Application of the superposition principle to the study of a charge transfer reaction in cyclic chronopotentiometry. Part II

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The general analytical expressions corresponding to the response obtained for a charge transfer process in cyclic chronopotentiometry are presented. The different geometries considered for the mass transport operator are planar, tubular and spherical. In the case of spherical electrodes (such as the dropping mercury electrode and the static mercury dropping electrode), we have analyzed the following two cases: solution soluble product and electrode soluble product or amalgamation. The solutions deduced here are independent of the method used in solving the differential equations system since we have applied the superposition principle for which we have only used the properties of the linear operators.

1. Introduction

Cyclic chronopotentiometry is a classical electrochemical technique consisting of the application of several successive current steps of alternating signs to a determined electrode without balance being recovered in the electrode-solution interphase. This technique was introduced by Herman and Bard in 1963 [1] who applied it to stationary plane electrodes and showed its use for the qualitative and quantitative study of electrode processes [2]. The method used by these authors to solve the corresponding differential equations was Laplace's transform method and the solution obtained was only valid for plane geometry.

In this paper, we obtain the general equations corresponding to the application of this technique for the study of a charge transfer process which takes place in plane and spherical electrodes (of constant and variable area) and also for tubular electrodes. The consideration of spherical geometry has allowed us to apply this technique to those processes in which the reaction product is a metal which is soluble in the mercury electrode (amalgamation process). The mathematical resolution of this kind of processes is complex and their response to this technique has not been

previously studied in the literature, in spite of the advantages that spherical electrodes offer as opposed to plane electrodes.

For the study of amalgamation, it is necessary to consider the spherical diffusion operator model for any mercury electrode because, as is well known, for plane electrodes the solution with amalgamation is equivalent to the solution without amalgamation in semi-infinite linear diffusion. This is a consequence of the invariance of the diffusion plane operator against the reflection $x \rightarrow -x$.

In a parallel manner to that of the previous paper, we have analyzed the boundary value problem in all the previously mentioned situations and we have demonstrated in all cases that the response corresponding to the successive application of j current steps can be expressed as a sum of j independent responses, in agreement with the superposition principle. Therefore, the solutions obtained here are valid for electrodes of any geometry and for any behaviour of the reaction product. Moreover, they are independent of the procedure used in solving the problem because for their deduction we have only used the properties of the linear operators [3,4].

2. Theory

Let us consider the following charge transfer reaction whose cathodic and anodic reaction orders a and b can take any positive value and are coincident with the stoichiometric coefficients for species A and B according to the scheme

$$aA + ne^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} bB, \tag{I}$$

where k_f and k_b are the rate constants of forward (reduction) and backward (oxidation) processes.

We will analyze the response of this electrode processes in cyclic chronopotentiometry, which is a powerful electrochemical technique which provides information similar to that of cyclic voltammetry [1,2]. However, the mathematical treatment is simpler, primarily because the total flux at the electrode surface at any time is known and constant.

This technique is based on the application of successive and alternating sign current steps to an electrode, in the manner indicated in the following scheme:

$$\left. \begin{array}{ll} I_1, & 0 \leqslant t_1 < \tau_1, \\ -I_2, & 0 \leqslant t_2 < \tau_2, \\ \vdots & \\ (-1)^{j+1} I_j, & 0 \leqslant t_j < \tau_j, \\ \vdots & \\ (-1)^{k+1} I_k, & 0 \leqslant t_k < \tau_k, \end{array} \right\} \tag{1}$$

where I_j $(1 \leqslant j \leqslant k)$ is the absolute value of each current step applied, t_j is the time during which a j step current is applied and τ_j is the time in which the change in sign is produced, as well as the absolute value. τ_j is lower than or equal to the transition time of the process taking place. For the sake of simplicity, we will suppose that each reversal of the current is produced precisely at the moment that the transition time corresponding to the reduction process A (forward) or to the reoxidation process B (backward) is reached.

