

Application of the superposition principle to the study of CEC, CE, EC and catalytic mechanisms in cyclic chronopotentiometry. Part III

A. Molina, J. González and M. López-Tenés

Departamento de Química-Física, Universidad de Murcia, Espinardo, 30100 Murcia, Spain

Received 4 February 1997; revised 5 November 1997

In this paper we have obtained the general analytical equations corresponding to the response of complicated charge transfer processes with coupled homogeneous chemical reactions in cyclic chronopotentiometry by applying the superposition principle. The analysis of different cycles of this response can be used to obtain accurate and contrasted values of kinetic parameters in each complex reaction scheme analysed. These parameters are of great interest for the chemist and the biochemist. These equations are also applicable to cyclic derivative chronopotentiometry which is a very useful method since the response is obtained with peaks in a similar way to cyclic voltammetry but its mathematical treatment is simpler.

0. Introduction

As has been pointed out in previous papers, electrochemical techniques in which the electrical perturbation (potential or current) is applied more than once are of great interest both analytically and kinetically [1,5,10].

When several potential steps are successively applied without balance in the interphase electrode solution being restored, the superposition principle can only be applied in the case of reversible processes and the analytical expressions for a slow charge transfer reaction have only been deduced for two and three potential steps [15]. On the other hand, in the case where several current steps with alternating sign are used successively, we have recently demonstrated that the superposition principle can be applied for electrodes of different geometry and is independent of the reversibility of the charge transfer process [11]. We have also found the general solution corresponding to a slow charge transfer reaction in planar, spherical and tubular electrodes in cyclic chronopotentiometry. The use of this technique presents great advantages both in the normal and also in the derivative mode, as has been shown recently in the literature [2,8,9].

With this in mind, the main aim of this paper is to propose a theory corresponding to the study of electrode processes with homogeneous chemical reactions (C) coupled to the heterogeneous electrochemical charge transfer step (E) in cyclic chronopoten-

tiometry. We will study the response of CEC, CE, EC, E and catalytic mechanisms in this technique at spherical electrodes such as the dropping mercury electrode (DME) and the static mercury drop electrode (SMDE), as well as at electrodes with planar geometry. The study of the electrochemical behaviour of these mechanisms is of great interest for the chemist and the biochemist.

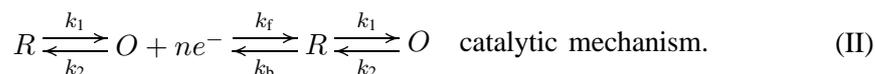
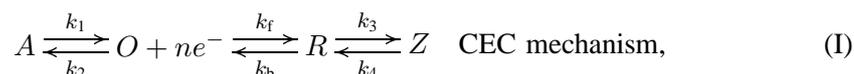
The equations deduced in this paper may be used directly in cyclic chronopotentiometry or in cyclic derivative chronopotentiometry. In the latter the inverse of that derivative is found from the response obtained, either analytically or numerically with respect to time. This technique is of great interest since responses are obtained with peaks that are barely affected by the charge current. The information obtained is similar to that of cyclic voltammetry but the mathematical treatment is simpler [2].

The mathematical resolution of the five above mentioned mechanisms in cyclic chronopotentiometry has been realised by demonstrating that the superposition principle can be applied in all these cases in such a way that the solutions obtained for these complex electrode process can be expressed in a general form for any number of applied current steps [11]. Moreover, the equations obtained here are easily applied to obtain kinetic and thermodynamic parameters and, therefore, permit a complete characterisation of each electrode process. To this extent, we include as an example of applications several figures that show the different behaviours of these reaction mechanisms, both in chronopotentiometry and in derivative chronopotentiometry, when two current steps are applied.

1. Theory

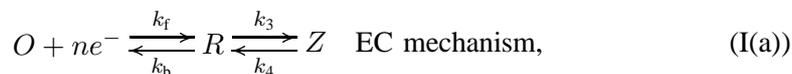
1.1. General treatment

We will simultaneously analyse the following two reaction schemes:

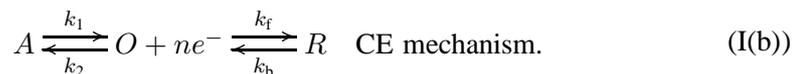


Scheme I corresponds to a CEC (chemical–electrochemical–chemical) mechanism in which both species participating in the electrode process, the oxidised O and the reduced R , are chemically coupled to different species.

The obtention of the general equations corresponding to the response of this scheme is of great interest because from the general expressions deduced for the CEC mechanism it is easy to deduce those corresponding to other interesting and simpler reaction schemes such as the EC mechanism given by the following scheme:



and also the CE mechanism which can be written as



Moreover, a catalytic electrode process, represented by scheme II, if both species R and O participating in the electrode process are initially present in the solution, can also be considered as a particular case of the CEC mechanism as will be seen below.

We will consider a dynamic electrode such as the dropping mercury electrode (DME) and we will analyse the response of CEC processes in cyclic chronopotentiometry. This technique, as was indicated in [11], consists of applying successive and alternating sign current steps, in the following way:

$$\left\{ \begin{array}{ll} I_1, & 0 \leq t_1 \leq T_1, \\ -I_2, & 0 \leq t_2 \leq T_2, \\ I_3, & 0 \leq t_3 \leq T_3, \\ \vdots & \\ (-1)^{j+1} I_j, & 0 \leq t_j \leq T_j, \\ \vdots & \\ (-1)^{k+1} I_k, & 0 \leq t_k \leq T_k, \end{array} \right. \quad (\text{III})$$

with I_j ($1 \leq j \leq k$) being the absolute value of each current step applied, t_j being the time during which an I_j current is applied and T_j is the time in which the change in sign is produced with $T_j \leq \tau_j$, with τ_j being the transition time corresponding to any reduction of O species (forward transition times, $\tau_1, \tau_3, \tau_5, \dots$) or to any oxidation of R species (reverse transition times, $\tau_2, \tau_4, \tau_6, \dots$). When τ_j is reached, the total time elapsed is given by

$$t = T_1 + T_2 + \dots + T_{j-1} + \tau_j. \quad (1)$$

For the CEC mechanism (scheme I), when the first current step I_1 is applied, the differential equations to be solved are

$$\left\{ \begin{array}{l} \widehat{\delta}_A c_A^1 = -k_1 c_A^1 + k_2 c_O^1, \\ \widehat{\delta}_O c_O^1 = k_1 c_A^1 - k_2 c_O^1, \\ \widehat{\delta}_R c_R^1 = -k_3 c_R^1 + k_4 c_Z^1, \\ \widehat{\delta}_Z c_Z^1 = k_3 c_R^1 - k_4 c_Z^1 \end{array} \right. \quad (2)$$

with $\widehat{\delta}_i$ ($i = A, O, R$ or Z) being the operator (see notation)

$$\widehat{\delta}_i = \frac{\partial}{\partial t} - D_i \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] + \frac{\zeta^3}{3r^2} \frac{\partial}{\partial r}. \quad (3)$$

Note that the operator $\widehat{\delta}_i$ given by equation (3) is linear and equations system (2) is also linear.

