Study of an EE mechanism using double potential step techniques

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Abstract

An analytical solution corresponding to the double potential step problem for a reversible EE mechanism is presented. This solution is applicable to any double pulse technique without restrictions on the duration of the first and second potential steps and is valid when several species are initially present in the solution. The influence of the duration of the two pulses on the characteristic of the current-potential curves on differential and reverse double pulse techniques in static and dynamic electrodes is also discussed.

Keywords: EE mechanism; Voltammetry; Polarography; Double potential step techniques

1. Introduction

Double pulse techniques in their many forms (differential normal pulse (DNP), differential pulse (DP), reverse pulse (RP)) are very useful electroanalytical tools. So, for example, differential normal pulse has proved to be an excellent and versatile technique for trace analysis, since in comparison with other voltammetric methods, the potential time sequence can be chosen to minimise the contribution of capacitative effects in the measured current [1]. In relation to the reverse pulse, its principal advantage is to characterise the product of an electrode reaction, especially with respect to stability [2].

The study of multistep electrode processes has received great attention in the literature, with the two step (EE mechanism) being the most analysed [3–8]. However, whereas analytical solutions have been deduced for an EE mechanism in dc or normal pulse techniques, there is an evident lack, not to say absence, of analytical solutions for an EE mechanism when more than one potential step is applied (multipulse potential techniques). This is because the theoretical treatment of this last problem is much more complex. In fact, only numerical solutions have been presented for EE mechanisms with multipulse potential techniques [9,10]. In consequence, a large part of the papers on systems with multiple charge transfer reactions in multistep potential techniques offer no more than a qualitative study [11–15].

In response to this situation, this paper aims to derive the rigorous analytical solution for a reversible EE process in any double potential step experiment in such a way that the two potentials $E^I$ and $E^II$ can be applied without restrictions on the intervals of times, $t_1$ and $t_2$, respectively. This solution is applicable to electrodes whose areas increase with an arbitrary power of time $z$, with $z = 0$ for a static electrode and $z = 2/3$ for a DME, and can, therefore, be used in double potential step chronoamperometry, DNP, DP, and RP voltammetries and polarographies, whose analytical expressions have not yet been established.

These expressions are applicable for any value of the difference of the formal potential of both steps, and also when all species participating in the electrode process are initially present in the solution. They can, therefore, be used for quantitative study of a reversible EE mechanism and can also be taken as a benchmark for more complex types of behaviour of this process, for example: the presence of adsorption or amalgamation, the consideration of no reversibility of any electrochemical step, high values of the rate constants of the electron exchange reaction in solution, etc.
2. Theory

We will consider a two-step reversible charge transfer process (EE mechanism), according to the following scheme

\[ O_1 + n_1e^- \rightleftharpoons O_2 \quad E^0_{i} \]

\[ O_2 + n_2e^- \rightleftharpoons O_3 \quad E^0_{f} \]

where \( E^0_{i} \) and \( n_1 \) (\( j = 1, 2 \)) are respectively the formal potential and the number of electrons of each step.

In the particular case in which \( D_1 = D_2 = D_3 \) the reaction

\[ n_1O_1 + n_1O_2 \xrightleftharpoons[k_2]{k_1} (n_1 + n_2)O_2 \]

cannot be detected with any electroanalytical technique for any values of \( k_1 \) and \( k_2 \) [16–18].

We have considered a planar electrode whose area \( A(t) \) increases with an arbitrary power of time \( z \), i.e. \( A(t) = A_0 t^z \) [19] to which two consecutive potential steps are applied. When a first potential step \( E = E^1 \) is applied during \( t \) with \( 0 \leq t \leq t_1 \), the expression obtained for the current for a reversible EE mechanism is the following (see Appendix A):

\[
J^1 = \frac{FA(t)\sqrt{D_1(2s + 1)}}{\sqrt{\pi t}} \left\{ X^1 c^* - (n_2\gamma_{31}c^*_2 - n_1c^*_1) \right\} \quad (1)
\]

\[
X^1 = \frac{(n_2\gamma_{31} - n_1J^1)}{1 + \gamma_{23}J^1 + \gamma_{13}J^1J^2} \quad (2)
\]

with

\[
J^1 = \exp \left\{ \frac{n_1F}{RT} (E^1 - E^0_1) \right\} \quad (3)
\]

\[
J^2 = \exp \left\{ \frac{n_2F}{RT} (E^2 - E^0_2) \right\} \quad (4)
\]

\[
J^2 = \exp \left\{ \frac{n_2F}{RT} (E^2 - E^0_2) \right\}
\]

\[
J^1 II = \exp \left\{ \frac{n_1F}{RT} (E^II - E^0_1) \right\}
\]

\[
J^2 II = \exp \left\{ \frac{n_2F}{RT} (E^II - E^0_2) \right\}
\]

and \( X^1 \) given by Eq. (2).

\[ I^II = I^II (c^*_2) + I^II (c^*_1) + I^II (c^*_1) \]

with \( I^II (c^*_i) \) being the current obtained when two consecutive potential steps are applied and only one species \( O_i \) (\( i = 1, 2, 3 \)) is initially present in the solution. Equation (8) is also fulfilled for the current corresponding to a single pulse \( I^1 \) (Eq. (1)) [20].

