_R(s_{R,2}, \xi_1, \alpha)}{\partial s_{R,2}} - 2 \alpha^2 \xi_1 \frac{\partial \hat{u}^{(2)}_R(s_{R,2}, \xi_1, \alpha)}{\partial \xi_1}
\end{align*}
\]

with the boundary value problem given by:

**Solution soluble product**

\[
\begin{align*}
\tau_2 \geq 0, & \quad r \to \infty \\
\tau_2 = 0, & \quad r \geq r_0 \\
\hat{u}^{(2)}_O(\infty) = \hat{u}^{(2)}_R(\infty) = 0 \\
\end{align*}
\]  
(B10)

**Electrode soluble product**

\[
\begin{align*}
\tau_2 \geq 0, & \quad r \to \infty \\
\tau_2 = 0, & \quad r \leq r_0 \\
\tau_2 \geq 0, & \quad r \to \infty \\
\tau_2 = 0, & \quad r \geq r_0 \\
\tau_2 > 0, & \quad r = r_0 \\
\end{align*}
\]

\[
\begin{align*}
s_{R,2} \to -\infty, & \quad \hat{u}^{(2)}_R(-\infty) = 0 \\
s_{O,2} \to \infty, & \quad \hat{u}^{(2)}_O(\infty) = 0 \\
\end{align*}
\]  
(B11)

By introducing expressions (B8) into Eq. (B3), the equation system becomes:

\[
\begin{align*}
\sigma^{(-)}_{i,j}(s_{O,2}) + 2s_{O,2} \sigma^{(-)}_{i,j}(s_{O,2}) - 2j \epsilon^{(-)}_{i,j}(s_{O,2}) &= -2(j - l - 2) \sigma^{(-)}_{i,j}(s_{O,2}) \\
\phi^{(\pm)}_{i,j}(s_{R,2}) + 2s_{R,2} \phi^{(\pm)}_{i,j}(s_{R,2}) - 2j \phi^{(\pm)}_{i,j}(s_{R,2}) &= -2(j - l - 2) \phi^{(\pm)}_{i,j}(s_{R,2}) \\
\end{align*}
\]  
(B14)

By considering expressions (B8) the boundary value problem is given by:

**Solution soluble product**

\[
\begin{align*}
\tau_2 \geq 0, & \quad r \to \infty \\
\tau_2 = 0, & \quad r \geq r_0 \\
s_{k,2} \to \infty (k \equiv O, R): & \quad \sigma^{(-)}_{i,j}(\infty) = 0 \\
\phi^{(\pm)}_{i,j}(\infty) = 0 & \quad \forall \ i, j
\end{align*}
\]  
(B15)

**Electrode soluble product**

\[
\begin{align*}
\tau_2 \geq 0, & \quad r \to -\infty \\
\tau_2 = 0, & \quad r \leq r_0 \\
\tau_2 \geq 0, & \quad r \to \infty \\
\tau_2 = 0, & \quad r \geq r_0 \\
\tau_2 > 0, & \quad r = r_0 \\
\end{align*}
\]

\[
\begin{align*}
s_{R,2} \to -\infty, & \quad \phi^{(\pm)}_{i,j}(-\infty) = 0 \\
s_{O,2} \to \infty, & \quad \sigma^{(-)}_{i,j}(\infty) = 0 & \quad \forall \ i, j
\end{align*}
\]  
(B16)

\[
\gamma \left[ \sigma^{(-)}_{i,j}(0) - \gamma \cdot \sigma^{(-)}_{i,j-1,0} \right] = \mp \left[ \phi^{(\pm)}_{i,j}(0) - \phi^{(\pm)}_{i,j-1,0} \right] & \quad \forall \ j
\]  
(B17)

\[
\sigma^{(-)}_{i,0}(0) - K_2 \phi^{(\pm)}_{i,0}(0) = K_2 \phi^{(\pm)}_{i,0}(0) - \sigma^{(-)}_{i,0}(0) & \quad j = 0
\]  
(B18)

where \(\phi^{(\pm)}_{i,0}(0)\) corresponds with the first potential pulse solution [2].

