Characterization of slow charge transfer processes in differential pulse voltammetry at spherical electrodes and microelectrodes

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**Abstract**

The use of differential pulse voltammetry at spherical electrodes for the study of the kinetic of charge transfer processes is analyzed. An analytical solution is presented, valid for any value of the electrode radius, the heterogeneous rate constant and the transfer coefficient. Several reversibility criteria are established based on the variation of DPV peak with the duration of the potential pulses and the electrode radius. Moreover, general working curves for extraction of kinetic parameters from DPV experiments are given. The anomalous shape of DPV curves for quasireversible processes with small values of the transfer coefficient is reported. The effect of the presence of both electroactive species on DPV curves for quasi reversible and irreversible systems is also studied.

The aim of this paper is to extend this study to spherical diffusion by deducing an explicit analytical expression applicable to DPV assuming that the duration of the first pulse is much longer than that of the second one (\(t_2 < t_1/50\)), since under these conditions the solution can be easily analyzed to extract kinetic parameters. In order to show the validity of the analytical solution, we have compared the analytical results with those obtained from numerical calculation, the difference being always smaller than 0.5%.

The equation derived is valid for spherical electrodes of any size and it considers the presence of either or both electroactive species forming an O/R redox couple in bulk solution. From this, we deduce, as limiting cases, the expressions corresponding to reversible processes \([10]\) as well as to planar electrodes \((t_0 \rightarrow \infty)\) and spherical ultramicroelectrodes \((t_0 \rightarrow 0)\). In this last case, the DPV stationary response is obviously similar to that obtained in square wave voltammetry (SWV) when the pulse height \((\Delta E)\) in DPV is equal to the double of square wave potential, i.e. \(2E_{SWV} = \Delta E\).

The effects of the heterogeneous rate constant \((k_t = k^0 \sqrt{\epsilon_t/D})\) and the transfer coefficient \((\alpha)\) on the \(\Delta I/E\) curves are analyzed, pointing out that for \(k^0\) values around \(10^{-3}\) cm/s an anomalous splitting in two peaks of DPV curve is observed for \(\alpha < 0.3\), one peak being situated at more positive potentials than \(E^0\) and the other one at more negative potentials. This phenomenon is more apparent for positive \(\Delta E\) values. This previously unobserved feature of DPV is important to report since the peak splitting might easily be mistaken by the experimentalist as indicating the presence of extra redox active species.
The characterization of electrode processes, that is, the extraction of kinetic parameters, is a major issue in electrochemistry [1,2,13–16]. In this paper several criteria of reversibility are given, for example, based on the asymmetry of the DPV peaks for $\Delta E < 0$ and $\Delta E > 0$ at different electrode radii, which depends on $k^0$ value. Another criterion could be based on the great influence of the variation of the double pulse duration on the peak current for quasireversible systems, whereas for totally irreversible ones the shift of the position of DPV peak towards more negative potentials is the most remarkable effect. It is also worth highlighting that whilst the initial presence of both electroactive species does not shape the DPV curve for reversible processes, this is considerably distorted for non-reversible systems in such a way that for totally irreversible processes two net separated peaks are obtained, one corresponding to the reduction of species O and the other one to the oxidation of species R. The greater the distortion is, the smaller the $k^0$ value. Finally, from the mathematical solutions presented, working curves are given for extraction of kinetic parameters from experimental data.

2. Theory

Let us consider the following charge transfer reaction:

$$O + e^{-} \rightarrow R$$

First, the applied potential is set at a value $E_1$ at a stationary spherical electrode during the interval $0 \leq t_1 \leq t_1$. The diffusion mass transport of the electroactive species towards or from the electrode surface is described by the following differential equation system:

$$\frac{\partial c^{(1)}_O(r,t)}{\partial t} - D \frac{\partial ^2 c^{(1)}_O(r,t)}{\partial r^2} = \frac{2}{r} \frac{\partial c^{(1)}_O(r,t)}{\partial r}$$

with:

$$\frac{\partial c^{(2)}_O(r,t)}{\partial t} = D \frac{\partial ^2 c^{(2)}_O(r,t)}{\partial r^2}$$

where we have assumed that both electroactive species have the same value of the diffusion coefficient ($D_O = D_R = D$).