3. Results and discussion

Equation (5), which corresponds to the rigorous solution for a reversible EE mechanism in a double potential step problem, will be applied to different electrochemical techniques. These techniques are called voltammetries, in a static electrode, or polarographies if the electrode used is the DME [21]. These cases correspond to values of \( z \) equal to 0 and \( 2/3 \), respectively, in all equations of this paper. In particular, double pulse techniques combine the faradaic currents at two different potential steps applied without the equilibrium being re-established and include differential normal pulse voltammetry (DNPV), differential pulse (DP) and reverse pulse (RP) techniques. The solutions corresponding to the techniques using single pulse (normal pulse voltammetry (NPV) and normal pulse polarography (NPP)) are also deduced as particular cases of those obtained in this paper.

3.1. Double pulse techniques with potential steps of constant amplitude: differential normal pulse voltammetry (DNPV) and polarography (DNPP)

In these techniques the difference \( \Delta E = E^II - E^1 \) is kept constant and the currents corresponding to both potential steps \( I^II \) and \( I^I \) are measured at times \( t_2 \) and \( t_1 \), respectively. The DNP current \( I^II - I^I \) is recorded versus \( E^1 \) with the pulse amplitude, \( \Delta E \), being scanned either in the negative (\( \Delta E < 0 \)) or in the positive direction (\( \Delta E > 0 \)) (see Scheme 1). This current is easily obtained without restriction on the times of the application of the two potential steps in DNPV (\( z = 0 \)) or DNPP (\( z = 2/3 \)). Thus, by subtracting Eqs. (5) and (1) we obtain:
Scheme 1. Potential–time waveform and points of current measurement for DNP techniques.

\[ I_{\text{DNP}} = \sqrt{2z + 1}(t_1 + t_2)^{-1/2} - (t_1)^{-1/2} \]
\[ \times \left( X^1 - \frac{n_2\gamma_3e^*}{c^*} - \frac{n_1e^*}{c^*} \right) + \frac{(t_1 + t_2)\gamma_3(j_{1\beta})}{\sqrt{I_2}} \]
\[ \times (X^{II} - X^I) \]  

(9)

with

\[ I_{\text{DNP}} = \frac{I^{II} - I^I}{FA_0e^*\sqrt{D_1/\pi}} \]  

(10)

When \( E^I, E^{II} \rightarrow \infty \) (\( J_1^I, J_2^I, J_1^{II} \) and \( J_2^{II} \rightarrow \infty \), see Eqs. (2) and (6)) (upper limit), Eq. (9) becomes

\[ I_{\text{DNP}}^{\text{upper}} = -\sqrt{2z + 1}(t_1 + t_2)^{-1/2} - (t_1)^{-1/2} \]
\[ \times \left\{ \frac{n_1\gamma_3e^*}{c^*} + \left( \frac{n_1 + n_2}{2} \right)\gamma_3e^* \right\} \]

(11)

and when \( E^I, E^{II} \rightarrow -\infty \) (\( J_1^I, J_2^I, J_1^{II} \) and \( J_2^{II} \rightarrow 0 \)) (lower limit) we have

\[ I_{\text{DNP}}^{\text{lower}} = \sqrt{2z + 1}(t_1 + t_2)^{-1/2} - (t_1)^{-1/2} \]
\[ \times \left\{ \frac{n_1\gamma_3e^*}{c^*} + \left( \frac{n_1 + n_2}{2} \right)\gamma_3e^* \right\} \]

(12)

Note that both the upper and lower limit currents in the DNP techniques (Eqs. (11) and (12), respectively) are dependent on the initial concentrations of species \( O_1 \), \( O_2 \) and \( O_3 \) and also on the duration of both pulses. So, for example, if the initial concentration of intermediate \( O_2 \) is zero and \( D_1 = D_2 = D_3 \), then from these limit currents the values of \((n_1 + n_2)e^*\) and \(n_1e^*\) can be easily determined.

Eqs. (9)–(12) are valid for any values of \( t_1 \) and \( t_2 \). We will now distinguish the two limit situations \( t_2 \ll t_1 \) and \( t_2 \gg t_1 \).

a) When \( t_2 \ll t_1 \), these equations become those corresponding to differential pulse (DP) techniques, and from Eq. (9) we obtain:

\[ I_{\text{DNP}}(t_2 \ll t_1) = I_{\text{DP}} = \frac{(t_1 + t_2)\gamma_3(j_{1\beta})}{\sqrt{I_2}}(X^{II} - X^I) \]  

(13)

with the upper and lower limiting currents being zero in these conditions (see Eqs. (11) and (12), respectively)

\[ I_{\text{DP}}^{\text{upper}} = I_{\text{DP}}^{\text{lower}} = 0 \]  

(14)

b) When \( t_2 \gg t_1 \), there are two cases to be distinguished: a static electrode (\( z = 0 \)) and a DME (\( z = 2/3 \)). For \( z = 0 \) the current corresponding to the second pulse, \( I^{II} \), is negligible in relation to that of the first pulse \( I^I \), i.e. \( I^{II} \ll I^I \). Introducing this condition in Eq. (10) the current obtained in DNP techniques will tend towards that obtained in dc voltammetry

\[ I_{\text{DNPv}}(t_2 \gg t_1) = \frac{-I^I}{FA_0e^*\sqrt{D_1/\pi}} \]  

(15)

with \( I^I \) given by Eq. (1).