Thus, initially a constant cathodic current I_1 is applied during $0 \leqslant t_1 < \tau_1$ (τ_1 being the first forward transition time). At time τ_1 the current is changed to an anodic value $-I_2$ during $0 \leqslant t_2 < \tau_2$ (τ_2 being the first backward transition time). The above operations can be continued by giving a series of forward ($\tau_1, \tau_3, \ldots$) and backward ($\tau_2, \tau_4, \ldots$) transition times, with the total time being

$$t = \tau_1 + \tau_2 + \ldots + \tau_{j-1} + t_j. \tag{2}$$

To deduce the general expressions corresponding to the response of the process (I) with this technique, we will consider:

(a) Different types of electrodes: we will obtain the solutions corresponding to planar, spherical and tubular electrodes of constant area and also planar and spherical electrodes of variable area, such as the dropping mercury electrode with the expanding plane electrode model and the expanding sphere electrode model.

(b) Different behaviours of the reaction product: We will consider the case where the reaction product is soluble in the solution, such as when the reaction product is soluble in the electrode (amalgam formation).

The mass transport is described by the differential equation system

$$\hat{\delta}_A C_A = \hat{\delta}_B C_B = 0, \tag{3}$$

where $\hat{\delta}_i$ ($i = A$ or B) is the diffusion operator corresponding to Fick's second law, which depends on the electrode geometry. We then have the following cases [5,6]:

(a) Expanding sphere electrode model for a DME:

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] + \frac{\zeta^3}{3r^2} \frac{\partial}{\partial r}. \tag{4}$$

(b) Expanding plane electrode model for a DME:

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2} - \frac{2x}{3t} \frac{\partial}{\partial x}. \tag{5}$$

(c) Stationary sphere electrode model for an SMDE:

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right]. \tag{6}$$

(d) Tubular electrode model (TE):

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \left[\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right]. \tag{7}$$

(e) Stationary plane electrode model (SPE):

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2}. \tag{8}$$

In eqs. (4)–(8), D_i ($i = A$ or B) is the diffusion coefficient of the i species.

The operators $\hat{\delta}_i$ given by eqs. (4)–(8) are always linear and the equation system (3) is also linear. In this paper, we will carry out the general development for the diffusion operator corresponding to the expanding sphere electrode model since, from the solutions obtained for that, we can deduce those corresponding to the operators given by eqs. (5), (6) and (8) as particular cases. In the case of tubular electrodes, (eq. (7)), the procedure followed is similar. For dynamic electrodes, the first current step I_1 must be used after a blank period t_{bp}. This blank period does not exist in the case of electrodes of constant area [7].

The boundary value problem corresponding to the first step current is given by

(a) Reaction product soluble in the electrolytic solution:

$$\left. \begin{array}{l} t_1 = 0; r \geqslant r_0 , \\ t_1 > 0; r \to \infty , \end{array} \right\} \quad \begin{array}{l} C_A^1(r, t) = C_A^* , \\ C_B^1(r, t) = C_B^* . \end{array} \tag{9}$$

(b) Reaction product soluble in the electrode (amalgam formation):

$$\left. \begin{array}{l} t_1 = 0; r \geqslant r_0 , \\ t_1 > 0; r \to \infty , \end{array} \right\} \quad \begin{array}{l} C_A^1(r, t) = C_A^* , \\ C_B^1(r, t) = 0 , \end{array} \tag{10}$$

$$\left. \begin{array}{l} t_1 = 0; r < r_0 , \\ t_1 > 0; r \to -\infty , \end{array} \right\} \quad \begin{array}{l} C_A^1(r, t) = 0 , \\ C_B^1(r, t) = C_B^* , \end{array} \tag{11}$$

$$t_1 > 0; r = r_0$$

$$\frac{D_A}{a} \left(\frac{\partial C_A^1}{\partial r} \right)_{r=r_0} = \mp \frac{D_B}{b} \left(\frac{\partial C_B^1}{\partial r} \right)_{r=r_0} = \frac{I_1}{nFA(t_s)} \tag{12}$$

with

$$A(t_s) = A_0 t_s^{2/3} \tag{13}$$

and t_s is given in Notations and definitions.

Throughout this paper the upper sign in any equation refers to a reaction product which is soluble in the electrolytic solution whilst the lower sign corresponds to a

product which is soluble in the electrode (amalgam formation). Furthermore, the superscript which appears in the concentrations of species A and B will refer to the number of the current step being considered.

The solutions for the concentration profiles of species A and B, $C_A^1(r, t)$ and $C_B^1(r, t)$, when the first step current, I_1, is applied, have been obtained previously [7] and their values for the electrode surface, $C_A^1(r_0, t)$ and $C_B^1(r_0, t)$, are given in Appendix (eqs. (A.1) and (A.2)).