Solutions of the differential equation system have the following form:

**when \(j - l = 0\) or \(j < 2\) (homogeneous differential equations)**

\[
\begin{align*}
\sigma^{(-)}_{i,j}(s_{O,2}) &= \lim_{s_{O,2} \to \infty} \frac{\sigma^{(-)}_{i,j}(s_{O,2})}{L_j + a_{i,j} \cdot \Psi^{(-)}_{j}(s_{O,2})} \\
\phi^{(\pm)}_{i,j}(s_{R,2}) &= \lim_{s_{R,2} \to \infty} \frac{\phi^{(\pm)}_{i,j}(s_{R,2})}{L_j + b_{i,j} \cdot \Psi^{(\pm)}_{j}(s_{R,2})} & \forall \ i, j
\end{align*}
\]  
(B19)

**when \(j - l \neq 0\) (nonhomogeneous differential equations)**

\[
\begin{align*}
\sigma^{(-)}_{i,j}(s_{O,2}) &= \lim_{s_{O,2} \to \infty} \frac{\sigma^{(-)}_{i,j}(s_{O,2})}{L_j + \sum_{m=0}^{j} a_{i,j,m} \cdot \Psi^{(-)}_{m}(s_{O,2})} \\
\phi^{(\pm)}_{i,j}(s_{R,2}) &= \lim_{s_{R,2} \to \infty} \frac{\phi^{(\pm)}_{i,j}(s_{R,2})}{L_j + \sum_{m=0}^{j} b_{i,j,m} \cdot \Psi^{(\pm)}_{m}(s_{R,2})} & \forall \ i, j
\end{align*}
\]  
(B20)
\[
\sigma_{i,j+1}^{(-)}(s_{0,2}) = \lim_{s_{0,2} \to -\infty} \frac{L_j}{\lim_{l_j \to -\infty}} + \sum_{m=0}^{j} a_{i,j+1,m} \cdot \Psi_{2m+1}^{(-)}(s_{0,2}) \tag{B21}
\]

where \( a_{i,j,m} \) and \( b_{i,j,m} \) are constants that we will determine by applying the boundary value problem, \( L_j \) are \( s_k \)-powers numeric series, and \( \Psi_{m}^{(\pm)}(s_k) \) (\( k \equiv 0, R \)) are Koutecký’s functions [13,14], which have the following properties:

\[
\Psi_{m}^{(\pm)}(0) = 1 \tag{B22}
\]

\[
\Psi_{m}^{(\pm)}(\pm\infty) = 0 \tag{B23}
\]

\[
\Psi_{m}^{(\pm)}(s_k) = \pm p_m \Psi_{m-1}^{(\pm)}(s_k) \tag{B24}
\]

\[
\Psi_{0}^{(\pm)}(s_k) = 1 \pm \text{erf}(s_k) \tag{B25}
\]

Finally, considering Eq. (9) we obtain the expression for the response corresponding to the second potential pulse (Eq. (10)).

The number of terms to be considered in series \( S^{\text{even}}(\alpha, \xi_1) \) and \( S^{\text{odd}}(\alpha, \xi_1) \) obviously depends on the electrode sphericity (through \( \xi_1 \)) and on the duration of the potential pulses (through \( \alpha \)), so that the higher sphericity and the greater \( \alpha \) value, the higher order of \( i \)-powers and \( j \)-powers, respectively, must be considered. In reference [1], a discussion about this point is presented, showing that to obtain a relative error less than 1% when \( \gamma = 0.7, E_1 \to -\infty, E_2 \to +\infty, t_1 = 1 \) s and \( t_2 = 0.5 \) s we need to consider up to the 11th order (\( \xi_1^{11} \)) for \( r_0 = 5 \times 10^{-3} \) cm, up to the 175th order (\( \xi_1^{175} \)) for \( r_0 = 10^{-3} \) cm, and up to the 275th order (\( \xi_1^{275} \)) for \( r_0 = 8 \times 10^{-4} \) cm, being in all cases up to \( \alpha^{75} \)-term considered.

References