Application of the superposition principle to the study of multistep electrode processes and systems with several components in chronopotentiometry with programmed current. Part I

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In this paper we present the solution to the differential equations system corresponding to the problem of multistep processes and systems with several components when a programmed current-time function is applied to planar and spherical electrodes. The analytical solutions have been obtained in both cases, by a recurrent procedure, which facilitates the numerical determination of results. This solution has been found for an expanding spherical electrode, since by using simple substitutions it is transformed into that corresponding to a stationary spherical electrode, to an expanding plane electrode or to a stationary plane electrode.

1. Introduction

From the point of view of both electrochemistry and chemical kinetics, the study of electrode processes in which oxidation or reduction reactions take place in several steps is of great interest. Thus, for example, fullerenes in general and C_{60} in particular can present up to five reversible one electron reductions [1,2].

The theoretical study of electrode processes that involve several successive steps in electrochemical techniques with controlled current is a very old one [3,4]. However, those papers which tackled these processes when a determined current is applied to an electrode have only considered the case of planar diffusion. Yet plane electrodes are not the most suitable for the study of such processes owning to their poorly reproducible surface which tends to accumulate contamination on the electrode-solution interface. More suitable, as is well known, are those electrodes of spherical geometry, such as the dropping mercury electrode (DME) and the static mercury electrode (SMDE), which show a clean, perfectly reproducible and con-

tamination-free surface. Moreover, by using a time-variable current in this last type of electrodes, it is possible to eliminate most of the double layer effects if we work with not very high concentrations of electroactive species and/or small electrode radii.

The main aim of this paper is to find a general analytical expression for the response of this type of electrode processes in chronopotentiometry with a programmed current. This technique consists of applying a current that is a known function of time through a function generator. Due to the fact that in chronopotentiometry the response obtained (potential-time curve) is a function of the concentrations of species participating in the surface of the electrode, it is possible, by determining the analytical expressions for these concentrations, to characterize the process thermodynamically and kinetically by analysis of the variation of the potential over time [5]. We have also deduced the expression corresponding to the response obtained for the system of several components whose deduction turns out to be much simpler than that corresponding to multistep processes.

The general study we present is applicable to small spherical electrodes of constant and variable area (SMDE and DME, respectively) and to planar electrodes, such as a stationary plane and the expanding plane electrode model for the DME. The solution for this type of problem is not easy. Nevertheless, certain situations do exist where it is easy to obtain such expressions for these cases. In these situations, a problem of k steps can be treated as k independent problems of only one step. To this end, we must demonstrate that not only is the system of equations posed linear but so is also the boundary value problem and, therefore, this can be expressed in the same general form for any step; i.e. the superposition principle is fulfilled [6,7]. Taking into account the above considerations, we have deduced general expressions for the concentrations of species participating in the different steps in terms of distance and time for the electrode models mentioned above.

From these general expressions, we obtain expressions which correspond to the concentrations at the surface of the electrode by substituting in them $r = r_0$ (for spherical diffusion) or $x = 0$ (for planar diffusion). Once the surface concentrations have been obtained, the potential-time response of the process is deduced immediately by substituting them in the Butler-Volmer equation or in the Nernst equation, depending on whether the charge transfer process is irreversible or reversible.

Due to the fact that these solutions have been obtained by a recurrent procedure based only on the linearity of the operators and on the related boundary value problem, they are independent of the method applied in solving the systems of differential equations participating in the first step. Moreover, the recurrent form of the solutions facilitates numerical determination of the results corresponding to the different steps.

Furthermore, using simple substitutions, the solution found for the expanding spherical electrode (DME) transforms into that corresponding to a stationary spherical electrode, to an expanding plane electrode or to a stationary plane elec-

trode. Thus, it can be concluded that for these processes, the superposition principle is fulfilled in chronopotentiometry for different geometries and for whatever the values of the diffusion coefficients of the participating species may be.

2. Theory

Let us suppose that species O_1 is reduced in k stages in line with the following scheme:

$$\left.\begin{aligned}
O_1 + n_1 e^- \, O_2\,, && E_1^0\,, \\
O_2 + n_2 e^- \, O_3\,, && E_2^0\,, \\
\vdots && \\
O_j + n_j e^- \, O_{j+1}\,, && E_j^0\,, \\
\vdots && \\
O_k + n_k e^- \, O_{k+1}\,, && E_k^0\,.
\end{aligned}\right\} \qquad (\mathrm{I})$$

Process (I) can only be studied with techniques using programmed current for the case in which the reduction potentials for the individual charge transfer steps are sufficiently well separated so that the chronopotentiometric response or potential-time curve shows perfectly defined k waves, each of which corresponds to individual steps in the overall process [4]. In any other case the initial and boundary conditions of this problem cannot be established reliably in terms of time.