The above explanation cannot be applied to the case of a DME (\( z = 2/3 \)) for which the growth of the electrode leads to:

\[ I_{\text{DP}}(t_2 \gg t_1) = \frac{I^I(E^{II}, t_2)}{FA_0e^*\sqrt{D_1/\pi}} \]  

(16)

i.e. a current is obtained which is formally identical to that of the first potential step ( Eq. (1)), but which corresponds to a potential \( E^{II} \) and to a time \( t_2 \).

Figs. 1 and 2 correspond to a static electrode and a DME, respectively. These figures show the influence of the duration of the second potential step, \( t_2 \), on the normalised DNP curves corresponding to a reversible EE process by supposing that \( n_1 = n_2 = 1 \), \( D_1 = D_2 = D_3 \) and \( E^0_2 - E^0_1 = -200 \text{ mV} \) for \( \Delta E = -50 \text{ mV} \). Figures a, b and c, correspond to the initial presence of species \( O_1 \), \( O_2 \) and \( O_3 \) respectively.

The behaviour shown in Fig. 1 is in line with Eqs. (9), (13)–(15). So, when \( t_2 \ll t_1 \) (see curve \( t_2 = 0.025 \text{ s} \) in Fig. 1a–c) the DNP technique behaves like the DP technique, whose response is the same whatever the specific species \( O_1 \), \( O_2 \) or \( O_3 \) initially present in solution (see Eq. (13)). In the converse case, when \( t_2 \gg t_1 \) the curves in DNPV tend to those obtained in dc voltammetry, according to Eq. (15). In this last technique the response obtained depends on the species initially present in the solution [20], with only cathodic current being obtained when only \( O_1 \) is initially present; cathodic and anodic currents are obtained when only \( O_2 \) is present; and only anodic current when only \( O_3 \) is present.

The evolution from the limit case \( t_2 \ll t_1 \) to \( t_2 \gg t_1 \) therefore, gives rise to a peculiar physical behaviour of the normalised DNP curves, depending on the species initially present, as is shown in these figures. So, except in the DP case \( t_2 = 0.025 \text{ s} \), when \( O_2 \) is initially present
the upper and lower limit currents are always different from zero (Fig. 1b), whereas in Fig. 1a and c the upper or lower limit current is respectively zero. Identical curves to those presented in Fig. 1b are obtained when both species O1 and O3 are also initially present in the solution with identical concentrations (see Eq. (9) with \( n_1 = n_2 = 1 \), \( D_1 = D_2 = D_3 \), \( T = 298.15 \text{ K} \), \( E_1^0 - E_2^0 = -200 \text{ mV} \), \( \Delta E = -50 \text{ mV} \), \( t_1 = 0.5 \text{ s} \). The values of \( t_2 \) (in s) are on the curves. (a) Only O1 is initially present in the solution, (b) only O2 is initially present in the solution, (c) only O3 is initially present in the solution.

Fig. 2 shows that the influence of \( t_2 \) on the DNP curves for a DME is qualitatively contrary to that corresponding to a static electrode, shown in Fig. 1. This is in accord with the fact that Eq. (9) for the DNP curves, in the limit \( t_2 \gg t_1 \), tends to Eq. (15) for a static electrode and to Eq. (16) in the case of a DME.

In Fig. 3 we have represented the DPV curves corresponding to a reversible EE process with \( n_1 = n_2 = 1 \), \( D_1 = D_2 = D_3 \) and \( \Delta E = -40 \text{ mV} \) at different values of \( E_2^0 - E_1^0 \). From this figure we deduce that the height of a peak for an EE mechanism with \( E_2^0 - E_1^0 \leq 100 \text{ mV} \) is considerably lower than that corresponding to an E simple process with two electrons [9,22] (which is coincident with the curves of \( E_2^0 - E_1^0 \geq 200 \text{ mV} \) in this figure) with a relative difference in heights of more than 5%. Therefore, both processes can be perfectly distinguishable in DPV even when the EE mechanism only
tends to decrease the current of the DPV curve. Fig. 4 shows the influence of pulse amplitude, \( \Delta E \), on the differential pulse voltamograms, \( I_{\text{DPV}}(E^3 - E^4) \), for an EE mechanism (Eq. (13) with \( z = 0 \)). \( \Delta E = -40 \) mV, \( t_1 = 1 \) s, \( t_2 = 0.03 \) s. The values of \( E^3 - E^4 \) (in mV) are on the curves. Other conditions as in Fig. 1.

Fig. 4 shows the influence of pulse amplitude, \( \Delta E \), on DPV curves. From this figure it is clear that for a given value of \( \Delta E^0 \) (\(-80 \) mV in this case), a decrease of \( |\Delta E| \) tends to decrease the current of the DPV curves and tends to separate out into two peaks in agreement with references [9,22].