At $t = \tau_1$, the current is reversed to an anodic value $-I_2$ during the interval $0 \leqslant t_2 < \tau_2$ $(t = \tau_1 + t_2)$, with the reoxidation of species B being produced.

The study of the application of the two successive, alternating sign current steps constitutes an electrochemical technique of great interest: "current reversal chronopotentiometry". This technique was introduced in 1953 by Delahay [8], who obtained the solutions corresponding to a plane electrode when both species are soluble in the electrolytic solution.

The solutions corresponding to the second step current for any of the operators given by eqs. (4)–(8), $C_A^2(r, t)$ and $C_B^2(r, t)$, can be expressed, due to the linearity of the equation system (3), in the following manner:

$$
\left.
\begin{aligned}
C_A^2(r, t) &= C_A^1(r, t) + \tilde{C}_A^2(r, t) , \\
C_B^2(r, t) &= C_B^1(r, t) + \tilde{C}_B^2(r, t) ,
\end{aligned}
\right\} \tag{14}
$$

where $C_A^1(r, t)$ and $C_B^1(r, t)$ are the solutions found in ref. [7] for the first step current and $\tilde{C}_A^2(r, t)$ and $\tilde{C}_B^2(r, t)$ are the new unknown quantities to be determined.

For this second current step, the boundary value problem, taking into account eqs. (9)–(12), can be expressed only in terms of the new unknown quantities $\tilde{C}_A^2(r, t)$ and $\tilde{C}_B^2(r, t)$, and is given by

$$
\left.
\begin{aligned}
t_2 &= 0; r \gtrless r_0 , \\
t_2 &> 0; r \to \pm\infty ,
\end{aligned}
\right\} \quad \tilde{C}_A^2(r, t) = \tilde{C}_B^2(r, t) = 0 , \tag{15}
$$

$t_2 > 0; r = r_0 ,$

$$
\frac{D_A}{a} \left(\frac{\partial \tilde{C}_A^2}{\partial r} \right)_{r=r_0} = \mp \frac{D_B}{b} \left(\frac{\partial \tilde{C}_B^2}{\partial r} \right)_{r=r_0} , \tag{16}
$$

$$
\frac{D_A}{a} \left(\frac{\partial \tilde{C}_A^2}{\partial r} \right)_{r=r_0} = \frac{-(I_1 + I_2)}{nFA(t_s)} . \tag{17}
$$

The solutions for this second step current, $C_A^2(r, t)$ and $C_B^2(r, t)$, have been obtained in a previous paper [7] and their expression for the electrode surface, $C_A^2(r_0, t)$ and $C_B^2(r_0, t)$, are given in Appendix (eqs. (A.5) and (A.6)).

For the jth step current $(-1)^{j+1} I_j$, we can express the solution in the form

$$C_i^j(r,t) = C_i^{j-1}(r,t) + \tilde{C}_i^j(r,t), \quad \text{where} \quad C_i^{j-1}(r,t) = C_i^1(r,t) + \sum_{m=2}^{j-1} \tilde{C}_i^m(r,t).$$

(18)

And from eqs. (15)–(17) and (18) it is easy to demonstrate through induction that the boundary value problem for any step current $(-1)^{j+1} I_j$ with $j > 1$ is given by

$$\left. \begin{aligned} & t_j = 0; r \gtrless r_0 \,, \\ & t_j > 0; r \to \pm\infty \,, \end{aligned} \right\} \quad \tilde{C}_A^j(r,t) = \tilde{C}_B^j(r,t) = 0 \,,$$

(19)

$$t_j > 0; r = r_0 \,,$$

$$\frac{D_A}{a} \left(\frac{\partial \tilde{C}_A^j}{\partial r} \right)_{r=r_0} = \mp \frac{D_B}{b} \left(\frac{\partial \tilde{C}_B^j}{\partial r} \right)_{r=r_0} ,$$

(20)

$$\frac{D_A}{a} \left(\frac{\partial \tilde{C}_A^j}{\partial r} \right)_{r=r_0} = (-1)^{j+1} \frac{(I_{j-1} + I_j)}{nFA(t_s)} .$$

(21)