Due to the fact that the surface of a dropping mercury electrode varies with time, being null at time zero, the first current step I_1 must be used after a blank period, t_{bp} , in order to avoid serious problems [14]. This fact complicates the mathematical treatment of this problem and, in the case of electrodes of constant area, this blank period has no physical sense. Nevertheless, in this paper we have solved the problem for the most complicated case of a dropping mercury electrode since, from the equations deduced for this electrode, by using the model of a sphere whose area increases with time (equation (3)) [7], the equations corresponding to others electrode models may be obtained through simple substitutions (see section 1.3).

The boundary value problem in this case is given by (see notation)

$$\begin{cases} t_1 = 0, & r \geq r_0, \\ t_1 > 0, & r \rightarrow \infty, \end{cases} \quad c_A^1 = c_A^*, \quad c_O^1 = c_O^*, \quad c_R^1 = c_R^*, \quad c_Z^1 = c_Z^*, \quad (4)$$

$$t_1 > 0, \quad r = r_0,$$

$$D_O \left(\frac{\partial c_O^1}{\partial r} \right)_{r=r_0} = -D_R \left(\frac{\partial c_R^1}{\partial r} \right)_{r=r_0} = \frac{I_1}{nFA(t_s)}, \quad (5)$$

$$D_A \left(\frac{\partial c_A^1}{\partial r} \right)_{r=r_0} = D_Z \left(\frac{\partial c_Z^1}{\partial r} \right)_{r=r_0} = 0 \quad (6)$$

with

$$\begin{cases} A(t_s) = A_0 t_s^{2/3}, \\ t_s = t_{bp} + t_1, \end{cases} \quad (7)$$

where t_{bp} is the blank period used for this electrode, t_1 is the time during which the first current step I_1 is applied and A_0 is a constant whose value for the dropping mercury electrode is given in notation. D_i and c_i^* ($i = A, O, R$ or Z) are the diffusion coefficient and the initial concentration of species i , respectively.

By introducing the variables

$$\begin{cases} \varepsilon^1 = c_A^1 + c_O^1, \\ \Delta^1 = c_R^1 + c_Z^1, \\ \phi^1 = (c_A^1 - K_{AO}c_O^1) e^{(k_1+k_2)t_1}, \\ \Omega^1 = (c_R^1 - K_{RZ}c_Z^1) e^{(k_3+k_4)t_1}, \end{cases} \quad (8)$$

with K_{AO} and K_{RZ} being the equilibrium constants of the first and the second chemical reactions, respectively, and which are given by

$$\begin{cases} K_{AO} = k_2/k_1 = c_A^*/c_O^*, \\ K_{RZ} = k_4/k_3 = c_R^*/c_Z^*, \end{cases} \quad (9)$$

and with the assumption

$$D_A = D_O \neq D_R = D_Z \quad (10)$$

the differential equations system (2) and the boundary value problem (equations (4)–(6)) are transformed into

$$\widehat{\delta}_A \varepsilon^1 = \widehat{\delta}_O \Delta^1 = \widehat{\delta}_R \phi^1 = \widehat{\delta}_Z \Omega^1 = 0, \quad (11)$$

$$\begin{cases} t_1 = 0, & r \geq r_0, \\ t_1 > 0, & r \rightarrow \infty, \end{cases} \quad \begin{cases} \phi^1 = \Omega^1 = 0, \\ \varepsilon^1 = c_A^* + c_O^*, \\ \Delta^1 = c_R^* + c_Z^*, \end{cases} \quad (12)$$

$$t_1 > 0, \quad r = r_0,$$

$$D_O \left(\frac{\partial \varepsilon^1}{\partial r} \right)_{r=r_0} = -D_R \left(\frac{\partial \Delta^1}{\partial r} \right)_{r=r_0} = \frac{I_1}{nFA(t_s)}, \quad (13)$$

$$\left(\frac{\partial \phi^1}{\partial r} \right)_{r=r_0} = -K_{AO} \left(\frac{\partial \varepsilon^1}{\partial r} \right)_{r=r_0} e^{(k_1+k_2)t_1}, \quad (14)$$

$$\left(\frac{\partial \Omega^1}{\partial r} \right)_{r=r_0} = \left(\frac{\partial \Delta^1}{\partial r} \right)_{r=r_0} e^{(k_3+k_4)t_1}. \quad (15)$$

The solution of this problem appears in [13] for a complex current time function, and for a current step I_1 it can be easily deduced from this reference by making $u = 0$ and $\omega = 0$. In this way, for the concentrations of species O and R in the electrode surface $c_O^1(r_0, t)$ and $c_R^1(r_0, t)$ we deduce the following expressions:

$$\frac{c_O^1(r_0, t)}{c_A^* + c_O^*} = \frac{1}{1 + K_{AO}} \left\{ 1 - N_s \frac{t_1^{1/2}}{t_s^{2/3}} [S_O(t_1) + K_{AO} X_O(t_1)] \right\}, \quad (16)$$

$$\frac{c_R^1(r_0, t)}{c_R^* + c_Z^*} = \frac{1}{1 + K_{RZ}} \left\{ K_{RZ} \mu_{\text{CEC}} + \gamma N_s \frac{t_1^{1/2}}{t_s^{2/3}} [K_{RZ} S_R(t_1) + X_R(t_1)] \right\}, \quad (17)$$

where

$$N_s = \frac{2I_1}{nFA_0 D_O^{1/2} (c_A^* + c_O^*)}, \quad (18)$$

$$\gamma = \sqrt{D_O/D_R}, \quad (19)$$

$$\mu_{\text{CEC}} = \frac{c_R^* + c_Z^*}{c_A^* + c_O^*}, \quad (20)$$

t_s is given by equation (7) and $S_i(t_1)$ and $X_i(t_1)$ (with $i = O$ or R) are functional series which are given in the appendix.