When two well-separated peaks are obtained (see curve of \( E^0 - E^4 = -200 \) mV in Fig. 3) the first and second peaks verify \( I_{1}^f, I_{1}^s \to \infty \) and \( I_{1}^f, I_{1}^s \to 0 \), respectively. With the above assumptions in Eq. (13) the expressions corresponding to the two separate DPV or DPP curves are:

\[
I_{\text{DP}}^\text{first} = \frac{(t_1 + t_2)h(z)}{\sqrt{t_2}} n_1 \gamma_{31} \left( \frac{1}{1 + \gamma_{12} J_{1}^f} - \frac{1}{1 + \gamma_{12} J_{1}^s} \right)
\]

(17)

\[
I_{\text{DP}}^\text{second} = \frac{(t_1 + t_2)h(z)}{\sqrt{t_2}} n_2 \gamma_{31} \left( \frac{1}{1 + \gamma_{23} J_{2}^f} - \frac{1}{1 + \gamma_{23} J_{2}^s} \right)
\]

(18)

and the peak parameters [22]

\[
E^4, \text{ first peak} = E^0 + \frac{RT}{n_1 F} \ln \gamma_{12} + \frac{|\Delta E|}{2}
\]

(19)

\[
I_{\text{DP}}^\text{first} = \frac{(t_1 + t_2)h(z)}{\sqrt{t_2}} n_1 \gamma_{32} \tan\left( \frac{n_1 F |\Delta E|}{4RT} \right)
\]

(20)

\[
E^4, \text{ second peak} = E^0 - \frac{RT}{n_2 F} \ln \gamma_{23} + \frac{|\Delta E|}{2}
\]

\[
I_{\text{DP}}^\text{second} = \frac{(t_1 + t_2)h(z)}{\sqrt{t_2}} n_2 \gamma_{31} \tan\left( \frac{n_2 F |\Delta E|}{4RT} \right)
\]

Note that Eqs. (13) and (17)–(20) are independent of which species are initially present in the solution but depend on the sum of the initial concentrations for all species present.

3.2. Double pulse techniques with potential steps of variable amplitude: reverse pulse voltammetry (RPV) and polarography (RPP)

In RP techniques the value of the first applied potential \( E^4 \) is kept constant at a value for which the surface concentrations of the species initially present in solution become zero, and the second potential \( E^3 \) varies. The RP current \( I^R \) is recorded versus \( E^3 \) (see Scheme 2). Thus, in order to obtain the expressions corresponding to these techniques, the species initially present in the solution must be specified as is clearly indicated in Refs. [23–25]. The same can be said about the normal pulse (NP) techniques, which are single pulse techniques whose response can be easily obtained from the general expressions developed in this paper. To do that, we must select the first pulse potential \( E^4 \) in such a way that the current \( I^p \) becomes zero, and so it is imperative to specify the species which are initially present in solution.
In the following, we will compare RP and NP techniques in order to show the analogies and differences between them in the following initial situations.

3.2.1. Case (a): only species $O_1$ or $O_3$ is initially present

When only species $O_1$ is initially present the RP current is deduced by making $E^I \to -\infty$ (i.e. $J^I_1 \to 0$ and $J^I_2 \to 0$) in Eq. (5) whereas to obtain the NP current we must make $E^I \to \infty$ (i.e. $J^I_1 \to \infty$ and $J^I_2 \to \infty$) in Eq. (5). So, we deduce

$$I_{RP}(c_1^r) = \sqrt{(2z+1)\beta(n_1 + n_2)\gamma_{31} - h_z(\beta)}$$

$$\times \left( n_2 \gamma_{21} J^I_2 + (n_1 + n_2) J^I_1 \right)$$

$$I_{NP}(c_1^r) = h_z(\beta) \left( n_1 + n_2 \right)$$

$$\times \left( \gamma_{31} J^I_2 + \gamma_{13} J^I_1 \right)$$

$$= \frac{I^I}{FA(c) \gamma_{31'}}$$

From Eqs. (21)-(24) it is clear that

$$I_{RP}(c_1^r) - I_{NP}(c_1^r) = I_{RP}(c_3^r) - I_{NP}(c_3^r)$$

$$= \sqrt{(2z+1)\beta(n_1 + n_2)\gamma_{31}}$$

Eq. (26) is of great interest since it signifies that the curves corresponding to RP and NP techniques when only $c_3^r$ is initially present in solution can be easily obtained from those corresponding to NP and RP techniques, respectively, when only $O_1$ is initially present.

Moreover, $I_{RP}(c_3^r)$ and $I_{NP}(c_3^r)$ verify

$$I_{RP}(c_3^r) - I_{NP}(c_3^r) = \sqrt{(2z+1)\beta - h_z(\beta)(n_1 + n_2)\gamma_{31}}$$

Therefore, we can conclude that it is sufficient to study only RP or NP curves, according to Eqs. (26) and (27).

It is also interesting to point out that the normalised $I_{RP}(c_i^r)/I_{NP}(c_i^r)$ curves, when only $O_1$ is initially present vary with $t_2$ in such a way that for $t_2 \ll t_1$ (i.e. $t_2 \to 0$ which is the most usual case) coincide with $I_{NP}(c_i^r)$ lower dashed line in Fig. 5 and with $I_{de}(c_i^r)$ upper dashed line in Fig. 5 when $t_2 \gg t_1$ (note that when $t_2 \gg t_1$ the NNP technique tends to dc polarography). Therefore, the $I_{RP}(c_i^r)$ curves vary between $I_{de}(c_i^r)$ and $I_{RP}(c_i^r)$ when $t_2$ varies, as is shown in Fig. 5 and Eqs. (26) and (27).