Since the boundary value problem can be expressed in a general form for any current step $(-1)^{j+1} I_j$ with $j > 1$, the surface concentrations of species A and B for any step can be expressed as a sum of j terms. In these conditions, the superposition principle is fulfilled and the following is obtained:

$$C_A^j(r_0,t) = C_A^* \left\{ 1 - N_s a \frac{1}{t_s^{2/3}} \sum_{n=1}^{j} (-1)^{n+1} \frac{I_n}{I_1} (t_{nj})^{1/2} H_{A,n}(1 + Q_n) \right\},$$

(22)

$$C_B^j(r_0,t) = C_B^* + C_A^* b \gamma_{A,B} N_s \frac{1}{t_s^{2/3}} \sum_{n=1}^{j} (-1)^{n+1} \frac{I_n}{I_1} (t_{nj})^{1/2} H_{B,n}(1 + Q_n)$$

(23)

with

$$\left. \begin{aligned} & Q_n = \frac{I_{n-1}}{I_n} \,, \quad \text{if } n > 1 \,, \\ & Q_1 = 0 \,. \end{aligned} \right\}$$

(24)

t_{nj} is given by eq. (A.11) and $H_{A,n}$ and $H_{B,n}$ are given by eq. (A.8) of Appendix. When species B is amalgamated into the electrode we must change $(\xi_{B,n})$ to $(-\xi_{B,n})$ in the $H_{B,n}$ series in eq. (23) (see Appendix). N_s and $\gamma_{A,B}$ are given by eqs. (A.3) and (A.4), respectively.

To obtain the transition time corresponding to the jth current step, $(-1)^{j+1} I_j$, we must impose that the concentration of the species that is oxidized or reduced be zero in the surface of the electrode.

If j is odd, a reduction process will take place. By imposing that $C_A^j(r_0, \tau_1 + \ldots + \tau_j) = 0$ in (22), we obtain the transition time for the reduction of species A,

$$\frac{(t_{bp} + \tau_{1j})^{2/3}}{aN_s} = \sum_{n=1}^{j}(-1)^{n+1}\frac{I_n}{I_1}(\tau_{nj})^{1/2}H_{A,n}(1 + Q_n). \tag{25}$$

If j is even, an oxidation process will be produced. By imposing $C_B^j(r_0, \tau_1 + \ldots + \tau_j) = 0$ in (23), we obtain, analogously to the previous case, the transition time corresponding to the oxidation of species B,

$$-\frac{(t_{bp} + \tau_{1j})^{2/3}}{b\gamma_{A,B}N_s} = \frac{C_A^*}{C_B^*}\sum_{n=1}^{j}(-1)^{n+1}\frac{I_n}{I_1}(\tau_{nj})^{1/2}H_{B,n}(1 + Q_n). \tag{26}$$

In these equations, τ_{nj} is given by

$$\tau_{nj} = \sum_{m=n}^{j}\tau_m. \tag{27}$$

Eqs. (25) and (26) for the particular case of a stationary plane electrode ($r_0 \to \infty$ and $t_{bp} \gg t$) of area $A = A_0 t_{bp}^{2/3}$ coincide with those obtained by Herman and Bard (eqs. (8) and (9), respectively, in ref. [1]).

From eqs. (22) and (23) for the surface concentrations obtained for an expanding spherical electrode model, it is possible to obtain solutions corresponding to the expanding plane electrode model (eq. (5)) by making $r_0 \to \infty$ in the series $H_{i,n}$ of eqs. (22), (23) and (25),(26). If in the previous equations we make $t_{bp} \gg t$, the expanding spherical electrode behaves like an electrode of constant area $A \cong A_0 t_{bp}^{2/3}$ (see Notations and definitions), making the series $H_{i,n}$ of eqs. (22), (23) and (25), (26) take the form given by eq. (A.14).

In Figs. 1 and 2 we have represented the potential time curves deduced (supposing that process (I) is reversible), by substituting eqs. (22) and (23) in Nernst's equation, obtaining

$$E(t) = E^0 + \frac{RT}{nF}\ln\frac{[C_A^j(r_0, t)]^a}{[C_B^j(r_0, t)]^b}. \tag{28}$$

We have used this equation to deduce the potential time response corresponding to the application of five current steps to a stationary spherical electrode.