The boundary conditions to be fulfilled by the solutions of the differential equations are given by:

$$\begin{align*}
\tau_1 & \geq 0, \quad r \rightarrow \infty & c^{(1)}_O(r,t) = c^{(2)}_O(r,t) = 0 \\
\tau_1 & = 0, \quad r \geq r_0 & c^{(1)}_O(r,t) = c^{(2)}_O(r,t) = \frac{1}{\theta_1 - 1} (1 - \mu K_1) / (1 + K_1) \\
\tau_1 & > 0, \quad r = r_0 & \left( \frac{\partial c^{(1)}_O(r,t)}{\partial r} \right)_{r=r_0} = - \left( \frac{\partial c^{(2)}_O(r,t)}{\partial r} \right)_{r=r_0} \\
\tau_1 & > 0, \quad r \rightarrow r_0 & \left( \frac{\partial c^{(2)}_O(r,t)}{\partial r} \right)_{r=r_0} = k^0 K^{-\alpha} c^{(2)}_O(r_0,t) - k^0 K^{-\alpha} c^{(4)}_R(r_0,t)
\end{align*}$$

where the different parameters are defined in Appendix A and Table 1.

By means of the mathematical procedure described in Appendix B, the expression for the current is derived:

$$I(t) = I_d(\infty) \cdot \frac{\theta_1 - 1}{\theta_1 (1 + K_1)} \left[ 1 + (\theta_2 - 1) \cdot F \left( \frac{X_1}{2} \right) \right]$$

where all the variables and functions are given Appendix A. This expression coincides with that obtained by Delmastro and Smith [17] when $D_O = D_R = D$.

At the time $t \geq t_1$, the applied potential is stepped from $E_1$ to $E_2$ and, analogously to the above, during this second period ($t = t_1 + t_2; 0 \leq t_2 \leq t_2$) the mass transport of species O and R is described by:

$$\delta c^{(2)}_O(r,t) = \delta c^{(2)}_R(r,t) = 0$$

with the following boundary value problem:

$$\begin{align*}
\tau_2 & \geq 0, \quad r \rightarrow \infty & c^{(2)}_O(r,t) = c^{(1)}_0, \quad c^{(2)}_R(r,t) = c^{(1)}_0 \\
\tau_2 & = 0, \quad r \geq r_0 & \left( \frac{\partial c^{(2)}_O(r,t)}{\partial r} \right)_{r=r_0} = - \left( \frac{\partial c^{(2)}_R(r,t)}{\partial r} \right)_{r=r_0} \\
\tau_2 & > 0, \quad r = r_0 & D \left( \frac{\partial c^{(2)}_O(r,t)}{\partial r} \right)_{r=r_0} = k^0 K^{-\alpha} c^{(2)}_O(r_0,t) - k^0 K^{-\alpha} c^{(4)}_R(r_0,t)
\end{align*}$$

Eq. (11) assumes that the transition state does not change with potential and so the same value of $\alpha$ applies to the forward and reverse processes.

From the mathematical procedure given in Appendix B, the expression for the current of the second potential pulse is obtained:

$$I_2 = I_1(t_1 + t_2) + I_d(\infty) \frac{\theta_2 - 1}{\theta_2 (1 + K_2)} \left[ 1 + (\theta_2 - 1) \cdot F \left( \frac{X_2}{2} \right) \right]$$

with all the variables and functions given in Appendix A.

The DPV technique consists of the application of successive double potential pulses, so that the initial equilibrium conditions are re-established after each one and the duration of the second pulse is much shorter than that of the first one ($t_2 << t_1$). The current is registered twice, at the end of the first pulse ($t_1$) and at the end of the second one ($t_1 + t_2$), and DPV curve is a plot of the difference between the two current samples ($\Delta I = I_2(t_1 + t_2) - I_1(t_1)$) vs a potential x-axis [1,2]. In a previous paper [10], we discussed the convenience of choosing the arithmetic average of both potential values ($E_{1,2} = (E_1 + E_2)/2$, see Fig. 1) as the potential-axis.

As mentioned above, in DPV technique initial equilibrium conditions are re-established before the application of each double potential pulse, for example, by renewal of the electrode (mercury drop electrode), by open circuiting the working electrode for a waiting period [10] or by setting the applied potential at a value at which no current flows [4]. Lovric has shown for reversible processes [3], and we have proved by numerical simulations, that a waiting period $\geq 5 \cdot t_1$ is long enough to achieve this condition at spherical electrodes; the smaller the electrode radius, the shorter the waiting period required. So, the expression for DPV response is immediately particularized from Eq. (12):

$$\frac{\Delta I}{I_d(\infty)} = \left( \frac{\theta_2 - 1}{\theta_2 (1 + K_2)} \right) \left[ 1 + (\theta_2 - 1) \cdot F \left( \frac{X_2}{2} \right) \right]$$

where:

$$X_2 = \frac{2r_0}{D^0} - \frac{t_1}{D^0} k^0 K^{-\alpha} (1 + K_1)$$
2.1. Particular cases