If we apply a cathodic current-time function $I(t)$ of the form

$$I(t) = I_0 t^u e^{\omega t} \quad \text{with} \quad I_0 > 0, u \geqslant 0, \omega \geqslant 0\,, \tag{1}$$

when O_1 is the only species initially present in the solution – which contains an excess of any electrolyte so that transport through conduction need not be taken into account – mass transport from the bulk of the solution to the electrode surface, for process (I), is described by the differential equation system

$$\hat{\delta}_{O_i} C_{O_i} = 0 \quad \text{for} \quad i = 1, 2, \ldots, k+1\,, \tag{2}$$

where $\hat{\delta}_{O_i}$ is the diffusion transport operator given by Fick's second law. For an expanding spherical electrode (i.e., the dropping mercury electrode, DME) the above operator is given by [8,9]

$$\hat{\delta}_{O_i} = \frac{\partial}{\partial t} - D_{O_i} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] + v \frac{\partial}{\partial r}\,, \tag{3}$$

where D_{O_i} is the diffusion coefficient of species O_i and v is the convection velocity of the electrode whose value is given by

$$v = \frac{\zeta^3}{3r^2} \tag{4}$$

with ζ being the radius of the DME for $t_s = 1$ s (see Notations and definitions).

If in eq. (3) the following change in variable is introduced:

$$x = r - \zeta t^{1/3}, \tag{5}$$

and if it is supposed that the thickness of the diffusion layer, which is of the order of $\sqrt{D_{O_i}t}$, is substantially less than the radius of the sphere and the second term in the square brackets on the right hand side of (3) is neglected, then this equation becomes [9]

$$\hat{\delta}_{O_i} = \frac{\partial}{\partial t} - D_{O_i} \frac{\partial^2}{\partial x^2} - \frac{2x}{3t} \frac{\partial}{\partial x}. \tag{6}$$

This operator corresponds to the model of the planar electrode in the expansion for the DME, which has been widely used for this electrode.

For stationary or constant area electrodes, the convective term must be removed, which yields

$$\hat{\delta}_{O_i} = \frac{\partial}{\partial t} - D_{O_i} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] \tag{7}$$

for a stationary spherical electrode, from eq. (3), and yields

$$\hat{\delta}_{O_i} = \frac{\partial}{\partial t} - D_{O_i} \frac{\partial^2}{\partial x^2} \tag{8}$$

for a stationary planar electrode, from eq. (6).

As the operators defined by eqs. (3) and (6)–(8) are linear, the system of differential equations (2) is linear in all cases [7]. In this paper, we consider the operator corresponding to a DME (eq. (3)) since it is the most complex and, it is possible to deduce solutions which correspond to remaining, simpler models (eqs. (6)–(8)) as particular cases of the solutions found for eq. (2).

We will suppose that by using a function generator [10] we apply the current-time function given by eq. (1), which is reduced to a power function of time when $\omega = 0$ ($I(t) = I_0 t^u$), to an exponential function of time when $u = 0$ ($I(t) = I_0 e^{\omega t}$), and to a current step or constant current when $u = \omega = 0$ ($I(t) = I_0$). In general, this current-time function must be used after a blank period, if it is applied to dynamic electrodes such as the DME. This blank period has no physical significance in stationary electrodes (eqs. (7) and (8)).

In order to analyse the response of process (I) to the application of a programmed current given by eq. (1), we will suppose, as hitherto expounded, that the normal potentials corresponding to the different steps fulfill the condition

$$E^0_{j-1} \ll E^0_j \ll E^0_{j+1} \tag{9}$$

and that step j takes place during a time t_j $(0 \leqslant t_j \leqslant \tau_{O_j})$, τ_{O_j} being the transition time of species O_j. When $t_j = \tau_{O_j}$, the electrode surface concentration of species O_j becomes zero. We must keep in mind, moreover, that the reduction of O_j (species produced in step $j - 1$) is accompanied by the reduction of the previous $j - 1$ species $(O_1, O_2, \ldots, O_{j-1})$, whose surface concentrations are null, due to their corresponding transition times $(\tau_{O_1}, \tau_{O_2}, \ldots, \tau_{O_{j-1}})$ having been already reached. When the transition time of step j, τ_{O_j}, is reached, the potential evolves to values of the order of E_{j+1}^0, for which species O_{j+1} (produced in step j) starts to be reduced.

Thus, the total time elapsed from the application of the current to step j is given by

$$\left. \begin{array}{l} t = \tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_{j-1}} + t_j , \\ 0 \leqslant t_j \leqslant \tau_{O_j} . \end{array} \right\} \tag{10}$$

For any step prior to j, $t_j = 0$, while for any step after j, t_j is constant $(= \tau_{O_j})$.

Bearing in mind the above, the boundary value problem for the first step $(0 \leqslant t_1 \leqslant \tau_{O_1})$, supposing that there is no accumulation of matter at the electrode surface, is given by

$$\left. \begin{array}{l} t_1 = 0; r \geqslant r_0 , \\ t_1 > 0; r \to \infty , \end{array} \right\} \quad \begin{array}{l} C_{O_1}^1(r, t) = C_{O_1}^* , \\ C_{O_i}^1(r, t) = 0 , \quad i = 2, 3, \ldots k + 1 , \end{array} \tag{11}$$

$$t_1 > 0; r = r_0 ,$$

$$D_{O_1} \left(\frac{\partial C_{O_1}^1}{\partial r} \right)_{r=r_0} = -D_{O_2} \left(\frac{\partial C_{O_2}^1}{\partial r} \right)_{r=r_0} = \frac{I_0 t_1^u e^{\omega t_1}}{n_1 F A(t_s)} \tag{12}$$

with

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

$$t_s = t_{bp} + t_1 . \tag{14}$$

Henceforth, the superscript in the concentrations of different O_j species (with $j = 1, 2, \ldots k + 1$) refers to the number of the step being considered (see Notations and definitions).