Fig. 1 shows how the influence of the amalgam formation, which does not affect the first transition time τ_1, makes the even transition times increase in relation to those obtained when B is soluble in the solution, the more so as the number of the current steps applied is increased. In the transition times corresponding to the reduction of A for $j = 3, 5, \ldots$ this effect is also obtained, but its origin is different. This behaviour can be used in the laboratory to characterize the amalgamation in a more conclusive manner than the proposal in reversal current chronopotentiometry, in which only two current step are applied. Fig. 2 shows the influence of the electrode sphericity in the response obtained when both species are soluble in the
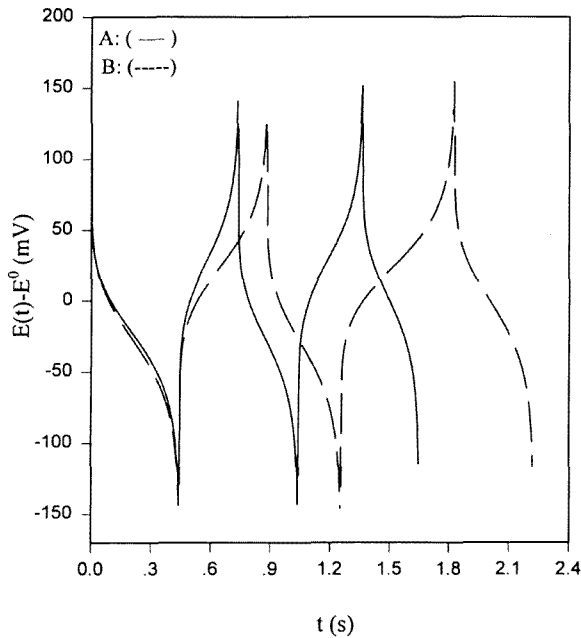
Fig. 1. Influence of the amalgam formation on the potential time curves in cyclic chronopotentiometry for the process (I) for a reversible charge transfer reaction (eq. (28)). $N_s = 3.0 \text{ s}^{-1/2}$, $D_A = D_B = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ($\gamma_{A,B} = 1.0$), $r_0 = 0.015$ cm, $Q_3 = Q_5 = 2$, $Q_2 = Q_4 = 1/2$, $a = b = 1$. In curve A, the reaction product is soluble in the solution and, in curve B the reaction product is soluble in the electrode.

electrolytic solution. In this figure, curve A corresponds to a plane electrode whose operator is given by eq. (8) and the solution corresponding to that is obtained by simultaneously making $r_0 \rightarrow \infty$ and $t_{bp} \gg t$ in eqs. (22), (23) and (25), (26). In the last case, the results obtained in this paper coincide with those published by Herman and Bard [1].

Finally, the solution corresponding to tubular electrodes is obtained by substituting series $H_{i,n}$ in (22),(23) by series $H_{i,n}^{TE}$ given by eq. (A.16). To deduce the cyclic chronopotentiometric response in tubular electrodes (see eq. (7)), we have taken into account the solution found by Aoki et al. for the application of a single current step [9] since we have shown that the superposition principle is fulfilled.

3. Notations and definitions

$C_i^j(r, t)$ concentration profiles of the i species (with $i = A$ or B) for the jth step current,

a, b cathodic and anodic reaction orders, respectively, which are coincident with the stoichiometric coefficients,
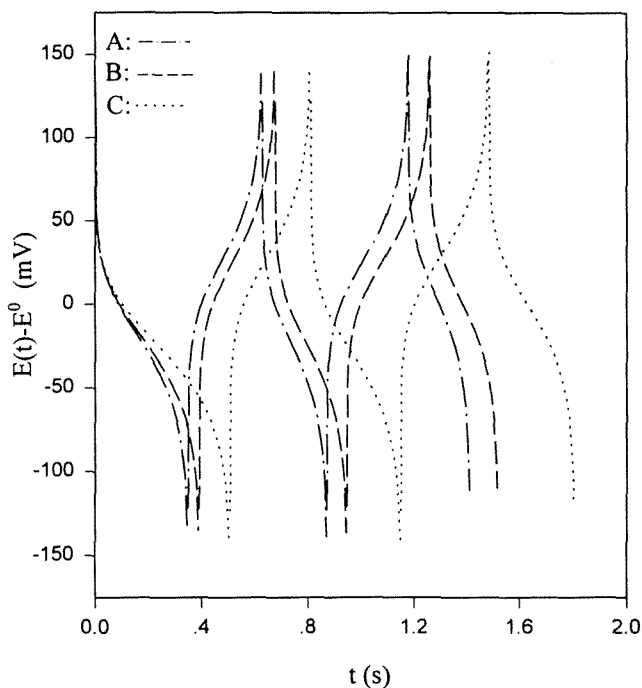
Fig. 2. Influence of the electrode sphericity on the potential time curves in cyclic chronopotentiometry for the process (I) for a reversible charge transfer reaction (eq. (28)). The values of r_0 in cm are: (A) $r_0 \to \infty$ (planar electrode), (B) 0.03 and (C) 0.01. Other conditions as Fig. 1.