Clearly, if only $O_3$ is initially present $I_{RP}(c_i^r)$ curves vary in a converse way.

Fig. 6 shows the influence of $E^I - E^0$ on the RP curves obtained when only $O_1$ species is initially present. As can be seen, all these curves have the same limit current and present a single wave for $E^I - E^0 > -100$ mV, which separates out into two waves for $E^I - E^0 < -150$ mV. This behaviour is similar to that previously described in Ref. [20] for the dc curves.

3.2.2. Case (b): only species $O_2$ is initially present or $O_1$, $O_2$ and $O_3$ are initially present with $c_2^r = c_3^r$

In this case according to the initial conditions we will suppose that $E^I_2 - E^I_1 << 0$ and to obtain the NP response from Eq. (5) we must substitute $E^I$ in the same, for an intermediate potential which fulfils $I^I = 0$ (see Eq. (1)).
This potential, \( E(\dot{I} = 0) \) when \( n_1 = n_2 = n \) and \( D_1 = D_3 \) for \( c_1^* = c_3^* \) and for any value of \( c_2^* \) is given by

\[
E(I^1) = \frac{E_1^0 + E_2^0}{2} \tag{28}
\]

by introducing Eq. (28) in Eq. (5) we deduce

\[
I_{NP}(c_1^*, c_2^*, c_3^*) = n h_z(\beta) \left\{ \frac{1 - J_1^{II} J_2^{II}}{1 + \gamma_{21} J_2^{II} + J_1^{II} J_2^{II}} \right\} \tag{29}
\]

In order to obtain the RP response we can select two values of \( E^1 \): for \( E_1^0 \rightarrow \infty \) conditions of lower limit current for species \( c_1^* \) and \( c_3^* \); or \( E_1^0 \rightarrow \infty \) on conditions of upper limit current for \( c_3^* \) and \( c_2^* \), by obtaining

\[
[I_{RP}(c_1^*, c_3^*, c_2^*)]_{E^1 \rightarrow \infty} = -n \left[ \sqrt{(2z + 1) \beta} - h_z(\beta) \right] \times \left\{ \frac{2 + \gamma_{21} J_2^{II} + J_1^{II} J_2^{II}}{1 + \gamma_{21} J_2^{II} + J_1^{II} J_2^{II}} \right\} \tag{30}
\]

\[
[I_{RP}(c_3^*, c_2^*, c_1^*)]_{E^1 \rightarrow \infty} = n \left[ \sqrt{(2z + 1) \beta} - h_z(\beta) \right] \times \left\{ \frac{2 J_1^{II} J_2^{II} + \gamma_{21} J_2^{II}}{1 + \gamma_{21} J_2^{II} + J_1^{II} J_2^{II}} \right\} \tag{31}
\]

By comparing Eqs. (29)–(31) it is easy to prove that

\[
(I_{RP})_{E^1 \rightarrow \infty} + (I_{RP})_{E^1 \rightarrow -\infty} = 2 I_{NP} \tag{32}
\]

Identical results are found when only species \( O_2 \) is initially present since \( c_1^* = c_3^* = 0 \) can be considered as a particular case of this section.

Fig. 7 shows the two RP curves (Eqs. (30) and (31)) and the NP curve (Eq. (29)) corresponding to this initial situation. These curves move, depending on the value of \( t_2 \), between the same limits \( I_{NP}(c_1^*) \) and \( I_{NP}(c_3^*) \), as explained in the above case.
DP or DNP, showing that whereas the position of the DNP response with respect to the zero current line depends on the species which are initially present in the solution, the DP curves are not affected, whatever the species initially present. We have also compared the DP curves deduced for an EE mechanism with the response obtained for a simple charge transfer reaction when the EE response only presents one peak. We have also pointed out how a decrease in the amplitude of pulse $|\Delta E|$ tends to decrease the current of the DP curves and to separate them out into two peaks.

We have also analysed the RP techniques, pointing out that the species initially present in the solution must be specified in order to select a suitable RP response. This is also the case in NP techniques (single pulse), whose equations can be easily obtained from the general expressions deduced in this paper. Thus, we have compared the response obtained in RP and NP techniques.

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Appendix A

A.1

First pulse

If we consider a planar electrode whose area $A(t)$ increases with an arbitrary power of time $z$, i.e. $A(t) = A_0 t^z$ [19], when a first potential step $E = E_i$ is applied during $t$ with $0 \leq t \leq t_1$, then the equation system that describes the mass transport to and from the electrode is given by

$$\delta_i^1 \frac{\partial c_i^1}{\partial x} (x, t) = \delta_i^2 \frac{\partial c_i^2}{\partial x} (x, t) = \delta_i^3 \frac{\partial c_i^3}{\partial x} (x, t) = 0 \quad \text{(A.1)}$$

where

$$\delta_i^l = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial x^2} + \frac{z x}{t} \frac{\partial}{\partial x} \right) \quad i = 1, 2, 3 \quad \text{(A.2)}$$

and the boundary value problem is

$$t > 0, \ x = 0 \quad D_1 \left( \frac{\partial c_1^1}{\partial x} \right)_{x = 0} + D_2 \left( \frac{\partial c_1^2}{\partial x} \right)_{x = 0} + D_3 \left( \frac{\partial c_1^3}{\partial x} \right)_{x = 0} = 0 \quad \text{(A.4)}$$

$$c_i^1 (x = 0) = J_i^1 c_i^1 (x = 0) \quad c_i^2 (x = 0) = J_i^2 c_i^2 (x = 0) \quad \text{(A.5)}$$

with $J_i^1$ and $J_i^2$ given by Eq. (3).