The problem for the first step given by eq. (2) for $i = 1, 2$ and eqs. (11)–(14) has been solved in a previous paper [11] in which solutions $C_{O_1}^1(r, t)$ and $C_{O_2}^1(r, t)$ were obtained. The particular values of these solutions at the surface of the electrode, $C_{O_1}^1(r_0, t)$ and $C_{O_2}^1(r_0, t)$, are given in Appendix (eqs. (A.1) and (A.2)). The transition time for the first step, τ_{O_1}, is attached when $C_{O_1}^1(r_0, \tau_{O_1}) = 0$. For $t_1 = \tau_{O_1}$, the potential evolves to values of the order of E_2^0 and it is then that the reduction of species O_2 occurs.

In the second step, the species participating are O_1, O_2 and O_3 (see scheme (I)).

As differential equations (2) are linear, any linear combination of their solutions

is also a solution for them. Thus, we will suppose that $C_{O_1}^2(r,t)$, $C_{O_2}^2(r,t)$ and $C_{O_3}^2(r,t)$ have the form

$$\left.\begin{aligned} C_{O_1}^2(r,t) &= C_{O_1}^1(r,t) + \tilde{C}_{O_1}^2(r,t)\,, \\ C_{O_2}^2(r,t) &= C_{O_2}^1(r,t) + \tilde{C}_{O_2}^2(r,t)\,, \\ C_{O_3}^2(r,t) &= \tilde{C}_{O_3}^2(r,t)\,, \end{aligned}\right\} \tag{15}$$

where $t = \tau_{O_1} + t_2$ and $t_s = t_{bp} + t$, with $0 \leqslant t_2 \leqslant \tau_{O_2}$, $C_{O_1}^1(r,t)$ and $C_{O_2}^1(r,t)$ are the solutions found in ref. [11] for the first step and $\tilde{C}_{O_1}^2(r,t)$, $\tilde{C}_{O_2}^2(r,t)$ and $\tilde{C}_{O_3}^2(r,t)$ are the new unknown quantities to be determined in this second step.

The boundary value problem for the second step is given by

$$\left.\begin{aligned} t_2 = 0; r \geqslant r_0\,, \\ t_2 > 0; r \to \infty\,, \end{aligned}\right\} \quad \begin{aligned} &C_{O_1}^2(r,t) = C_{O_1}^1(r,t), C_{O_2}^2(r,t) = C_{O_2}^1(r,t)\,, \\ &C_{O_3}^2(r,t) = 0\,, \end{aligned} \tag{16}$$

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

$$C_{O_1}^2(r_0,t) = 0\,, \tag{17}$$

$$D_{O_1}(n_1 + n_2)\left(\frac{\partial C_{O_1}^2}{\partial r}\right)_{r=r_0} + D_{O_2}n_2\left(\frac{\partial C_{O_2}^2}{\partial r}\right)_{r=r_0} = \frac{I_0 t^u e^{\omega t}}{FA(t_s)}\,, \tag{18}$$

$$D_{O_1}\left(\frac{\partial C_{O_1}^2}{\partial r}\right)_{r=r_0} + D_{O_2}\left(\frac{\partial C_{O_2}^2}{\partial r}\right)_{r=r_0} + D_{O_3}\left(\frac{\partial C_{O_3}^2}{\partial r}\right)_{r=r_0} = 0 \tag{19}$$

with

$$t_s = t_{bp} + \tau_{O_1} + t_2\,. \tag{20}$$

Condition (17) refers to the fact that for $t > \tau_{O_1}$, the surface concentration of species O_1 is zero for any step after the first one. Eqs. (18) and (19) refer to the surface flow produced by the current applied and the non-accumulation of matter at the electrode surface, respectively.

By introducing eqs. (15) into eqs. (16)–(19) and taking into account that $C_{O_1}^1(r,t)$ and $C_{O_2}^1(r,t)$ fulfill condition (12) for any t, we obtain the following simplified initial and limit conditions for the second step; these conditions have the advantage that they have null initial values:

$$\left.\begin{aligned} t_2 = 0; r \geqslant r_0\,, \\ t_2 > 0; r \to \infty\,, \end{aligned}\right\} \quad \tilde{C}_{O_i}^2(r,t) = 0\,, \quad i = 1, 2, 3\,, \tag{21}$$