When the second current step $-I_2$ is applied, as this problem is linear (see equations (2) and (3)), we assume that the solutions of the equations system (2) are now $c_A^2(r, t)$, $c_O^2(r, t)$, $c_R^2(r, t)$ and $c_Z^2(r, t)$, which can be written

$$\begin{cases} c_A^2(r, t) = c_A^1(r, t) + \tilde{c}_A^2(r, t), \\ c_O^2(r, t) = c_O^1(r, t) + \tilde{c}_O^2(r, t), \\ c_R^2(r, t) = c_R^1(r, t) + \tilde{c}_R^2(r, t), \\ c_Z^2(r, t) = c_Z^1(r, t) + \tilde{c}_Z^2(r, t). \end{cases} \quad (21)$$

Therefore, if we define the new variables

$$\begin{cases} \varepsilon^2 = c_A^2 + c_O^2 = \varepsilon^1 + \tilde{\varepsilon}^2, \\ \Delta^2 = c_R^2 + c_Z^2 = \Delta^1 + \tilde{\Delta}^2, \\ \phi^2 = (c_A^2 - K_{AO}c_O^2) e^{(k_1+k_2)t} = \phi^1 + \tilde{\phi}^2, \\ \Omega^2 = (c_R^2 - K_{RZ}c_Z^2) e^{(k_3+k_4)t} = \Omega^1 + \tilde{\Omega}^2, \end{cases} \quad (22)$$

where ε^1 , Δ^1 , ϕ^1 and Ω^1 have already been obtained for the previous step, the boundary value problem now has the following, simplified form in terms only of the new unknown functions $\tilde{\varepsilon}^2$, $\tilde{\Delta}^2$, $\tilde{\phi}^2$ and $\tilde{\Omega}^2$:

$$\begin{cases} t_2 = 0, & r \geq r_0, \\ t_2 > 0, & r \rightarrow \infty, \end{cases} \quad \tilde{\varepsilon}^2 = \tilde{\Delta}^2 = \tilde{\phi}^2 = \tilde{\Omega}^2 = 0, \quad (23)$$

$$t_2 > 0, \quad r = r_0,$$

$$D_O \left(\frac{\partial \tilde{\varepsilon}^2}{\partial r} \right)_{r=r_0} = -D_R \left(\frac{\partial \tilde{\Delta}^2}{\partial r} \right)_{r=r_0}, \quad (24)$$

$$D_O \left(\frac{\partial \tilde{\varepsilon}^2}{\partial r} \right)_{r=r_0} = -\frac{(I_1 + I_2)}{nFA(t_s)}, \quad (25)$$

$$\left(\frac{\partial \tilde{\phi}^2}{\partial r} \right)_{r=r_0} = -K_{AO} \left(\frac{\partial \tilde{\varepsilon}^2}{\partial r} \right)_{r=r_0} e^{(k_1+k_2)t}, \quad (26)$$

$$\left(\frac{\partial \tilde{\Omega}^2}{\partial r} \right)_{r=r_0} = \left(\frac{\partial \tilde{\Delta}^2}{\partial r} \right)_{r=r_0} e^{(k_3+k_4)t} \quad (27)$$

with

$$t_s = t_{bp} + T_1 + t_2. \quad (28)$$

By substituting (21) in (22), and through a similar procedure for the resolution of this problem as that in [13] for the first step, the following expressions for $c_O^2(r, t)$ and $c_R^2(r, t)$ are deduced:

$$\frac{c_O^2(r_0, t)}{c_A^* + c_O^*} = \frac{1}{1 + K_{AO}} \left\{ 1 - \frac{N_s}{t_s^{2/3}} \left[(T_1 + t_2)^{1/2} \{ S_O(T_1 + t_2) + K_{AO} X_O(T_1 + t_2) \} - \frac{I_2 + I_1}{I_1} t_2^{1/2} \{ S_O(t_2) + K_{AO} X_O(t_2) \} \right] \right\}, \quad (29)$$

$$\frac{c_R^2(r_0, t)}{c_R^* + c_Z^*} = \frac{1}{1 + K_{RZ}} \left\{ K_{RZ} \mu_{CEC} + \frac{\gamma N_s}{t_s^{2/3}} \left[(T_1 + t_2)^{1/2} \{ K_{RZ} S_R(T_1 + t_2) + X_R(T_1 + t_2) \} - \frac{I_2 + I_1}{I_1} t_2^{1/2} \{ K_{RZ} S_R(t_2) + X_R(t_2) \} \right] \right\}. \quad (30)$$

Equations (29) and (30) are of great importance since they correspond to the surface concentrations for a CEC mechanism in cyclic chronopotentiometry with two current steps. These expressions have not previously been obtained in the literature. The particular case of the cyclic chronopotentiometry with two current steps leads to the technique known as *current reversal chronopotentiometry*. This technique is of great interest for the study of reaction mechanisms. To date, it has only been applied to planar electrodes because their treatment is less complicated from the theoretical point of view [3,4]. Nevertheless, from a practical viewpoint, this technique offers far more advantages when applied to spherical electrodes like the static mercury drop electrode (SMDE) and the dropping mercury electrode (DME).

The mathematical treatment used for the first and the second current steps can be easily generalised by induction for any number of current steps. Indeed, for the j th step the solutions to the differential equations system can be written in the following way:

$$\begin{cases} \alpha^j = \alpha^{j-1} + \tilde{\alpha}^j, \\ \alpha^{j-1} = \alpha^1 + \sum_{m=2}^{j-1} \tilde{\alpha}^m \end{cases} \quad (31)$$

with $\alpha^j = \varepsilon^j, \Delta^j, \phi^j$ or Ω^j , which fulfil

$$\widehat{\delta}_A \varepsilon^j = \widehat{\delta}_O \Delta^j = \widehat{\delta}_R \phi^j = \widehat{\delta}_Z \Omega^j = 0. \quad (32)$$

Therefore the generalised boundary value problem now has the form

$$\begin{cases} t_j = 0, & r \geq r_0, & \tilde{\varepsilon}^j = \tilde{\Delta}^j = \tilde{\phi}^j = \tilde{\Omega}^j = 0, \\ t_j > 0, & r \rightarrow \infty, \end{cases} \quad (33)$$

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

$$D_O \left(\frac{\partial \tilde{\varepsilon}^j}{\partial r} \right)_{r=r_0} = -D_R \left(\frac{\partial \tilde{\Delta}^j}{\partial r} \right)_{r=r_0}, \quad (34)$$

$$D_O \left(\frac{\partial \tilde{\varepsilon}^j}{\partial r} \right)_{r=r_0} = (-1)^{j+1} \frac{(I_j + I_{j-1})}{nFA(t_s)}, \quad (35)$$

$$\left(\frac{\partial \tilde{\phi}^j}{\partial r} \right)_{r=r_0} = -K_{AO} \left(\frac{\partial \tilde{\varepsilon}^j}{\partial r} \right)_{r=r_0} e^{(k_1+k_2)t}, \quad (36)$$

$$\left(\frac{\partial \tilde{\Omega}^j}{\partial r} \right)_{r=r_0} = \left(\frac{\partial \tilde{\Delta}^j}{\partial r} \right)_{r=r_0} e^{(k_3+k_4)t} \quad (37)$$

with t given by equation (1) and $t_s = t_{bp} + t$.