From Eq. (13), expressions under some interesting conditions can be derived:

- **Planar electrodes** \((r_0 \to \infty)\). Expression (13) becomes:

\[
\Delta \frac{I}{I_d(t_2)} = \left\{ 1 - \mu K_2 - (1 - \mu K_1) \left( \frac{1 + K_2}{1 + K_1} \right) \right\} \times \left[ 1 + \left( \frac{1 + K_1}{1 + K_2} \right)^{\alpha} \cdot F \left( \frac{\Delta E}{2} \right) \right]
\]

which, in the case of reversible systems \((k^0 \to \infty)\), is equivalent to that obtained in Square Wave Voltammetry under steady-state conditions [18]. Note that the use of this equation is quite restricted since the reach of steady state conditions in DPV requires the use of very small electrodes due to the duration of the second potential pulse \((t_2)\) is very short.

- **Ultramicroelectrodes** (UME). When \(r_0 \ll \sqrt{\pi D t_2}\), Eq. (13) tends to:

\[
\Delta \frac{I}{I_d(\infty)} = k^\text{micro} \left[ \frac{K_2^{-\alpha} (1 - \mu K_2)}{\theta_2} - \frac{K_1^{-\alpha} (1 - \mu K_1)}{\theta_1} \right]
\]

which coincides with that deduced in Ref. [10] for \(D_0 = D_R\).

3. Results and discussion

As discussed in Appendix B, for the resolution of the problem we have supposed that the mathematical concentration profiles of the first pulse for the total time \(t_1 + t_2\) is not disturbed by the application of the second one (Eq. (B35)). This assumption is fully valid for any electrode radius in DPV technique, where the duration of the second pulse is much shorter than that of the first one \((t_1 \gg t_2)\). We have confirmed the validity of the analytical Eqs. (7) and (12) in DPV conditions by comparison with numerical results [19], since non-significant deviations are obtained (less than 0.5%) around the peak potential when \(t_1/t_2 > 50\).

All the calculations have been performed in quadruple precision with homemade programs written in FORTRAN 90 (available as Supporting information).

![Fig. 1. Differential pulse voltammetry: (a) Potential-time function; after each double pulse, the initial equilibrium conditions are restored; (b) technique parameters; (c) current samples; (d) signals for normal ((ΔE < 0)) and reverse (ΔE > 0) DPV modes.](image-url)

![Fig. 2. Influence of the heterogeneous rate constant (k^0) on DPV curves (Eq. (13)). k^0 values are marked on the curves. t_0 = 30 \mu m, \alpha = 0.5, \Delta E = +20 mV, t_1 = 1 s, t_1/t_2 = 100, D = 10^{-8} cm^2/s, \mu = 0.](image-url)
In Fig. 2 the effect of the reversibility of the electron transfer process on DPV peaks is studied at conventional spherical microelectrodes ($\alpha = 0.2$, which corresponds to an electrode radius $r_0 = 30 \mu m$ for $t_2 = 10 ms$ and $D = 10^{-5} \text{cm}^2/\text{s}$).

As previously depicted for planar electrodes [1,14], the decrease of the heterogeneous rate constant gives rise to the diminution of the peak current, the increase of the peak half width and the shift of the peak potential towards more negative values. For completely irreversible systems (very small $k_0$ values), it is observed that the current peak and the peak half width become independent of the rate constant, whereas the position of the peak (i.e., the peak potential $E_{\text{peak}}$) is sensitive to $k_0$.

For the above study the usual value of the transfer coefficient $\alpha = 0.5$ has been considered. With small $\alpha$ values, DPV peaks are found to show a special shape under certain conditions.

As can be seen in Fig. 3a, for $\alpha < 0.3$ $\Delta I - E$ curves corresponding to quasireversible processes with $k_0 \sim 10^{-3} \text{cm/s}$ presents a striking splitting of the peak, a sharper peak appearing at more anodic potentials. This phenomenon is promoted by small transfer constants and it is more obvious for positive pulse heights ($\Delta E > 0$, reverse mode) and for planar electrodes (see Fig. 3b), where the anodic peak is even greater than the cathodic one. The description of this phenomenon is of great interest since this could lead to erroneous interpretation of experimental data for real quasireversible systems with low $\alpha$ values [14,20].