This problem has an easy solution, which is given by Eq. (8) in Ref. [20]. From this reference we can write, for $i = 1, 2, 3$:

$$c_i^1 (x, t) = e_i^* + [c_i^i (x = 0) - c_i^*] \text{erfc} \left( \sqrt{\frac{2z + 1}{4D_i} t} x \right) \quad \text{(A.6)}$$

being

$$c_i^1 (x = 0) = \frac{J_i^1 J_i^2 e_i^*}{1 + \gamma_{23} J_i^2 + \gamma_{13} J_i^1 J_i^2} \quad \text{(A.7)}$$

where

$$\gamma_{mp} = \sqrt{\frac{D_m}{D_p}} \quad \text{(A.8)}$$

and $e_i^*$ is given in Eq. (4). The current observed for the EE mechanism, $I_i$, is given by Eq. (1) in this paper [20].

A.2

Second pulse

If at time $t_1$ the potential is stepped from $E_i$ to $E_{ii}$, which is applied during $t_2$ with $0 \leq t_2 \leq t_2$ and $t = t_1 + t_2$, the equation system to solve is now

$$\delta_i^1 c_i^1 (x, t) = \delta_i^2 c_i^2 (x, t) = \delta_i^3 c_i^3 (x, t) = 0 \quad \text{(A.9)}$$

where

$$\delta_i^l = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial x^2} + \frac{z x}{(t_1 + t_2)} \frac{\partial}{\partial x} \right) \quad i = 1, 2, 3 \quad \text{(A.10)}$$

and the boundary value problem can be now written as

$$t_1 > 0, \ x \geq 0 \quad t_2 > 0, \ x \rightarrow \infty \quad c_i^l = c_i^l (x, t) \quad i = 1, 2, 3 \quad \text{(A.11)}$$

$$t_2 > 0, \ x = 0 \quad D_1 \left( \frac{\partial c_i^l}{\partial x} \right)_{x = 0} + D_2 \left( \frac{\partial c_i^l}{\partial x} \right)_{x = 0} + D_3 \left( \frac{\partial c_i^l}{\partial x} \right)_{x = 0} = 0 \quad \text{(A.12)}$$
\[ c_{i}^{II}(x = 0) = J_{i}^{II} \]
\[ c_{j}^{II}(x = 0) = J_{j}^{II} \]
\[ \text{(A.13)} \]

with \( J_{i}^{II} \) and \( J_{j}^{II} \) given by Eq. (7).

Taking into account that the operator \( \delta_{s}^{H} \) given by Eq. (A.10) is linear, the solutions corresponding to the second potential step, \( c_{i}^{II}(x, t) \) can be written as (see Eq. (A.9))

\[ c_{i}^{II}(x, t) = c_{i}^{I}(x, t) + \tilde{c}_{i}^{II}(x, \tau_{2}) \quad i = 1, 2, 3 \]  \[ \text{(A.14)} \]

where \( c_{i}^{I}(x, t) \) are the solutions corresponding to the first potential step \( E_{1}^{I} \) (see Eq. (A.6)) and \( \tilde{c}_{i}^{II}(x, \tau_{2}) \) are the new unknown partial solutions.

By introducing Eq. (A.14) in Eqs. (A.9), (A.10), (A.11), (A.12) and (A.13) and taking into account Eqs. (A.1), (A.2), (A.3), (A.4) and (A.5) for the first pulse, we deduce that the boundary value problem of this second pulse is given only in terms of the new unknown variables \( \tilde{c}_{i}^{II}(x, \tau_{2}) \), and has the advantage of having null initial conditions. In effect, we have

\[ \tilde{c}_{1}^{II}(x, \tau_{2}) = 0, \quad x \geq 0 \]
\[ \tilde{c}_{2}^{II}(x, \tau_{2}) = 0, \quad x < 0 \]
\[ \tilde{c}_{3}^{II}(x, \tau_{2}) = 0, \quad 0 < x < \infty \]  \[ \text{(A.15)} \]

\[ D_{1} \frac{\partial^{2} \tilde{c}_{1}^{II}}{\partial x^{2}}(x, \tau_{2}) + D_{2} \frac{\partial^{2} \tilde{c}_{2}^{II}}{\partial x^{2}}(x, \tau_{2}) + D_{3} \frac{\partial^{2} \tilde{c}_{3}^{II}}{\partial x^{2}}(x, \tau_{2}) = 0 \]  \[ \text{(A.16)} \]

\[ \tilde{c}_{1}^{II}(x = 0) = J_{1}^{II} c_{1}^{II}(x = 0) + (J_{1}^{II} - J_{1}^{I}) c_{1}^{I}(x = 0) \]
\[ \tilde{c}_{2}^{II}(x = 0) = J_{2}^{II} c_{2}^{II}(x = 0) + (J_{2}^{II} - J_{2}^{I}) c_{2}^{I}(x = 0) \]  \[ \text{(A.17)} \]