Conditions (23)–(27) for $j = 2$ (current reversal chronopotentiometry) have a general form identical to the initial and surface conditions (33)–(37) for any $j \geq 2$ (cyclic chronopotentiometry). Therefore, it is evident that we can write (see equations (29) and (30))

$$\frac{c_O^j(r_0, t)}{c_A^* + c_O^*} = \frac{1}{1 + K_{AO}} \left\{ 1 - \frac{N_s}{t_s^{2/3}} \times \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} \{ S_O(t_{n,j}) + K_{AO} X_O(t_{n,j}) \} \right\}, \quad (38)$$

$$\frac{c_R^j(r_0, t)}{c_R^* + c_Z^*} = \frac{1}{1 + K_{RZ}} \left\{ K_{RZ} \mu_{CEC} + \frac{\gamma N_s}{t_s^{2/3}} \times \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} \{ K_{RZ} S_R(t_{n,j}) + X_R(t_{n,j}) \} \right\} \quad (39)$$

with

$$I_0 = 0, \quad (40)$$

$$\begin{cases} t_{n,j} = \sum_{m=n}^{j-1} T_m + t_j, \\ t_{j,j} = t_j. \end{cases} \quad (41)$$

Equations (38) and (39) show that the surface concentrations of species O and R (and also species A and Z which are not shown for the sake of simplicity), can be expressed as a sum of j terms of the same general form due to the fact that the superposition principle is fulfilled in these conditions.

1.2. Other mechanisms

Equations (29) and (30) for current reversal chronopotentiometry and (38) and (39) for cyclic chronopotentiometry can be transformed into those corresponding to EC, CE (schemes I(a) and I(b), respectively) and E processes by making the following simple substitutions:

1.2.1. EC mechanism

In this case, condition $K_{AO} = 0$ (i.e., $c_A^* = 0$) must be fulfilled in order to obtain the response to an EC mechanism. Scheme I becomes scheme I(a), and $c_O^j(r_0, t)$ and $c_R^j(r_0, t)$ take the simpler form

$$\frac{c_O^j(r_0, t)}{c_O^*} = 1 - \frac{N_s}{t_s^{2/3}} \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} S_O(t_{n,j}), \quad (42)$$

$$\frac{c_R^j(r_0, t)}{c_O^*} = \frac{1}{1 + K_{RZ}} \left\{ K_{RZ} \frac{c_R^* + c_Z^*}{c_O^*} + \frac{\gamma N_s}{t_s^{2/3}} \times \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} \{ K_{RZ} S_R(t_{n,j}) + X_R(t_{n,j}) \} \right\}. \quad (43)$$

1.2.2. CE mechanism

The equations corresponding to this process are obtained by making $K_{RZ} = \infty$ (i.e., $c_Z^* = 0$) in equations (38) and (39). Thus, scheme I becomes scheme I(b), and $c^j(r_0, t)$ and $c_R^j(r_0, t)$ now take the form

$$\frac{c_O^j(r_0, t)}{c_A^* + c_O^*} = \frac{1}{1 + K_{AO}} \left\{ 1 - \frac{N_s}{t_s^{2/3}} \times \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} \{ S_O(t_{n,j}) + K_{AO} X_O(t_{n,j}) \} \right\}, \quad (44)$$

$$\frac{c_R^j(r_0, t)}{c_A^* + c_O^*} = \frac{c_R^*}{c_A^* + c_O^*} + \frac{\gamma N_s}{t_s^{2/3}} \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} S_R(t_{n,j}). \quad (45)$$

1.2.3. E mechanism

In this case, $K_{AO} = 0$ and $K_{RZ} = \infty$ must be simultaneously fulfilled, and equations (38) and (39) for $c^j(r_0, t)$ and $c_R^j(r_0, t)$ are transformed into equations (22) and (23) in [11].

1.2.4. Catalytic mechanism (scheme II)

In this case, the deduction is simpler than in the CEC mechanism due to the fact that the solutions corresponding to any current step $(-1)^{j+1} I_j$ can fulfil

$$c_O^j(r, t) + c_R^j(r, t) = c_O^* + c_R^* = cte \quad (46)$$

for any value of $j = 1, 2, 3, \dots$, $r \geq r_0$ and t .

In these conditions, equations (38) and (39) corresponding to a CEC process are transformed into that corresponding to a catalytic mechanism by making

$$\begin{cases} \gamma = 1, \\ \varepsilon^j = \Delta^j = c_O^* + c_R^*, \\ K_{AO} = K_{RZ} = K = c_R^*/c_O^*, \end{cases} \quad (47)$$

so we obtain

$$\frac{c_O^j(r_0, t)}{c_O^* + c_R^*} = \frac{1}{1 + K} \left\{ 1 - \frac{N_s}{t_s^{2/3}}(1 + K) \times \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} X_O(t_{n,j}) \right\}, \quad (48)$$

$$\frac{c_R^j(r_0, t)}{c_O^* + c_R^*} = \frac{1}{1 + K} \left\{ K + \frac{N_s}{t_s^{2/3}}(1 + K) \times \sum_{n=1}^j (-1)^{n+1} (t_{n,j})^{1/2} \frac{I_n + I_{n-1}}{I_1} X_R(t_{n,j}) \right\}. \quad (49)$$

1.3. Other electrode models

1.3.1. Expanding plane electrode model for a DME

In this case, the diffusion operator that appears in the differential equations system that describes the mass transport to the electrode surface is given by

$$\widehat{\delta}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2} - \frac{2x}{3t} \frac{\partial}{\partial x}. \quad (50)$$

The equations for this electrode model are obtained by making $\xi_i^{n,j} = 0$ (see appendix) in series S_i and X_i (with $i = O$ or R) which appear in the expressions of the surface concentrations of species O and R , $c_O^j(r_0, t)$ and $c_R^j(r_0, t)$, throughout this paper.

1.3.2. Static sphere electrode model for an SMDE

In this case, the diffusion operator is given by

$$\widehat{\delta}_i = \frac{\partial}{\partial t} - D_i \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right]. \quad (51)$$

We can obtain the expressions for a static mercury drop electrode (SMDE) of constant area $A = A_0 t_{bp}^{2/3}$ by making $t_{bp} \gg 1$ in all expressions of $c^j(r_0, t)$ and $c_R^j(r_0, t)$ (see equations (A.16)–(A.19)).

1.3.3. Static plane electrode model

For this electrode model, the diffusion operator is given by

$$\widehat{\delta}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2}. \quad (52)$$

The solutions corresponding to a static plane electrode are obtained by making both $t_{bp} \gg 1$ and $\xi_i^{n,j} = 0$ (with $i = O$ or R) in the expressions of $c_O^j(r_0, t)$ and $c_R^j(r_0, t)$ (see equations (A.23) and (A.24)). In this case, from these substitutions the responses obtained for an EC and catalytic mechanisms are identical to those deduced by Herman and Bard [6].

1.4. Transition times

In order to obtain the transition time corresponding to species O and R in the different steps, we make $c_O^j(r_0, \tau_j) = 0$ in equation (38) when $j = 1, 3, 5, \dots$, and $c_R^j(r_0, \tau_j) = 0$ in equation (39) when $j = 2, 4, 6, \dots$.