It is worth highlighting that this anomalous behaviour is characteristic of quasireversible processes with $k_0 \sim 10^{-3} \text{cm/s}$, and the splitting is not observed for greater ($k_0 \geq 10^{-2} \text{cm/s}$) or smaller ($k_0 \leq 10^{-4} \text{cm/s}$) rate constants, where the usual single peak is obtained regardless of $\alpha$ value. In the same way, for $\alpha \geq 0.5$ the typical shape of DPV curves is found for any $k_0$.

In Fig. 4 we compare the variation of DPV (Fig. 4a) and normal pulse voltammetry (NPV, Fig. 4b) curves with $k_0$ when both electroactive species are initially present in the solution ($\mu = c_0^e/c_0^o \neq 0$).

From this figure we can observe that the initial presence of the reaction product has no influence on the shape of DPV curves for quasireversible processes, though the signal is proportional to the total bulk concentration $c_0^e + c_0^o$ according to Eq. (17).

However, the shape of DPV curve for non-reversible systems is considerably affected by the initial presence of the reduced species, the greater the distortion, the smaller the $k_0$ value. For completely irreversible systems there exist two well-separated peaks: the cathodic one associated to the reduction process of species O and the anodic one to the oxidation of species R, as can be deduced by comparing DPV and NPV results (Fig. 4b). As expected, each peak only depends on the corresponding reactive species, since the backward process does not take place at such extreme potentials.

Note that due to the subtractive character of DPV technique, both peaks exhibit positive values of DPV current since the sign of $\Delta I$ depends on the sign of the pulse height ($\Delta E$) and not on the process taking place (reduction or oxidation). So, the initial presence of both electroactive species may be also mistaken for an EE mechanism in DPV.
3.1. Characterization and determination of kinetic parameters of the charge transfer process

From the equations obtained for DPV, it is deduced that the reversibility of an electrode process can be characterized by varying the time scale of the DPV experiment or by varying the electrode radius. As shown in the following figures, when the charge transfer process is not reversible, the peak current and/or the peak potential are affected by these variables.

Fig. 5 demonstrates that, when the ratio \( t_1/t_2 \) remains constant, the double pulse duration has no influence either on \( \Delta I_{\text{peak}}/I_d(t_2) \) or the peak potential for reversible electrode processes at planar electrodes. For quasi-reversible processes \( (10^{-2} < k_0^0 \text{cm/s} < 10^{-3}) \) the peak height is greatly affected by the duration of the double potential step \( (t_1 + t_2) \), while the peak potential slightly varies. On the other hand, for totally irreversible processes the peak potential notably varies with the time scale of the experiment. So, the reversibility degree of the charge transfer process is easily characterizable from the time behaviour of the height and position of the normalized DPV peak.

The dependence of \( \Delta I_{\text{peak}} \) with \( 1/\sqrt{t_2} \), keeping constant experimental variables, provides a very simple and reliable criterion to test reversibility in DPV. As shown in Fig. 6 and Eq. (17), for a diffusion-controlled reversible process \( \Delta I_{\text{peak}} \) is linearly dependent on \( 1/\sqrt{t_2} \) for any electrode radius, while this dependence turns non-linear and always lower for quasi-reversible or totally irreversible charge transfer reaction. This criterion is very easy to apply experimentally, since from measurements at different \( t_2 \)-values, we can obtain different differential pulse voltammograms in a single experiment. The behaviour of the peak current with \( t_2 \) is also valuable to discard adsorption, because in presence of adsorption a characteristic linear dependence of \( \ln \left( \Delta I_{\text{peak}} \right) \) with \( t_2 \) is found, which does not hold when both electroactive species are in solution phase.

For quantitative characterization of the system, in Fig. 7a we study the variation of the peak position with respect to the pulse duration at planar electrodes. It can be seen that for totally irreversible systems the position of the DPV peak has a linear relationship with respect to the logarithm of the dimensionless rate constant \( (k_0 = k_0^0 \sqrt{t_2}/D) \). Thus, a simple expression for the peak potential is obtained, which permits us to readily determine kinetic parameters:

\[
E_{\text{peak}}^{\text{irrev,plane}} = A + \frac{R^\alpha}{\alpha F} \ln(k_0^0) + \frac{R^\alpha}{\alpha F} \ln(2.311_0^0) \tag{18}
\]

where

\[
E_{1/2}^{\text{plane}} = E^0' + \frac{RT}{\alpha F} \ln(2.311_0^0) \quad \text{and} \quad A = 49.7 \text{ mV for the typical values } \alpha = 0.5, \Delta E = +50 \text{ mV and } t_1/t_2 = 100.
\]