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

$$\tilde{C}_{O_1}^2(r_0, t) = -C_{O_1}^1(r_0, t) \,, \tag{22}$$

$$D_{O_1}(n_1 + n_2)\left(\frac{\partial \tilde{C}_{O_1}^2}{\partial r}\right)_{r=r_0} + D_{O_2}n_2\left(\frac{\partial \tilde{C}_{O_2}^2}{\partial r}\right)_{r=r_0} = 0 \,, \tag{23}$$

$$\sum_{i=1}^{3} D_{O_i}\left(\frac{\partial \tilde{C}_{O_i}^2}{\partial r}\right)_{r=r_0} = 0 \,. \tag{24}$$

This problem has been recently solved for a dropping mercury electrode [12] and the solutions for this step, $C_{O_1}^2(r, t)$, $C_{O_2}^2(r, t)$ and $C_{O_3}^2(r, t)$, are given in Appendix (eqs. (A.16)–(A.18)) for $r = r_0$. Furthermore, the expression corresponding to the second transition time, τ_{O_2}, is given in eq. (A.22).

For $t = \tau_{O_1} + \tau_{O_2} + t_3$ (with $0 \leqslant t_3 \leqslant \tau_{O_3}$), the third step takes place and species O_3 is reduced.

For this step, the concentrations of the implicated species O_1, O_2, O_3 and O_4, can be written in the following way:

$$\left.\begin{array}{l} C_{O_1}^3(r, t) = C_{O_1}^2(r, t) + \tilde{C}_{O_1}^3(r, t) \,, \\[4pt] C_{O_2}^3(r, t) = C_{O_2}^2(r, t) + \tilde{C}_{O_2}^3(r, t) \,, \\[4pt] C_{O_3}^3(r, t) = C_{O_3}^2(r, t) + \tilde{C}_{O_3}^3(r, t) \,, \\[4pt] C_{O_4}^3(r, t) = \tilde{C}_{O_4}^3(r, t) \,. \end{array}\right\} \tag{25}$$

As the transition times of O_1 and O_2 have already been attached, for the surface electrode the following must be fulfilled:

$$C_{O_1}^3(r_0, t) = C_{O_2}^3(r_0, t) = 0 \,. \tag{26}$$

Taking into account eqs. (26), (17)–(19) and also eqs. (25), the boundary value problem for the third step is given by

$$\left.\begin{array}{l} t_3 = 0; r \geqslant r_0 \,, \\[6pt] t_3 > 0; r \to \infty \,, \end{array}\right\} \quad \tilde{C}_{O_i}^3(r, t) = 0 \,, \quad i = 1, \ldots, 4 \,, \tag{27}$$

$$t_3 > 0; r = r_0 \,,$$

$$\tilde{C}_{O_1}^3(r_0, t) = 0 \,, \tag{28}$$

$$\tilde{C}_{O_2}^3(r_0, t) = -C_{O_2}^2(r_0, t) \,, \tag{29}$$

$$\sum_{i=1}^{3} D_{O_i}\left[\sum_{l=i}^{3} n_l\right]\left(\frac{\partial \tilde{C}_{O_i}^3}{\partial r}\right)_{r=r_0} = 0 \,, \tag{30}$$

$$\sum_{i=1}^{4} D_{O_i} \left(\frac{\partial \tilde{C}_{O_i}^3}{\partial r} \right)_{r=r_0} = 0. \tag{31}$$

For any step $j \geqslant 2$, the linearity of the system of equations (2) enables us to write in general

$$\left. \begin{array}{l} C_{O_j}^j(r,t) = C_{O_j}^{j-1}(r,t) + \tilde{C}_{O_j}^j(r,t)\,, \\[2mm] C_{O_{j+1}}^j(r,t) = \tilde{C}_{O_{j+1}}^j(r,t) \end{array} \right\} \tag{32}$$

with

$$t = \tau_{O_1} + \ldots + \tau_{O_{j-1}} + t_j\,. \tag{33}$$

Taking into account that for any intermediate step $j > 1$, the condition

$$C_{O_1}^j(r_0,t) = C_{O_2}^j(r_0,t) = \ldots = C_{O_{j-1}}^j(r_0,t) = 0 \tag{34}$$

for the previous $j - 1$ steps is fulfilled, since $j - 1$ transition times have already been attached, it is easily demonstrated by induction that the boundary value problem is only dependent on the unknown quantities $\tilde{C}_{O_i}^j$ ($i = 1, 2, \ldots j + 1$) and on the concentration of the species $j - 1$ in the previous step. These are given in the following general form for any intermediate step j with $3 \leqslant j \leqslant k$ and t given by eq. (33):

$$\left. \begin{array}{l} t_j = 0; r \geqslant r_0\,, \\[3mm] t_j > 0; r \to \infty\,, \end{array} \right\} \quad \tilde{C}_{O_i}^j(r,t) = 0 \quad i = 1,\ldots,j+1, \tag{35}$$

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

$$\tilde{C}_{O_i}^j(r_0,t) = 0, \quad i = 1,2,\ldots,j-2\,, \tag{36}$$

$$\tilde{C}_{O_{j-1}}^j(r_0,t) = -C_{O_{j-1}}^{j-1}(r_0,t)\,, \tag{37}$$

$$\sum_{i=1}^{j} D_{O_i} \left[\sum_{l=i}^{j} n_l \right] \left(\frac{\partial \tilde{C}_{O_i}^j}{\partial r} \right)_{r=r_0} = 0\,, \tag{38}$$

$$\sum_{i=1}^{j+1} D_{O_i} \left(\frac{\partial \tilde{C}_{O_i}^j}{\partial r} \right)_{r=r_0} = 0\,. \tag{39}$$