1.5. Potential time response

The potential time response corresponding to any of the above studied mechanisms, when the j th current step is applied, can be easily deduced by substituting the expressions of the surface concentrations of the oxidized and the reduced species, $c_O^j(r_0, t)$ and $c_R^j(r_0, t)$, for the j th current step (equations (38) and (39), respectively) in the Butler–Volmer equation, in the following way:

$$\frac{I_j}{nFA(t_s)k_s^0} e^{\alpha\eta(t)} = (-1)^{j+1} [c_O^j(r_0, t) - e^{\eta(t)} c_R^j(r_0, t)] \quad (53)$$

with

$$\eta(t) = \frac{nF}{RT} (E(t) - E^0), \quad (54)$$

where k_s^0 is the apparent heterogeneous rate constant of charge transfer at $E(t) = E^0$, with E^0 being the formal standard potential of the electrode reaction.

2. Some applications

In figure 1 we have plotted the different potential time responses obtained when two current steps, I_1 and $I_2 = -I_1$, are applied to a static spherical electrode in similar conditions for all the mechanisms analysed in this paper (equations (38) and (39), (42) and (43) and (44) and (45) for the CEC, EC and CE mechanisms, respectively, and (48) and (49) for the catalytic mechanism). As can be observed in this figure, the CEC and CE mechanisms have an identical transition time τ_1 corresponding to the first reduction. However, the reoxidation transition times of both processes, τ_2 , are not equal. Moreover, we can also observe that the first reduction transition time

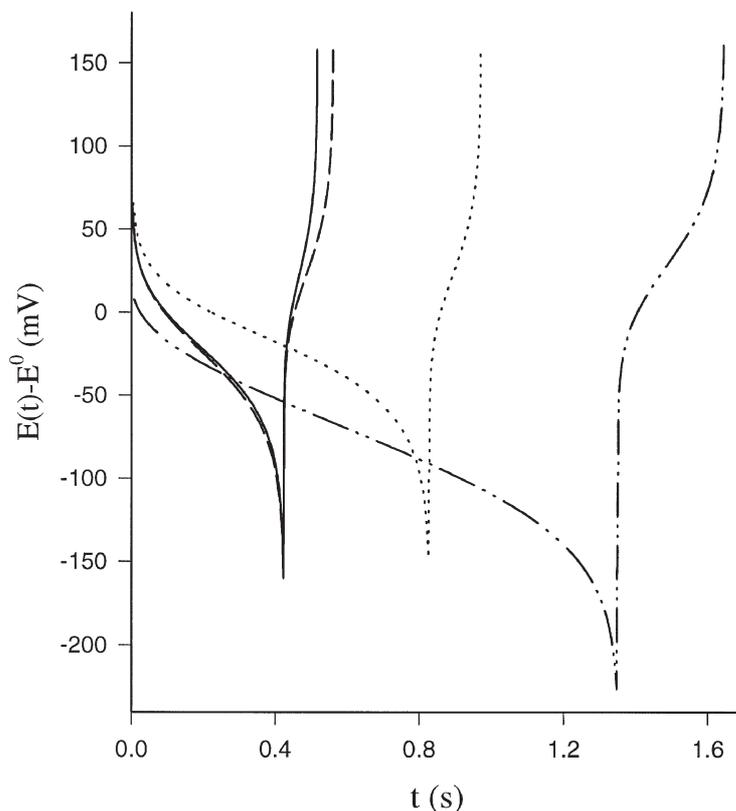


Figure 1. Potential time curves in current reversal chronopotentiometry ($j = 2$) at a static mercury drop electrode (equation (53)). $N_s = 2 \text{ s}^{-1/2}$, $r_0 = 0.06 \text{ cm}$, $\gamma = 1$, $T = 298 \text{ K}$, $n = 1$, $D_O = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $I_2/I_1 = 1$, $k_s = 10^{-3} \text{ cm s}^{-1}$. The values of the rate and equilibrium constants are: CEC (—) $K_{AO} = K_{RZ} = 0.5$, $k_1 + k_2 = k_3 + k_4 = 2 \text{ s}^{-1}$; CE (---) $K_{AO} = 0.5$, $k_1 + k_2 = 2 \text{ s}^{-1}$; EC (···) $K_{RZ} = 0.5$, $k_3 + k_4 = 2 \text{ s}^{-1}$; catalytic (— · — ·) $K = 0.5$, $k_1 + k_2 = 2 \text{ s}^{-1}$.

corresponding to an EC process is greater than in the case of the CE and CEC mechanisms. This fact is in agreement with the schemes of the mechanisms CEC, CE and EC (see schemes I, I(a) and I(b)) since in the EC mechanism no homogeneous chemical reaction competes with the reduction of species O and, therefore, the concentration of the latter on the electrode surface is always greater for an EC mechanism than for the CEC and the CE mechanisms.

In the case of a catalytic process, for the values of the rate constant of the chemical step analysed in figure 1 ($k_1 + k_2 = 2 \text{ s}^{-1}$), transition time τ_1 is much longer than that corresponding to the other processes. This fact is also in agreement with the very nature of the mechanism (see scheme II), in which species O , which is electrochemically consumed on the electrode surface in order to give R , is then regenerated through a homogeneous chemical reaction.

Figure 2 shows the variation of $(dE/dt)^{-1}$ vs. $E - E^0$ (derivative chronopotentiometry) obtained from the data in figure 1. As can be observed, clearly distinguished

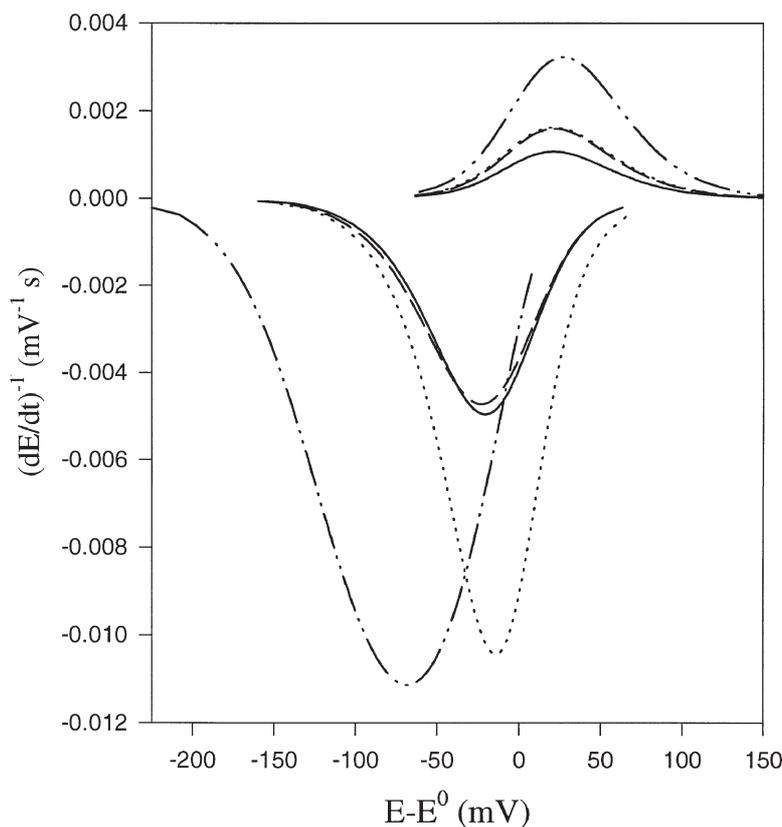


Figure 2. Cyclic derivative chronopotentiograms corresponding to CEC (—), CE (---), EC (···) and catalytic (-·-·-) mechanisms at a static mercury drop electrode. Other conditions as in figure 1.

peaks are obtained with this technique, as we have mentioned in the introduction to this paper. Their height and situation is characteristic for a determined electrode process [2,8,9].