So, by varying the potential pulse duration (keeping the ratio \( t_1/t_2 \) constant) the value of the transfer coefficient \( (\alpha) \) can be directly determined from the slope of the plot \( E_{\text{peak}}^{\text{irrev,plane}} \) vs \( \ln \left( \sqrt{t_2}/D \right) \). Once \( \alpha \) value is known, the formal potential \( (E^0') \) or the heterogeneous rate constant \( (k_0^0) \) is accessible from the intercept of the straight line.

In a similar way, at ultramicroelectrodes a linear relationship is obtained between the peak potential and the logarithm of the electrode radius, as observed in Fig. 7b. A simple expression is also deduced for this case:

\[
E_{\text{peak}}^{\text{UME}}^{1/2} = E_{\text{irrev,UME}}^0 + \frac{RT}{\alpha F} \ln(k_0^0) \tag{20}
\]

which is totally coincident with the half-wave potential for irreversible processes due to the time-independent response. According to this equation, the kinetic parameters could be...
obtained from the variation of the peak potential for different ultramicroelectrode radii.

Besides the time scale of the experiment, the electrode radius is other variable we can work with in order to elucidate the system reversibility. In Fig. 8 we study its influence on DPV curves for the three general situations: reversible (Fig. 8a), quasireversible (Fig. 8b) and irreversible (Fig. 8c) electrode processes. In all cases, we have considered the application of negative \( \Delta E < 0 \) (normal mode) and positive \( \Delta E > 0 \) (reverse mode) pulse heights.

For a reversible system (Fig. 8a), the peak potential is not affected by the electrode sphericity \( (\xi_2) \), and it takes the value \( E_{\text{rev}}^{\pm} = E_0' \) \([10]\). Moreover, for a given electrode radius, DPV peaks corresponding to the normal and the reverse modes have the same peak potential and the same peak current so that they are fully symmetrical. This complete symmetry of the peaks, as well as the independence of the peak potential with \( r_0 \), are characteristic features of DPV curves of reversible behaviour, and so they constitute simple diagnostic criteria of reversibility.

In Fig. 8b and c the quasireversible and irreversible cases are respectively analyzed. Contrarily to that observed for reversible processes, the peak potential depends on the electrode size, taking more negative values as \( \xi_2 \) increases, that is, as \( r_0 \) diminishes and/or the second pulse duration is longer. Both experimental variables can be readily modified in such a way that the shift of the peak for different \( \xi_2 \) values gives information about the reversibility of the electrode reaction. Moreover, the values of the peak current in normal and reverse mode for a given \( \xi_2 \) value are different.

For determination of kinetic parameter with DPV technique, the variation of the peak potential and the normalized peak current \( \Delta I_{\text{peak}}/I_d(\xi_2) \) with the determining dimensionless parameters are proposed as working surfaces in Figs. 9a and 10a, respectively. The plots vs \( \log(\xi_2) = 2 \sqrt{D \xi_2/r_0} \) are also plotted in Figs. 9b and 10b for different \( k_{\text{micro}}' = k' r_0/D \) values. Note that given a \( k_{\text{micro}}' \) value, the variation of the parameter \( \xi_2 \) is equivalent to the variation of the double pulse duration; so, they are general working curves from which the kinetic parameters of the electrode process can be easily obtained, once \( D \) value is known, by measurement of the peak.
potential and the peak current for different values of the double pulse duration, keeping constant the ratio $t_1/t_2$.

Regarding the peak potential (Fig. 9), the duration of the double pulse has no influence on the peak position for reversible processes, taking the $E^0$ value which corresponds to the "plateau" observed in Fig. 9a. On the other hand, for quasireversible and irreversible systems the peak potential shifts towards less negative values when the double pulse duration increases. So, the analysis of the time behaviour of the peak potential is very appropriate to determine kinetic parameters for irreversible and quasireversible systems.

With respect to the normalized peak current, in Fig. 10 we can see that for both reversible and totally irreversible processes $\Delta I_{\text{peak}}/I_{d(t_2)}$ is not sensitive to $k_0^0$ value. Contrarily, for quasireversible processes the duration of the double pulse has a great influence on $\Delta I_{\text{peak}}/I_d(t_2)$ (see also Fig. 5) so that we can determine the kinetic parameters from Fig. 10b.