Therefore, for $j \geqslant 3$, the superposition principle is fulfilled [7] since the general expressions for the boundary value problem for any step j with $3 \leqslant j \leqslant k$ (eqs. (35)–(39)) are identical to those for the third step (eqs. (27)–(31)), i.e. we have reduced a problem of k steps to one of k independent problems of only one step. Taking into account the solutions found for the first and second steps and conditions (35)–(39),

we deduce that the concentrations of the different species for $j \geqslant 2$ are given by the following recurrent general expressions:

$$C_{O_j}^j(r_0, t) = C_{O_j}^{j-1}(r_0, t) + \gamma_{j-1,j} \frac{n_{j-1} + n_j}{n_j} C_{O_{j-1}}^{j-1}(r_0, t) G_{O_{j-1},O_j}^j, \tag{40}$$

$$C_{O_{j+1}}^j(r_0, t) = -\gamma_{j-1,j+1} \frac{n_{j-1}}{n_j} C_{O_{j-1}}^{j-1}(r_0, t) G_{O_{j-1},O_{j+1}}^j, \tag{41}$$

where G_{O_i,O_l}^j series is given by eq. (A.23) and $\gamma_{i,l}$ is given in Notations and definitions.

Owing to the simplicity of eqs. (40) and (41) and the easiness of their calculation implied by their recurrent form, they offer important advantages in finding the concentrations of the different intermediate species and the different transition times. The calculation of the transition time of step j is immediate, since it suffices to make $C_{O_j}^j(r_0, t) = 0$ in eq. (40) with $t = \tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j}$.

3. Particular cases

(a) Spherical electrodes with $D_{O_1} = D_{O_2} = \ldots = D_{O_{j+1}}$

In this case the following is fulfilled:

$$\gamma_{i,l} = 1 \quad \text{with} \quad i = 1, 2, \ldots, j - 1 \quad \text{and} \quad l = (i + 1) \text{ or } (i + 2), \tag{42}$$

and the G_{O_i,O_l}^j series for the intermediate j step is simplified to

$$G_{O_i,O_l}^j = 1 \quad \text{with} \quad i = j - 1 \quad \text{and} \quad l = j \text{ or } j + 1 \tag{43}$$

The general expressions for the surface concentrations (eqs. (40) and (41)) and the transition time for step j are notably simplified. In this case, the following is fulfilled for any value of r and t:

$$C_{O_1}^j(r, t) + C_{O_2}^j(r, t) + \ldots + C_{O_{j+1}}^j(r, t) = C_{O_1}^*, \tag{44}$$

and taking into account the expressions for $C_{O_1}^1(r_0, t)$ and $C_{O_2}^1(r_0, t)$ given by eqs. (A.1) and (A.2), eqs. (40) and (41) take the simpler form

$$C_{O_j}^j(r_0, t) = \frac{\sum_{i=1}^j n_i}{n_j} C_{O_1}^* - \frac{n_1}{n_j} C_{O_1}^* N_s \frac{t^{u+1/2}}{t_s^{2/3}} S_{DME,O_1}, \tag{45}$$

$$C_{O_{j+1}}^j(r_0, t) = -\frac{\sum_{i=1}^{j-1} n_i}{n_j} C_{O_1}^* + \frac{n_1}{n_j} C_{O_1}^* N_s \frac{t^{u+1/2}}{t_s^{2/3}} S_{DME,O_1} \tag{46}$$

with

$$t_s = t_{bp} + \tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_{j-1}} + t_j \,. \tag{47}$$

S_{DME,O_1} is given by eq. (A.5), t by eq. (33) and N_S by eq. (A.3).

In order to deduce the transition time of step j, we impose $C_{O_j}^j(r_0, \tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j}) = 0$ in eq. (45), obtaining

$$\frac{(\tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j})^{u+1/2}}{(t_{bp} + \tau_{O_1} + \ldots + \tau_{O_j})^{2/3}} = \frac{\sum_{i=1}^{j} n_i}{n_1 N_s S_{DME,O_1}} \,, \tag{48}$$

where S_{DME,O_1} has to be calculated for $t = \tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j}$.

The expression for the transition time corresponding to a stationary spherical electrode of constant area $A = A_0 t_{bp}^{2/3}$ is obtained by introducing the condition $t_{bp} \gg t$ in eq. (48),

$$(\tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j})^{u+1/2} = \frac{\sum_{i=1}^{j} n_i}{n_1 N_s^* S_{SMDE,O_1}} \tag{49}$$

with

$$N_s^* = \frac{2I_0}{n_1 FA \sqrt{D_{O_1}} \, C_{O_1}^*} \tag{50}$$

and S_{SMDE,O_1} is given by eq. (A.14).