Figures 3 and 4 are an example of application of cyclic chronopotentiometry with $j = 2$ (current reversal chronopotentiometry) in order to determine the rate constants corresponding to the chemical step in an EC mechanism (see scheme I(a)).

In these figures we have plotted values of $((\tau_2 + T_1)/\tau_2)^{1/2}$ or τ_2/T_1 vs. $(k_3 + k_4)T_1$, respectively, for a plane electrode, where T_1 is the time in which the sign of the applied current I_1 is reversed to a value $-I_2$ ($I_2/I_1 = 1$ in this case) with $T_1 \leq \tau_1$, and τ_2 is the transition time corresponding to the second current step (i.e., to the first oxidation of species R), which varies when T_1 changes according to the following equations:

$$\left(\frac{\tau_2 + T_1}{\tau_2}\right)^{1/2} = \frac{(1 + (I_2/I_1))[K_{RZ}/\sqrt{\pi} + X_R^{PL}(\tau_2)]}{K_{RZ}/\sqrt{\pi} + X_R^{PL}(T_1 + \tau_2)}, \quad (55)$$

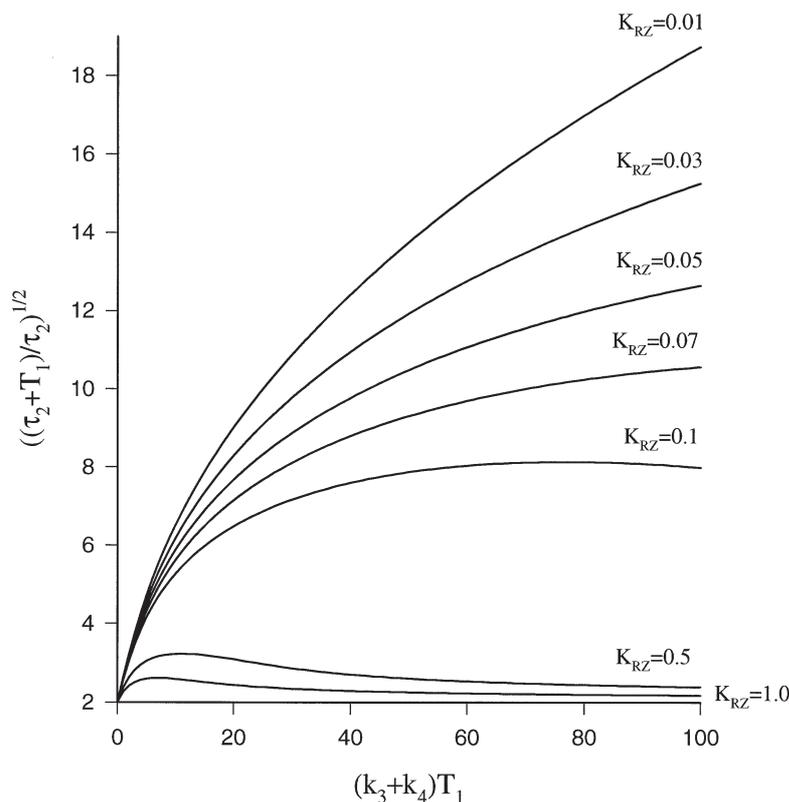


Figure 3. Working curves deduced from current reversal chronopotentiograms in a plane electrode at different values of time in which the current is reversed for an EC mechanism (equation (55)). $I_2/I_1 = 1$. The values of K_{RZ} are on the curves.

$$\frac{\tau_2}{T_1} = \left\{ \left(\left[1 + \frac{I_2}{I_1} \left(2 + \frac{I_2}{I_1} \right) \right] \left[\frac{K_{RZ}/\sqrt{\pi} + X_R^{PL}(\tau_2)}{K_{RZ}/\sqrt{\pi} + X_R^{PL}(T_1 + \tau_2)} \right] \right)^2 - 1 \right\}^{-1}. \quad (56)$$

These equations can be obtained by making $c_R^2(r_0, \tau_2 + T_1) = 0$ in equation (43) with $j = 2$, and $(c_R^* + c_Z^*) = 0$ for the particular case of a plane electrode (see equations (A.23) and (A.24) of the appendix).

The curves shown in figures 3 and 4 can be used by the experimentalist as working curves to determine, from measurements of τ_2 and fixed T_1 , the values of $(k_3 + k_4)$ in s^{-1} by proceeding in the following way:

First, determine the value of the relation $((\tau_2 + T_1)/\tau_2)^{1/2}$ either using figure 3 or τ_2/T_1 in figure 4 and then, once the equilibrium constant K_{RZ} is known, the value of $(k_3 + k_4)$ in s^{-1} can be immediately determined as the abscissa corresponding to the value of the previous time ratios in the appropriate working curve. The curves in figure 3 are suitable for values of $K_{RZ} < 0.1$ and those in figure 4 for values of $K_{RZ} > 0.1$. It should be noted that in this last figure, more than one measurement of τ_2/T_1 is necessary to determine $(k_3 + k_4)$ when the corresponding working curve presents a minimum.

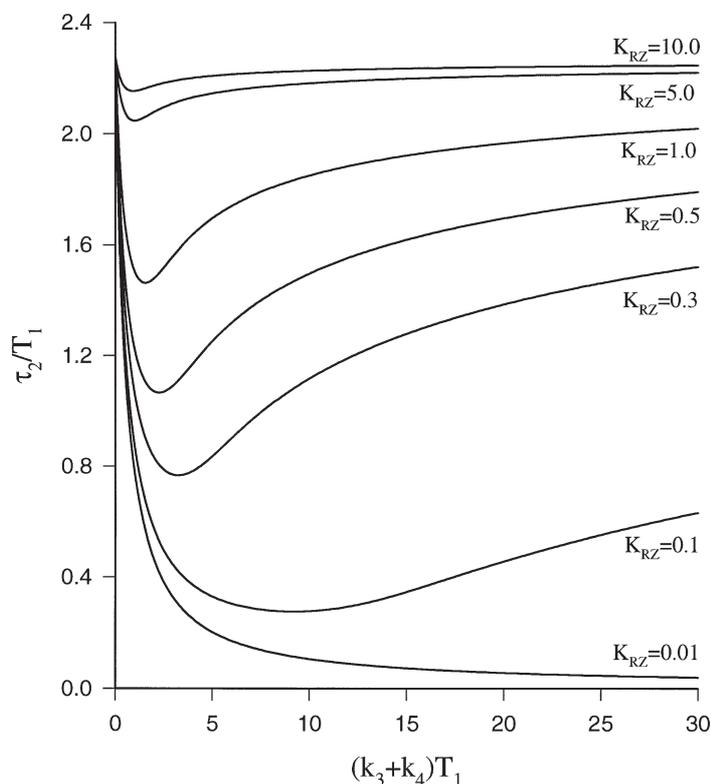


Figure 4. Working curves deduced from current reversal chronopotentiograms in a plane electrode at different values of time in which the current is reversed for an EC mechanism (equation (56)). $I_2/I_1 = 0.2$. The values of K_{RZ} are on the curves.