Note that, in all cases, the diminution of the electrode radius gives rise to the diminution of the "apparent" reversibility of the system under study, due to the enhancement of the diffusion transport [1,2]. So, the range of applicability of the above-proposed characterization methods reaches faster electrode processes (greater $k_0^0$ values) when smaller electrodes are used.

For the working curves, the general case $\alpha = 0.5$ has been considered. Nevertheless, the proposed methodology is general, so that from the simultaneous analysis of the variation of the peak potential and the peak current with the double pulse duration, the complete characterization of a charge transfer process is possible, permitting us to obtain the values of both the rate constant and the transfer coefficient.

4. Conclusions

Analytical expressions for the response of slow charge transfer reactions at spherical electrodes in differential pulse voltammetry are obtained, valid whatever the electrode size and the reversibility degree of the electron transfer process.

From this solution, the influence of the electrode kinetics, the electrode sphericity and the initial presence of the reaction product are studied. Thus, the anomalous shape of DPV curves for quasireversible processes with $k_0^0 \sim 10^{-3}$ cm/s and small values of the transfer coefficient is reported, which can lead to misinterpretation of experimental data. When both electroactive species are initially present two peaks are obtained when the electrode process is quasireversible or irreversible, corresponding to the reduction and oxidation processes.

The value of DPV for elucidation of the electrode process reversibility is also demonstrated. Several diagnosis criteria are proposed, based on the variation of the DPV curve with the duration
of the double pulse, the electrode radius and the reaction product concentration. Moreover, general working curves are given for determination of kinetic parameters from the position and height of DPV peak.

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Appendix A. Variables and functions

\[ F(x) = \exp(x^2 - \text{erfc}(x)) \] (A.1)
\[ \mu = \frac{C_k}{C_0} \] (A.2)
\[ I_d(\infty) = \frac{FAC_0 D}{r_0} \] (A.3)
\[ I_d(t_2) = \frac{FAC_0 \sqrt{D}}{\sqrt{\pi} r_2} \] (A.4)
\[ \eta_j = \frac{F}{R T} (E_j - E^0) \quad j = 1, 2 \] (A.5)
\[ K_j = \exp(\eta_j) \quad j = 1, 2 \] (A.6)
\[ \theta_1 = 1 + k_micr K_1^{-\alpha}(1 + K_1) \] (A.7)
\[ \theta_2 = 1 + k_micr K_2^{-\alpha}(1 + K_2) \] (A.8)
\[ \chi_1 = \xi_1 + \chi_1^p \] (A.9)
\[ \xi_1 = \frac{2 \sqrt{D} (t_1 + t_2)}{r_0} \] (A.10)
\[ \chi_1^p = \frac{2 \sqrt{t_1 + t_2}}{D} k^0 K_1^{-\alpha}(1 + K_1) = (\chi_1)|_{\xi_1=0} \] (A.11)
\[ \chi_2 = \xi_2 + \chi_2^p \] (A.12)
\[ \xi_2 = \frac{2 \sqrt{D} - t_2}{r_0} \] (A.13)
\[ \chi_2^p = \frac{2 \sqrt{t_2}}{D} k^0 K_2^{-\alpha}(1 + K_2) = (\chi_2)|_{\xi_2=0} \] (A.14)
\[ f(x) = 1 - \mu K_2 - (1 - \mu K_1) \left( \frac{K_2}{K_1} \right)^2 \left[ \frac{\theta_2}{\theta_1} + \left( 1 - \frac{\theta_2}{\theta_1} \right) \cdot F(x) \right] \] (A.15)

Table 1. Definitions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>( r_o )</td>
<td>radius of the electrode</td>
</tr>
<tr>
<td>( t_j ), ( j = 1, 2 )</td>
<td>duration of the j-th potential pulse</td>
</tr>
<tr>
<td>( t_j ), ( j = 1, 2 )</td>
<td>time during which the j-th potential pulse is applied</td>
</tr>
<tr>
<td>( D_i ), ( i = O, R )</td>
<td>diffusion coefficient of the electroactive species</td>
</tr>
<tr>
<td>( c_{i*} ), ( i = O, R )</td>
<td>bulk concentration of species i for the j-th potential pulse</td>
</tr>
<tr>
<td>( c_{i*}^0 ), ( i = O, R )</td>
<td>concentration profile of species i for the j-th potential pulse</td>
</tr>
<tr>
<td>( k_j ), ( k_0 )</td>
<td>heterogeneous rate constants of reduction, oxidation processes</td>
</tr>
<tr>
<td>( k^0 )</td>
<td>standard heterogeneous rate constant</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>transfer coefficient</td>
</tr>
<tr>
<td>( E_j ), ( j = 1, 2 )</td>
<td>potential applied during the j-th pulse</td>
</tr>
<tr>
<td>( \Delta E )</td>
<td>pulse height</td>
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Appendix B.