(b) Planar electrodes and any value of D_{O_i}

To obtain the general expressions for planar electrodes, we have imposed $r_0 \to \infty$ such that eq. (43) is fulfilled for any value of the diffusion coefficients. It is also fulfilled for any value of distance x,

$$\sqrt{D_{O_1}} \, C_{O_1}^j(x,t) + \sqrt{D_{O_2}} \, C_{O_2}^j(x,t) + \ldots + \sqrt{D_{O_{j+1}}} \, C_{O_{j+1}}^j(x,t) = \sqrt{D_{O_1}} \, C_{O_1}^* \,. \tag{51}$$

This equation is valid for the stationary planar electrode model (eq. (8)) and for the expanding plane electrode model (eq. (6)). This equation was obtained by Testa and Reinmuth [3] for a three step process and only for the case of stationary plane electrodes and when $I(t)$ is constant.

If we apply the condition $r_0 \to \infty$ to eqs. (40) and (41), we obtain the expressions for the surface concentrations of the O_j and O_{j+1} species corresponding to the expanding plane electrode model,

$$C_{O_j}^j(x = 0, t) = \gamma_{1,j} \frac{\sum_{i=1}^{j} n_i}{n_j} C_{O_1}^* - \frac{n_1}{n_j} \gamma_{1,j} C_{O_1}^* N_s \frac{t^{u+1/2}}{t_s^{2/3}} S_{EPE} \,, \tag{52}$$

$$C_{O_{j+1}}^j(x = 0, t) = -\gamma_{1,j+1} \frac{\sum_{i=1}^{j-1} n_i}{n_j} C_{O_1}^* + \frac{n_1}{n_j} \gamma_{1,j+1} C_{O_1}^* N_s \frac{t^{u+1/2}}{t_s^{2/3}} S_{EPE} \,, \tag{53}$$

where S_{EPE} is given by eq. (A.13).

The expression for the transition time of the j step is obtained by making $C_{O_j}^j(x = 0, \tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j}) = 0$ in eq. (52),

$$\frac{(\tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j})^{u+1/2}}{(t_{bp} + \tau_{O_1} + \ldots + \tau_{O_j})^{2/3}} = \frac{\sum_{i=1}^{j} n_i}{n_1 N_s S_{EPE}}, \tag{54}$$

where S_{EPE} has to be calculated for $t = \tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j}$.

The equation for the transition time for the case of a stationary planar electrode of constant area $A = A_0 t_{bp}^{2/3}$ is obtained by making $t_{bp} \gg t$ in eq. (54),

$$(\tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j})^{u+1/2} = \frac{\sum_{i=1}^{j} n_i}{n_1 N_s^* S_{SPE}}, \tag{55}$$

where S_{SPE} is given by eq. (A.15).

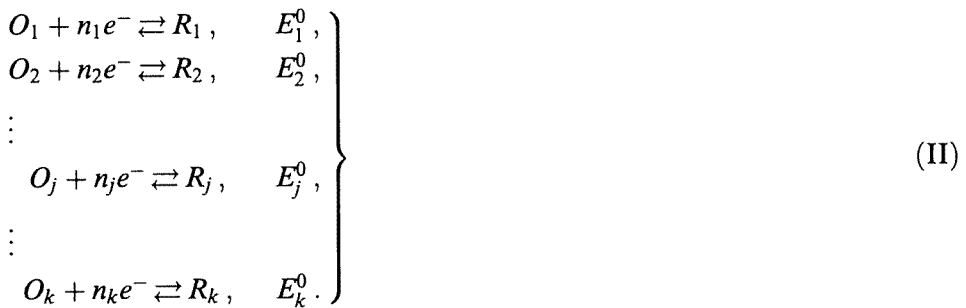For the particular case of a potential current-time function ($\omega = 0$; $I(t) = I_0 t^u$), eq. (55) becomes

$$(\tau_{O_1} + \tau_{O_2} + \ldots + \tau_{O_j})^{u+1/2} = \frac{p_{u,0,1} \sum_{i=1}^{j} n_i}{n_1 N_s^*}, \tag{56}$$

where $p_{u,0,1}$ is given by eq. (A.12) with $h = 0$. The right hand side of eq. (56) is constant for a given value of u. This equation was deduced by McDonald [4] for a current step ($u = 0$) for which

$$p_{0,0,1} = \sqrt{\pi}. \tag{57}$$

4. Multicomponents systems

The reaction scheme in this case is given by

$$\left.\begin{array}{ll} O_1 + n_1 e^- \rightleftarrows R_1, & E_1^0, \\ O_2 + n_2 e^- \rightleftarrows R_2, & E_2^0, \\ \vdots & \\ O_j + n_j e^- \rightleftarrows R_j, & E_j^0, \\ \vdots & \\ O_k + n_k e^- \rightleftarrows R_k, & E_k^0. \end{array}\right\} \tag{II}$$