Notation and definitions

- $c_i^j(r, t_s)$, concentration profiles of the i species (with $i = A, O, R$ or Z) for the j th current step;
- k_f and k_b , rate constants of forward (reduction) and backward (oxidation) processes;
- k_s^0 , apparent heterogeneous rate constant of charge transfer at E^0 ;
- I_j , absolute value of the j th current step applied;
- D_i , diffusion coefficient of species i ($i = A, O, R$ or Z);
- c_i^* , bulk concentration of species i ($i = A, O, R$ or Z);
- k_1, k_2 , rate constants of the preceding chemical reaction in a CEC process; rate constants of the chemical reaction in a catalytic or in a CE process;
- k_3, k_4 , rate constants of the subsequent chemical reaction in a CEC process; rate constant of the chemical reaction in a EC process;

K_{AO} ,	equilibrium constant of the preceding chemical reaction in a CEC process (k_2/k_1); equilibrium constant of the chemical reaction of a CE process;
K_{RZ} ,	equilibrium constant of the subsequent chemical reaction in a CEC process (k_4/k_3); equilibrium constant of the chemical reaction of an EC process;
K ,	equilibrium constant of a catalytic process;
r ,	distance from the centre of the spherical electrode;
r_0 ,	$\left\{ \begin{array}{l} \text{electrode radius at time } t_s (= \zeta t_s^{1/3}) \text{ for a DME,} \\ \text{constant electrode radius for a SMDE;} \end{array} \right.$
t_{bp} ,	blank period used only for a dropping mercury electrode;
t ,	time elapsed between application of the first and the j th current step ($= T_1 + \dots + T_{j-1} + t_j$);
t_j ,	time during which a j current step is applied ($0 \leq t_j \leq T_j$);
τ_j ,	transition time of the j th current step. If j is odd, τ_j corresponds to a reduction process, whereas if j is even, τ_j corresponds to an oxidation one;
T_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 dropping mercury electrode ($= (3m_{Hg}/4\pi d)^{1/3}$);
m_{Hg} and d ,	rate of flow and density of mercury;
$A(t_s)$,	time dependent electrode area of a dropping mercury electrode ($= A_0 t_s^{2/3}$);
A_0 ,	$(4\pi)^{2/3} (3m_{Hg}/d)^{2/3}$ in $s^{-2/3}$;
A ,	constant electrode area for static spherical or planar electrodes;
γ ,	$= \sqrt{D_O/D_R}$;
μ_{CEC} ,	$= (c_A^* + c_O^*)/(c_R^* + c_Z^*)$;
$E(t)$,	time-dependent potential;
E^0 ,	formal standard potential of the electrode reaction;
Γ ,	Euler Gamma function.

Other definitions are conventional.

Appendix

The series S_O and S_R which appear in general equations (38) and (39) and in most of the equations deduced in this paper are given by the expressions

$$S_O(t_{n,j}) = \frac{J^{(0)}(\beta_{n,j})}{\sqrt{\pi}} - \xi_O^{n,j} J^{(1)}(\beta_{n,j}) + (\xi_O^{n,j})^2 \frac{J^{(2)}(\beta_{n,j})}{\sqrt{\pi}} \quad (\text{A.1})$$

and

$$S_R(t_{n,j}) = \frac{J^{(0)}(\beta_{n,j})}{\sqrt{\pi}} - \xi_R^{n,j} J^{(1)}(\beta_{n,j}) + (\xi_R^{n,j})^2 \frac{J^{(2)}(\beta_{n,j})}{\sqrt{\pi}}, \quad (\text{A.2})$$

where

$$\begin{cases} \beta_{n,j} = (t_{n,j}/(t_{bp} + t_{1,j}))^{1/3} & \text{for a dropping mercury electrode,} \\ \beta_{n,j} = 0 & \text{for a static drop mercury electrode} \\ & \text{or a static plane electrode,} \end{cases} \quad (\text{A.3})$$

$$\xi_O^{n,j} = \frac{2\sqrt{D_O t_{n,j}}}{r_0}, \quad (\text{A.4})$$

$$\xi_R^{n,j} = \frac{2\sqrt{D_R t_{n,j}}}{r_0} \quad (\text{A.5})$$

with $r_0 = cte \times t_s^{2/3}$ for a dropping mercury electrode, and r_0 is constant for a static mercury drop electrode (see notation),

$$J^{(0)}(\beta_{n,j}) = 1 + \frac{1}{9}\beta_{n,j}^3 + \frac{7}{270}\beta_{n,j}^6 + \frac{20}{2835}\beta_{n,j}^9 + \dots, \quad (\text{A.6})$$

$$J^{(1)}(\beta_{n,j}) = \frac{1}{4} + \frac{1}{16}\beta_{n,j}^3 + \frac{1}{64}\beta_{n,j}^6 + \dots, \quad (\text{A.7})$$

$$J^{(2)}(\beta_{n,j}) = \frac{1}{6} + \frac{1}{15}\beta_{n,j}^3 + \dots. \quad (\text{A.8})$$

Equations (A.1) and (A.2) have been deduced by making $m = -1/6$ and $k = 0$ in equation (26) in [12]. In this reference we deduced the equations corresponding to the application of a single perturbation to a DME. The equations deduced in this reference correspond to a current which is a function of time and become those corresponding to a current step by making the previously indicated substitutions. As we have demonstrated in this paper, by virtue of the superposition principle, the equations deduced for a single applied current step are valid for any number of successive steps in cyclic chronopotentiometry, by substituting the suitable time intervals in each case, as equations (A.1) and (A.2) indicate.