In order to solve the problem we introduce the following variable change,

\[ u_i^{(j)}(r, t) = \frac{\psi_i^{(j)}(r, t) \cdot r}{c_0^* \cdot r_0} \quad i \equiv O, R \quad j = 1, 2 \] (B1)

Considering the new variable, \( u_i^{(j)}(r, t) \), the differential equation system and the corresponding boundary value problem for the first potential pulse \((t = t_1; 0 \leq t_1 \leq t_1)\) become,

\[ \frac{\partial^2 u_i^{(1)}(r, t)}{\partial r^2} = D \frac{\partial^2 u_i^{(1)}(r, t)}{\partial r^2} \] (B2)
\[ \frac{\partial^2 u_R^{(1)}(r, t)}{\partial r^2} = D \frac{\partial^2 u_R^{(1)}(r, t)}{\partial r^2} \] (B3)

\[ t \geq 0, \quad r \rightarrow \infty \quad t = 0, \quad r \geq r_0 \] \[ u_i^{(1)}(r) = \frac{r_0}{r}; \quad u_R^{(1)}(r) = \mu \frac{r}{r_0} \] (B4)

\[ u_i^{(1)}(r_0) = \frac{r_0}{r_0}; \quad u_R^{(1)}(r_0) = \mu \frac{r_0}{r_0} \] (B5)

By applying Koutecky’s dimensionless parameter method \([21,22]\), we suppose that solutions are functional series of the dimensionless variable \( \xi = \frac{2 \sqrt{D} r}{r_0} \).

\[ u_O^{(1)}(r, t) = u_O^{(1)}(s, \xi) = \sum_{k} \alpha_k^{(1)}(s) \xi^k \] (B6)
\[ u_R^{(1)}(r, t) = u_R^{(1)}(s, \xi) = \sum_{k} \rho_k^{(1)}(s) \xi^k \] (B7)

Taking into account the dimensionless variables \( s = \frac{r - n - \pi / \Delta E}{2 \sqrt{D}} \) and \( \xi \), the differential equation system and the boundary value problem turn into,

\[ \frac{\partial^2 u_i^{(1)}}{\partial s^2} + 2 \xi \frac{\partial u_i^{(1)}}{\partial s} - 2 \xi^2 \frac{\partial u_i^{(1)}}{\partial \xi} = 0 \] (B8)

\[ \frac{\partial^2 u_R^{(1)}}{\partial s^2} + 2 \xi \frac{\partial u_R^{(1)}}{\partial s} - 2 \xi^2 \frac{\partial u_R^{(1)}}{\partial \xi} = 0 \] (B9)

\[ u_O^{(1)}(s, \xi) = 1 + s \xi; \quad u_R^{(1)}(s, \xi) = \mu (1 + s \xi) \] (B10)

\[ \left( \frac{\partial u_A^{(1)}}{\partial s} \right)_{s=0} - \xi \left( u_A^{(1)} \right)_{s=0} = \left( \frac{\partial u_R^{(1)}}{\partial s} \right)_{s=0} - \xi \left( u_R^{(1)} \right)_{s=0} \] (B11)
By introducing the expressions (B6) and (B7) into Eq. (B8), the differential equation system becomes,

$$
\begin{align*}
\sigma_k^{(1)}(s) + 2s\sigma_k^{(1)}(s) - 2k\sigma_k(s) &= 0 \\
\rho_k^{(1)}(s) + 2s\rho_k^{(1)}(s) - 2k\rho_k(s) &= 0
\end{align*}
$$

(B12)

the solutions of which have the following form,

$$
\begin{align*}
\sigma_k^{(1)}(s) &= \sigma_k^{(1)}(\infty) L_k + \rho_k^{(1)} \cdot \Psi_k(s) \\
\rho_k^{(1)}(s) &= \frac{\phi_k^{(1)}(\infty)}{L_k} L_k + b_k^{(1)} \cdot \Psi_k(s)
\end{align*}
$$