Following a similar procedure to the one given above, it is possible to generalize the boundary value problem for any step $j > 2$ in the following way:

$$\left.\begin{array}{l} t_j = 0; r \geqslant r_0, \\ t_j > 0; r \to \infty, \end{array}\right\} \quad \tilde{C}_{O_i}^j(r, t) = \tilde{C}_{R_i}^j(r, t) = 0, \quad i = 1, \ldots, j, \tag{58}$$

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

$$\tilde{C}_{O_i}^j(r_0, t) = 0 \,, \quad i = 1, 2, \ldots j - 2 \,, \tag{59}$$

$$\tilde{C}_{O_{j-1}}^j(r_0, t) = -C_{O_{j-1}}^{j-1}(r_0, t) \,, \tag{60}$$

$$\sum_{i=1}^{j} D_{O_i} n_i \left(\frac{\partial \tilde{C}_{O_i}^j}{\partial r} \right)_{r=r_0} = 0 \,, \tag{61}$$

$$D_{O_i} \left(\frac{\partial \tilde{C}_{O_i}^j}{\partial r} \right)_{r=r_0} = -D_{R_i} \left(\frac{\partial \tilde{C}_{R_i}^j}{\partial r} \right)_{r=r_0} \,, \quad i = 1, 2, \ldots j \,. \tag{62}$$

The solution to this problem is simpler than the previous one due to the absence of reaction intermediates which might complicate the overall process (see scheme II). Under these conditions, the surface concentration expressions for species O_j and R_j, $C_{O_j}^j(r_0, t)$ and $C_{R_j}^j(r_0, t)$ are given by

$$C_{O_j}^j(r_0, t) = C_{O_j}^* + \sqrt{\frac{D_{O_{j-1}}}{D_{O_j}}} \frac{n_{j-1}}{n_j} C_{O_{j-1}}^{j-1}(r_0, t) G_{O_{j-1}, O_j}^j \,, \tag{63}$$

$$C_{R_j}^j(r_0, t) = -\sqrt{\frac{D_{O_{j-1}}}{D_{R_j}}} \frac{n_{j-1}}{n_j} C_{O_{j-1}}^{j-1}(r_0, t) G_{O_{j-1}, R_j}^j \,. \tag{64}$$

G_{O_{j-1}, R_j}^j in eq. (64) is also given by eq. (A.23) by changing D_{O_l} to D_{R_l}.

5. Notations and definitions

E_j^0	normal reduction potential of the jth step,
n_j	number of electrons transferred in the jth step,
I_0	value of $I(t)$ at $u = \omega = 0$,
$C_{O_j}^l(r, t)$	concentration profiles of species O_j in the jth step $(l \geqslant j)$,
D_{O_j}	diffusion coefficient of species O_j,
r	distance from the center of the spherical electrode,
r_0	$\begin{cases} \text{electrode radius at time } t_s \ (= \zeta t_s^{1/3}) \text{ for a DME,} \\ \text{constant electrode radius for a SMDE,} \end{cases}$
ζ	electrode radius at $t_s = 1$ s for a DME,
m_{Hg} and d	rate of flow and density of mercury,
t_{bp}	blank period used only for a DME,

t	time elapsed between current application and the jth step ($= t_1$ for the first step and $t = \tau_{O_1} + \ldots + \tau_{O_{j-1}} + t_j$ for any jth step with $j > 1$),
t_j	time during which the jth step takes place ($0 \leqslant t_j < \tau_{O_j}$),
τ_{O_j}	transition time of species O_j for which the condition $C_{O_j}^j(r_0, \tau_{O_1} + \ldots + \tau_{O_j}) = 0$ is fulfilled,
t_s	total time ($= t_{bp} + t$),
$A(t_s)$	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),
$\gamma_{i,l}$	$= \sqrt{D_{O_i}/D_{O_l}}$ with $i = 1, 2, \ldots k - 1$ and $l = i + 1$ or $i + 2$,
DME	dropping mercury electrode for which the expanding sphere electrode model (eq. (3)) and the expanding plane electrode model (eq. (6)) are used,
SMDE	stationary spherical electrode model or static mercury dropping electrode (eq. (7)),
EPE	expanding plane electrode model (for the DME),
SPE	stationary plane electrode.

Other definitions are conventional.

Acknowledgements

Appendix

A.1. FIRST STEP

By using the dimensionless parameters method, we obtain [11] the following expressions for the surface concentrations of the O_1 and O_2 species for the first step, corresponding to the expanding sphere electrode model (eq. (3)):

$$C_{O_1}^1(r_0, t) = C_{O_1}^* \left\{ 1 - N_s \frac{t^{u+1/2}}{t_s^{2/3}} S_{DME,O_1} \right\}, \tag{A.1}$$

$$C_{O_2}^1(r_0, t) = C_{O_1}^* \gamma_{1,2} N_s \frac{t^{u+1/2}}{t_s^{2/3}} S_{DME,O_2}. \tag{A.2}$$