Likewise, series X_O and X_R which appear in this paper are given by

$$X_O(t_{n,j}) = e^{-(k_1+k_2)t_{n,j}} \sum_{z=0} (H_O)_z(t_{n,j}) \frac{((k_1 + k_2)t_{n,j})^z}{z!}, \quad (\text{A.9})$$

$$X_R(t_{n,j}) = e^{-(k_3+k_4)t_{n,j}} \sum_{z=0} (H_R)_z(t_{n,j}) \frac{((k_3 + k_4)t_{n,j})^z}{z!}, \quad (\text{A.10})$$

where

$$(H_O)_z(t_{n,j}) = J_z^{(0)}(\beta_{n,j}) - \xi_O^{n,j} J_z^{(1)}(\beta_{n,j}) + (\xi_O^{n,j})^2 J_z^{(2)}(\beta_{n,j}), \quad (\text{A.11})$$

$$(H_R)_z(t_{n,j}) = J_z^{(0)}(\beta_{n,j}) - \xi_R^{n,j} J_z^{(1)}(\beta_{n,j}) + (\xi_R^{n,j})^2 J_z^{(2)}(\beta_{n,j}), \quad (\text{A.12})$$

and

$$J_z^{(0)}(\beta_{n,j}) = 1 + \frac{1}{3(2z+3)}\beta_{n,j}^3 + \frac{7}{18(2z+3)(2z+5)}\beta_{n,j}^6 + \frac{20}{27(2z+3)(2z+5)(2z+7)}\beta_{n,j}^9 + \dots, \quad (\text{A.13})$$

$$J_z^{(1)}(\beta_{n,j}) = \frac{1}{4(z+1)} + \frac{1}{8(z+1)(z+2)}\beta_{n,j}^3 + \frac{1}{32(z+1)(z+2)(z+3)}\beta_{n,j}^6 + \dots, \quad (\text{A.14})$$

$$J_z^{(2)}(\beta_{n,j}) = \frac{1}{2(2z+3)} + \frac{1}{(2z+3)(2z+5)}\beta_{n,j}^3 + \dots. \quad (\text{A.15})$$

The series S_O , S_R , X_O and X_R take a simpler form for electrodes whose areas are not dependent on time as in the following cases.

Static spherical electrode

Equations (A.1)–(A.15) are transformed into those corresponding to a static spherical electrode by making $t_{bp} \gg t$. Indeed, in this case the variable on time area $A(t)$ becomes a constant area $A \cong A_0 t_{bp}^{2/3}$. If we take that into account, this assumption implies also that $\beta_{n,j} = 0$, and equations (A.1) and (A.2) are simplified to

$$S_O^{SPH}(t_{n,j}) = \frac{1}{\sqrt{\pi}} - \frac{\xi_O^{n,j}}{4} + (\xi_O^{n,j})^2 \frac{1}{6\sqrt{\pi}} - \dots, \quad (\text{A.16})$$

$$S_R^{SPH}(t_{n,j}) = \frac{1}{\sqrt{\pi}} - \frac{\xi_R^{n,j}}{4} + (\xi_R^{n,j})^2 \frac{1}{6\sqrt{\pi}} - \dots, \quad (\text{A.17})$$

and

$$X_O^{SPH}(t_{n,j}) = e^{-(k_1+k_2)t_{n,j}} \sum_{z=0} \left(\frac{1}{p_{2z+1}} - \frac{\xi_O^{n,j}}{4(z+1)} + \frac{(\xi_O^{n,j})^2}{2(2z+3)p_{2z+1}} - \dots \right) \times \frac{((k_1+k_2)t_{n,j})^z}{z!}, \quad (\text{A.18})$$

$$X_R^{SPH}(t_{n,j}) = e^{-(k_3+k_4)t_{n,j}} \sum_{z=0} \left(\frac{1}{p_{2z+1}} - \frac{\xi_R^{n,j}}{4(z+1)} + \frac{(\xi_R^{n,j})^2}{2(2z+3)p_{2z+1}} - \dots \right) \times \frac{((k_3+k_4)t_{n,j})^z}{z!}, \quad (\text{A.19})$$

$$p_{2z+1} = \frac{2\Gamma(1+(2z+1)/2)}{\Gamma(1/2+(2z+1)/2)}. \quad (\text{A.20})$$

Moreover, in all the expressions of the surface concentrations, $c_O^j(r_0, t)$ and $c_R^j(r_0, t)$, we must change $N_s/t_s^{2/3}$ for N_s' with

$$N_s' = \frac{2I_1}{nFA\sqrt{D_O}(c_O^* + c_A^*)}, \quad (\text{A.21})$$

where

$$A = A_0 t_{\text{bp}}^{2/3} = \text{cte}. \quad (\text{A.22})$$

Static planar electrode

To obtain the solutions corresponding to a planar electrode of area A , we must make $r_0 \rightarrow \infty$ ($\xi_O^{n,j} = \xi_R^{n,j} = 0$) in equations (A.16)–(A.19), so we deduce

$$S_O^{PL}(t_{n,j}) = S_R^{PL}(t_{n,j}) = \frac{1}{\sqrt{\pi}}, \quad (\text{A.23})$$

$$X_O^{PL}(t_{n,j}) = X_R^{PL}(t_{n,j}) = e^{-kt_{n,j}} \sum_{z=0}^{\infty} \frac{(kt_{n,j})^z}{p_{2z+1} z!}, \quad (\text{A.24})$$

where $k = k_1 + k_2$ for X_O , and $k = k_3 + k_4$ for X_R . In this case, we must also change in all the expressions of surface concentrations $c_O^j(r_0, t)$ and $c_R^j(r_0, t)$, $N_s/t_s^{2/3}$ for N_s' given in equation (A.21).

Acknowledgements

The authors greatly appreciate financial support from the Dirección General de Investigación Científica y Técnica (Project No. PB96-1095) and the Comunidad Autónoma de la Región de Murcia (Project No. FI-con 96/9).

References

- [1] A.J. Bard and L.R. Faulkner, *Electrochemical Methods* (Wiley, New York, 1980) chapter 5.
- [2] S. Bi and J. Yu, *J. Electroanal. Chem.* 405 (1996) 51.
- [3] O. Dracka, *Collect. Czech. Chem. Comm.* 25 (1960) 338.
- [4] O. Fischer and O. Dracka, *J. Electroanal. Chem.* 75 (1977) 301.
- [5] Z. Galus, *Fundamentals of Electrochemical Analysis*, 2nd edn. (Ellis Horwood, Chichester, 1994).
- [6] H.B. Herman and A.J. Bard, *Anal. Chem.* 36 (1964) 510.
- [7] J. Heyrovsky and J. Kuta, *Principles of Polarography* (Academic Press, New York, 1996) chapter 2.
- [8] M.J. Honeychurch and M.J. Ridd, *J. Electroanal. Chem.* 418 (1996) 185.
- [9] W. Jin and J. Wang, *J. Electroanal. Chem.* 306 (1991) 31.
- [10] D.D. McDonald, *Transient Techniques in Electrochemistry* (Plenum Press, New York, 1977) chapter 3.
- [11] A. Molina, J. González, C. Serna and L. Camacho, *J. Math. Chem.* 20 (1996) 169.
- [12] A. Molina, M. López-Tenés and C. Serna, *J. Electroanal. Chem.* 278 (1990) 35.
- [13] A. Molina, M. López-Tenés and C. Serna, *J. Electroanal. Chem.* 346 (1993) 53.

- [14] A. Molina, F. Martínez-Ortiz, J. Zapata and J. Albaladejo, *J. Electroanal. Chem.* 227 (1987) 1.
- [15] C. Serna, A. Molina, L. Camacho and J.J. Ruiz, *Anal. Chem.* 65 (1993) 215.