(B13)

where $a_k^{(1)}$ and $b_k^{(1)}$ are constants that will be determined from the boundary value problem, $L_k$ are $s_1$-powers numeric series, and $\Psi_k(s_1)$ are Koutecký’s functions which have the following properties,

$$
\begin{align*}
\Psi^{(1)}(0) &= 1 \\
\Psi^{(1)}(\infty) &= 0 \\
\Psi'_{k}(x) &= -p_k \Psi_{k-1}(x) \\
\Psi_0(x) &= 1 - erf(x)
\end{align*}
$$

(B14)-(B17)

Taking into account the form of the solutions (Eq. (B13)) along with the properties of Koutecký’s functions, the boundary value problem is given by,

$$
\begin{align*}
\sigma_0^{(1)}(s) &= 1, \quad \rho_0^{(1)}(s) = \mu \\
\sigma_0^{(1)}(s) &= s, \quad \rho_0^{(1)}(s) = \mu \cdot s \\
\sigma_k^{(1)}(s) &= 0, \quad \rho_k^{(1)}(s) = 0, \quad k > 1 \\
\sigma_k^{(1)}(0) - \sigma_{k-1}^{(1)}(0) &= -\rho_k^{(1)}(0) + \rho_{k-1}^{(1)}(0) \\
\sigma_k^{(1)}(0) - \sigma_k^{(1)}(0) &= \frac{r_0 k_0 K_1^{(1)} a}{D} \left[ \sigma_k^{(1)}(s) - K_1 \rho_k^{(1)}(0) \right]
\end{align*}
$$

(B18)-(B20)

By applying Eqs. (B18)-(B20), we obtain the expressions for $\sigma_k^{(1)}(s)$ and $\rho_k^{(1)}(s)$, and by introducing them in Eqs. (B6) and (B7) we find the solutions of the problem ($u_1^{(1)}(r, t)$ and $u_1^{(1)}(r, t)$). From these, the $I-E$ expression for the application of the first potential pulse at spherical electrodes (Eq. (7)) is obtained.

Regarding the application of the second potential step ($t = t_1 + t_2; 0 \leq t_1 \leq t_2$), due to that the diffusion operator $\delta$ (given by Eq. (3)) is linear, the solutions of the differential equation system can be written as,

$$
u_1^{(1)}(r, t) = u_1^{(1)}(r, t) + u_1^{(2)}(r, t_2)
$$

(i.e. O, R

(B21)

being $u_1^{(2)}(r, t_2)$ the new unknown partial solutions with null initial conditions,

$$
\begin{align*}
\frac{\partial u_1^{(2)}(r, t_2)}{\partial t_2} &= D \frac{\partial^2 u_1^{(2)}(r, t_2)}{\partial r^2} \\
\frac{\partial u_1^{(2)}(r, t_2)}{\partial r} &= D \frac{\partial^2 u_1^{(2)}(r, t_2)}{\partial r^2}
\end{align*}
$$

(B22)

$$
\begin{align*}
\sigma_k^{(2)}(s) &= \frac{\sigma_k^{(2)}(\infty)}{L_k} L_k + a_k^{(2)} \cdot \Psi_k(s) \\
\phi_k^{(2)}(s) &= \frac{\phi_k^{(2)}(\infty)}{L_k} L_k + b_k^{(2)} \cdot \Psi_k(s)
\end{align*}
$$

(B23)-(B32)
which must fulfil the following limit and surface conditions:

\[
\lim_{s_2 \to \infty} \sigma_k^{(2)}(\infty) = 0; \quad \rho_k^{(2)}(\infty) = 0 \quad \forall k
\]

(B33)

\[
\sigma_k^{(2)}(0) - \sigma_k^{(2)}(0) = -\rho_k^{(2)}(0) + \rho_k^{(2)}(0)
\]

(B34)

As can be seen, the surface condition (B35) introduces dependence with the first potential pulse. Given that in DPV technique we have that \(t_1 \gg t_2\), we assume that the mathematical form of the solutions corresponding to the first pulse \(u^{(1)}(r, t)\) and \(u^{(1)}(r, t)\) is not disturbed by the application of the second one.

By applying the conditions given by Eqs. (B33)–(B35), we deduce the expressions for \(\sigma_k^{(2)}(s_2)\) and \(\rho_k^{(2)}(s_2)\), and taking into account Eqs. (B21), (B26) and (B27), the solutions \(u^{(2)}(r, t)\) are obtained. From these, the equation for the current corresponding to the second potential pulse (Eq. (12)) is derived.

Appendix C. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2010.04.024.

References