Note that the conditions which must fulfill \( \tilde{c}_{1}^{II}(x = 0) \), \( \tilde{c}_{2}^{II}(x = 0) \) and \( \tilde{c}_{3}^{II}(x = 0) \) (Eqs. (A.17), (A.18) and (7)), have a similar form to that corresponding to the first potential step, \( E_{1}^{I} \) (Eqs. (A.4) and (A.5) and Eq. (3), respectively), except in the value of the constants \( (J_{1}^{II} - J_{1}^{I}) c_{1}^{I}(x = 0) \) and \( (J_{2}^{II} - J_{2}^{I}) c_{2}^{I}(x = 0) \) in Eq. (A.18), since the surface concentrations corresponding to the first potential step, \( c_{1}^{I}(x = 0), c_{2}^{I}(x = 0) \) and \( c_{3}(x = 0) \) are independent of time (see Eq. (A.7)). However, the \( \delta_{s}^{H} \) operator corresponding to this second pulse is more complex than that corresponding to the first pulse \( \delta_{s}^{I} \) (compare Eq. (A.10) and Eq. (A.2), respectively). In these conditions, in order to solve the differential equation system (Eq. (A.15)), it is necessary to introduce in addition the usual variable

\[ s_{i} = \frac{x}{2 \sqrt{D_{i} \tau_{2}}} \quad i = 1, 2, 3 \]  \[ \text{(A.19)} \]

the new dimensionless variable

\[ \beta = \frac{\tau_{2}}{t_{1} + \tau_{2}} \]  \[ \text{(A.20)} \]

If we also suppose that the functions \( \tilde{c}_{i}^{II}(x, \tau_{2}) \) are of the form:

\[ \tilde{c}_{i}^{II}(x, \tau_{2}) = \sum_{k=0}^{\infty} \sigma_{i,k}(s_{i}) \beta^{k} \quad i = 1, 2, 3 \]  \[ \text{(A.21)} \]

the equation system (Eq. (A.15)) is transformed into:

\[ \sigma_{i,k}(s_{i}) + 2 \sigma_{i,k-1}(s_{i}) - 4k \sigma_{i,k}(s_{i}) \]
\[ = -4 \zeta \sigma_{i,k-1}(s_{i}) - 4(k - 1) \sigma_{i,k}(s_{i}) \quad i = 1, 2, 3 \]  \[ \text{(A.22)} \]

and Eqs. (A.16), (A.17) and (A.18), corresponding to the boundary conditions, transform to:

\[ s_{i} \to \infty \quad \sigma_{i,k} = 0 \quad i = 1, 2, 3 \]  \[ \text{(A.23)} \]

\[ \sum_{i=1}^{3} \sqrt{D_{i}} \sigma_{i,k}(s_{i} = 0) = 0 \]  \[ \text{(A.24)} \]

\[ \sigma_{1,0}(s_{1}) = J_{1}^{II} \sigma_{1,0}(s_{2} = 0) + (J_{1}^{II} - J_{1}^{I}) \sigma_{1}(x = 0) = 0 \]  \[ \text{(A.25)} \]

\[ \sigma_{2,0}(s_{2} = 0) = J_{2}^{II} \sigma_{2,0}(s_{3} = 0) + (J_{2}^{II} - J_{2}^{I}) \sigma_{2}(x = 0) = 0 \]  \[ \text{(A.26)} \]

By proceeding in the way described in Ref. [26], we obtain the following expressions for the functions \( \sigma_{i,k}(s_{i}) \) \( i = 1, 2, 3 \),

\[ k = 0 \quad \sigma_{i,0}(s_{i}) = c_{i}^{II}(0) \text{erfc}(s_{i}) \]  \[ \text{(A.27)} \]

\[ k = 1 \quad \sigma_{i,1}(s_{i}) = -\frac{z}{\sqrt{\pi}} c_{i}^{II}(x = 0)s_{i}e^{-s_{i}^{2}} \]  \[ \text{(A.28)} \]

\[ k = 2 \quad \sigma_{i,2}(s_{i}) = -\frac{z}{2 \sqrt{\pi}} c_{i}^{II}(x = 0) \left[ \frac{z + 4}{6} s_{i} - zs_{i} \right] e^{-s_{i}^{2}} \]  \[ \text{(A.29)} \]

\[ k = 3 \quad \sigma_{i,3}(s_{i}) = \frac{z}{6 \sqrt{\pi}} c_{i}^{II}(x = 0) \]  \[ \times \left[ \frac{4 - z^{2}}{4} s_{i} - z(z + 2)s_{i}^{3} + z^{3}s_{i}^{5} \right] e^{-s_{i}^{2}} \]  \[ \text{(A.30)} \]

\[ k = 4 \quad \sigma_{i,4}(s_{i}) = -\frac{z}{24 \sqrt{\pi}} c_{i}^{II}(x = 0) \]  \[ \times \left[ \frac{3z^{3} + 56z^{2} + 96z - 96}{40} s_{i} + \frac{z(5z + 8)(z - 8)}{12} s_{i}^{3} \right. \]  \[ + \left. \frac{2z^{2}(z + 8)}{4} s_{i}^{5} - z^{3}s_{i}^{7} \right] e^{-s_{i}^{2}} \]  \[ \text{(A.31)} \]
So, taking into account Eq. (A.21), the concentration profiles given by Eq. (A.14) can be expressed as \((i = 1, 2, 3)\):

\[
c^i(x, t) = c^i(0, t) + \sum_{k=0}^{\infty} \sigma_{i,k}(s) \beta^k
\]

(A.33)

with the functions \(\sigma_{i,k}(s)\) given by Eqs. (A.27), (A.28), (A.29), (A.30) and (A.31).