k_f and k_b	rate constants of forward (reduction) and backward (oxidation) processes,
I_j	absolute value of the jth current step applied,
D_i	diffusion coefficient of species i,
r	distance from the center of the spherical electrode,
r_0	$\begin{cases} \text{electrode radius at time } t_s \ (= \zeta t_s^{1/3}) \text{ for a DME,} \\ \text{constant electrode radius for a SMDE,} \end{cases}$
t_{bp}	blank period used only for a DME,
t	time elapsed between application of the first and the jth current step $(= \tau_1 + \ldots + \tau_{j-1} + t_j)$,
t_j	time during which a j step current is applied $(0 \leqslant t_j < \tau_j)$,
τ_j	time in which the change in sign of the current is produced, as well as the absolute value,
t_s	total time $(= t_{bp} + t)$,
ζ	electrode radius at $t_s = 1$ s for a DME $(= (3m_{Hg}/4\pi d)^{1/3})$,
m_{Hg} and d	rate of flow and density of mercury,
$A(t_s)$	time dependent electrode area of a DME $(= A_0 t_s^{2/3})$,
A_0	$= (4\pi)^{2/3}(3m_{Hg}/d)^{2/3}$ in cm^2 s$^{-2/3}$,

A electrode area ($= A_0 t_{bp}^{2/3}$) when $t_{bp} \gg t$ (static spherical or planar electrodes),

$\gamma_{A,B}$ $= \sqrt{D_A/D_B}$,

DME   dropping mercury electrode for which the expanding sphere electrode model (eq. (4)) and the expanding plane electrode model (eq. (5)) are used,

SMDE   stationary spherical electrode model or static mercury dropping electrode (eq. (6)),

EPE   expanding plane electrode model (for the DME)

SPE   stationary plane electrode (eq. (8)),

TE   tubular or cylindrical electrode (eq. (7)).

Other definitions are conventional.

Acknowledgements

Appendix

A.1. FIRST STEP CURRENT

By using the dimensionless parameters method, we obtained [7] the following expressions for the surface concentrations of the A and B species for the first step, corresponding to the expanding sphere electrode model (eq. (4)):

$$C_A^1(r_0, t) = C_A^* - a C_A^* N_s \frac{t^{1/2}}{t_s^{2/3}} H_{A,1}, \tag{A.1}$$

$$C_B^1(r_0, t) = C_B^* + b C_A^* \gamma_{A,B} N_s \frac{t^{1/2}}{t_s^{2/3}} H_{B,1}. \tag{A.2}$$

Moreover,

$$N_s = \frac{2 I_1}{n F \sqrt{D_A}\, A_0 C_A^*}, \tag{A.3}$$

$$\gamma_{A,B} = \sqrt{\frac{D_A}{D_B}}. \tag{A.4}$$

A.2. SECOND STEP CURRENT

For the second step current ($0 \leqslant t_2 \leqslant \tau_2$) we deduced the following expressions for the surface concentrations of the A and B species [7]:

$$C_A^2(r_0, t) = C_A^* - aC_A^* N_s \frac{1}{t_s^{2/3}} \left\{ (\tau_1 + t_2)^{1/2} H_{A,1} - (1 + Q_2) \frac{I_2}{I_1} (t_2)^{1/2} H_{A,2} \right\},$$

$$\tag{A.5}$$

$$C_B^2(r_0, t) = C_B^* + bC_A^* N_s \gamma_{A,B} \frac{1}{t_s^{2/3}} \left\{ (\tau_1 + t_2)^{1/2} H_{B,1} - (1 + Q_2) \frac{I_2}{I_1} (t_2)^{1/2} H_{B,2} \right\}$$

$$\tag{A.6}$$

with

$$Q_2 = \frac{I_1}{I_2} \, . \tag{A.7}$$

The $H_{i,n}$ series has a general expression which does not depend on the step current considered,

$$H_{i,n} = F(\beta_n) \mp \xi_{i,n} F_1(\beta_n) + (\xi_{i,n})^2 F_2(\beta_n) \, , \tag{A.8}$$

where

$$\beta_n = \left(\frac{t_{nj}}{t_{bp} + t_{1j}} \right)^{1/3} , \tag{A.9}$$

$$\xi_{i,n} = \frac{2\sqrt{D_i t_{nj}}}{\zeta t_s^{1/3}} \, , \tag{A.10}$$

$$\left. \begin{aligned} t_{nj} &= \sum_{m=n}^{j-1} \tau_m + t_j \, , \\ t_{jj} &= t_j \, , \end{aligned} \right\} \tag{A.11}$$

$$\left. \begin{aligned} F(\beta_n) &= \frac{1}{\pi^{1/2}} \left(1 + \frac{1}{9} \beta_n^3 + \frac{7}{270} \beta_n^6 + \frac{4}{567} \beta_n^9 + \frac{11}{5832} \beta_n^{12} + \cdots \right), \\ F_1(\beta_n) &= \frac{1}{4} \left(1 + \frac{1}{4} \beta_n^3 + \frac{1}{16} \beta_n^6 + \cdots \right), \\ F_2(\beta_n) &= \frac{1}{6\pi^{1/2}} \left(1 + \frac{2}{5} \beta_n^3 + \cdots \right). \end{aligned} \right\} \tag{A.12}$$

Throughout this appendix, when two signs appear, the upper sign in an equation refers to a reaction product which is soluble in the electrolytic solution whilst the lower sign corresponds to a product which is amalgamated in the electrode (this is equivalent to changing $(\xi_{i,n})$ to $(-\xi_{i,n})$).

A.3. PARTICULAR CASES OF THE H-SERIES

(a) If $r_0 \to \infty$ ($\xi_{i,n} = 0$) the above expressions are simplified notably and become those corresponding to an expanding plane electrode (EPE). So, eq. (A.8) is simplified to

$$H_{i,n}^{\text{EPE}} = F(\beta_n) . \tag{A.13}$$

(b) By making $t_{bp} \gg t$ in eqs. (A.1) and (A.2), we obtain the expressions corresponding to a stationary sphere electrode model (SMDE) of area $A = A_0 t_{bp}^{2/3}$. In this situation, eq. (A.8) becomes

$$H_{i,n}^{\text{SMDE}} = \pm \frac{1}{\xi_{i,n}} \left(1 - \exp \left(\left(\frac{\xi_{i,n}}{2} \right)^2 \right) \left(1 \mp \text{erf} \left(\frac{\xi_{i,n}}{2} \right) \right) \right) . \tag{A.14}$$

(c) If $r_0 \to \infty$ and $t_{bp} \gg t$, we deduce the equations corresponding to a stationary plane electrode (SPE) of area $A = A_0 t_{bp}^{2/3}$ and eq. (A.8) is transformed to

$$H_{i,n}^{\text{SPE}} = \frac{1}{\pi^{1/2}} . \tag{A.15}$$

(d) For a tubular electrode (TE), the mathematical treatment for the first current step is given in ref. [9] and for any current step $j > 1$ we deduce, taking into account that the superposition principle is fulfilled, that the series $H_{i,n}$ in eqs. (22) and (23) is given by

$$H_{i,n}^{\text{TE}} = \frac{1}{\sqrt{\pi}} - \frac{1}{8} \xi_{i,n} + \frac{1}{16\sqrt{\pi}} \xi_{i,n}^2 - \frac{3}{256} \xi_{i,n}^3 + \frac{21}{2560\sqrt{\pi}} \xi_{i,n}^4$$

$$- \frac{9}{4096} \xi_{i,n}^5 + \frac{633}{286720\sqrt{\pi}} \xi_{i,n}^6 - \cdots . \tag{A.16}$$

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