The surface concentrations \(c^i_0(x = 0)\) corresponding to an EE mechanism for this second potential step can be calculated by making \(x = 0\) in Eq. (A.33). So, we have the following (expected) expressions

\[
c^0_1(x = 0) = \frac{J^{11}_0 J^{11}_1 e^*}{1 + \gamma_{23}^{11} J^{11}_2 + \gamma_{13}^{11} J^{11}_1 J^{11}_2} - \frac{1}{1 + \gamma_{23}^{11} J^{11}_2 + \gamma_{13}^{11} J^{11}_1 J^{11}_2}
\]

\[
c^0_2(x = 0) = \frac{J^{11}_0 e^*}{1 + \gamma_{23}^{11} J^{11}_2 + \gamma_{13}^{11} J^{11}_1 J^{11}_2} - \frac{1}{1 + \gamma_{23}^{11} J^{11}_2 + \gamma_{13}^{11} J^{11}_1 J^{11}_2}
\]

\[
c^0_3(x = 0) = \frac{e^*}{1 + \gamma_{23}^{11} J^{11}_2 + \gamma_{13}^{11} J^{11}_1 J^{11}_2}
\]

(A.34)

Note that, as in the case of a reversible E simple process [27], the surface concentrations of species \(O_1, O_2\), and \(O_3\) are independent of time and take the same form for the first and second potential steps (compare Eq. (A.7) and Eq. (A.34)). These surface concentrations fulfil the following relation for any potential step

\[
c^i_0(x = 0)^{n_i+e_i} = c^i(x = 0)^{n_i} \exp \left\{ \frac{n_i n_2 F (E^i - E^0)}{RT} \right\} = K
\]

(A.35)

with \(K\) being the equilibrium constant corresponding to the electron exchange reaction (ii).

Once the concentration profiles for this second potential step \(E^{11}\) have been obtained (Eq. (A.33)) and taking into account Eqs. (A.27), (A.28), (A.29), (A.30) and (A.32), the partial currents \(I^{11}_1\) and \(I^{11}_2\) are given by

\[
I^{11}_1 = I^1_1 + n_1 FA(t) \sqrt{\frac{D_1}{\pi \tau_2}} h_2(\beta) \times [c^1_1(x = 0) - c^1_1(x = 0)]
\]

\[
I^{11}_2 = I^1_1 + n_2 FA(t) \sqrt{\frac{D_1}{\pi \tau_2}} h_2(\beta) \times [c^1_1(x = 0) - c^1_1(x = 0)]
\]

(A.36)

where \(I^1_1\) and \(I^1_2\) are the partial currents corresponding to the application of the first potential pulse \(E^1\), whose expressions are [20]

\[
I^1_1 = n_1 FA(t) \sqrt{\frac{D_1(2z + 1)}{\pi t}} [c^* - c^1_1(x = 0)]
\]

\[
I^1_2 = n_2 FA(t) \sqrt{\frac{D_1(2z + 1)}{\pi t}} \times \{[c^* - c^1_1(x = 0)] + \gamma_2 [c^* - c^1_1(x = 0)]\}
\]

(A.37)

and

\[
h_2(\beta) = \sqrt{\frac{7\beta}{3(1 - (1 - \beta)^{2z + 1})}}
\]

(A.39)

In the particular cases \(z = 0\) (static electrode) and \(z = 2/3\) (DME), the function \(h_2(\beta)\) takes the form

\[
h_{2/3}(\beta) = \frac{7\beta}{3(1 - (1 - \beta)^{2/3})}
\]

(A.40)

where \(h_{2/3}(\beta \rightarrow 0) = 1\); \(h_{2/3}(\beta \rightarrow 1) = \sqrt{7}/3\). The current observed, \(I^0\), corresponding to this second potential step is deduced by adding Eq. (A.36) and Eq. (A.37) such that

\[
I^0 = I^{11}_1 + I^{11}_2
\]

(A.41)

so, we deduce

\[
I^0 = I^1 + FA(t) \sqrt{\frac{D_1}{\pi \tau_2}} h_2(\beta) \times \{(n_1 + n_2)[c^1_1(x = 0) - c^1_1(x = 0)] + n_2 \gamma_2 [c^1_2(x = 0) - c^1_2(x = 0)]\}
\]

(A.42)

where \(I^0\) is the current corresponding to the first potential (Eq. (1)). By introducing Eq. (A.7) and Eq. (A.34) into Eq. (A.42) we obtain Eq. (5) of the theory.

References