Moreover,

$$N_s = \frac{2I_0}{n_1 F \sqrt{D_{O_1}} \, A_0 C_{O_1}^*} \, , \tag{A.3}$$

$$\gamma_{1,2} = \sqrt{\frac{D_{O_1}}{D_{O_2}}} \, , \tag{A.4}$$

$$S_{DME,O_l} = \sum_{h=0} \left\{ \frac{J_u^0(h, \beta)}{p_{u,h,1}} - \frac{2\sqrt{D_{O_l}t}}{r_0} J_u^1(h, \beta) + \left(\frac{2\sqrt{D_{O_l}t}}{r_0} \right)^2 \frac{J_u^2(h, \beta)}{p_{u,h,1}} \right\} \frac{\Omega^h}{h!} \, , \tag{A.5}$$

$$\Omega = \omega t \, , \tag{A.6}$$

$$\beta = \left(\frac{t}{t_{bp} + t} \right)^{1/3} \, , \tag{A.7}$$

$$\left. \begin{aligned} J_u^0(h, \beta) &= 1 + A_u^0(h)\beta^3 + B_u^0(h)\beta^6 + C_u^0(h)\beta^9 + \dots \, , \\ J_u^1(h, \beta) &= A_u^1(h) + B_u^1(h)\beta^3 + C_u^1(h)\beta^6 + \dots \, , \\ J_u^2(h, \beta) &= A_u^2(h) + B_u^2(h)\beta^3 + \dots \, , \end{aligned} \right\} \tag{A.8}$$

$$\left. \begin{aligned} A_u^0(h) &= 1/3(2u + 2h + 3) \, , \\ B_u^0(h) &= 7/[12(2u + 2h + 3)(2u + 2h + 5)] \, , \\ C_u^0(h) &= 20/[9(2u + 2h + 3)(2u + 2h + 5)(2u + 2h + 7)] \, , \end{aligned} \right\} \tag{A.9}$$

$$\left. \begin{aligned} A_u^1(h) &= 1/2(u + h + 1) \, , \\ B_u^1(h) &= 1/[8(u + h + 1)(u + h + 2)] \, , \\ C_u^1(h) &= 9/[32(u + h + 1)(u + h + 2)(u + h + 3)] \, , \end{aligned} \right\} \tag{A.10}$$

$$\left. \begin{aligned} A_u^2(h) &= 1/[2(2u + 2h + 3)] \, , \\ B_u^2(h) &= 1/[(2u + 2h + 3)(2u + 2h + 5)] \, , \end{aligned} \right\} \tag{A.11}$$

$$p_{u,h,1} = p_{2u+2h+1} = \frac{2\Gamma\left(1 + \dfrac{2u + 2h + 1}{2} \right)}{\Gamma\left(\dfrac{1}{2} + \dfrac{2u + 2h + 1}{2} \right)} \, . \tag{A.12}$$

Eqs. (A.1) and (A.2) are valid for $u \geqslant 0$ and $\omega \geqslant 0$ for the current-time function involved.

A.1.1. Particular cases of S-series

(a) If $r_0 \to \infty$, the above expressions are simplified notably and become those corresponding to an expanding plane electrode (EPE). So, eq. (A.5) is simplified to

$$S_{EPE} = \sum_{h=0} \frac{J_u^0(h, \beta)}{p_{u,h,1}} \frac{\Omega^h}{h!} . \tag{A.13}$$

(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.5) becomes

$$S_{SMDE,O_l} = \sum_{h=0} \left\{ \frac{1}{p_{2u+2h+1}} - \frac{3}{2(6u+6h+6)} \frac{2\sqrt{D_{O_l}t}}{r_0} \right.$$
$$+ \frac{3}{2(6u+6h+9)p_{2u+2h+1}} \left(\frac{2\sqrt{D_{O_l}t}}{r_0} \right)^2$$
$$\left. - \frac{9}{4(6u+6h+6)(6u+6h+12)} \left(\frac{2\sqrt{D_{O_l}t}}{r_0} \right)^3 + \dots \right\} \frac{\Omega^h}{h!} . \tag{A.14}$$

(c) If $r_0 \to \infty$ and $t_{bp} \gg t$, we deduce equations corresponding to a static plane electrode (SPE) of area $A = A_0 t_{bp}^{2/3}$ and eq. (A.5) is transformed to

$$S_{SPE} = \sum_{h=0} \frac{1}{p_{2u+2h+1}} \frac{\Omega^h}{h!} . \tag{A.15}$$

A.2. SECOND STEP

We deduced for the second step $(0 \leqslant t_2 \leqslant \tau_{O_2})$ the following expressions for the surface concentrations of the participating species [12]:

$$C_{O_1}^2(r_0, t) = 0 , \tag{A.16}$$

$$C_{O_2}^2(r_0, t) = C_{O_2}^1(r_0, t) + \gamma_{1,2} \frac{n_1 + n_2}{n_2} C_{O_1}^1(r_0, t) G_{O_1,O_2}^2 , \tag{A.17}$$

$$C_{O_3}^2(r_0, t) = -\gamma_{1,3} \frac{n_1}{n_2} C_{O_1}^1(r_0, t) G_{O_1,O_3}^2 \tag{A.18}$$

with

$$t = \tau_{O_1} + t_2 , \tag{A.19}$$

$$G_{O_1,O_l}^2 = 1 - (1 - \gamma_{1,l}) \left\{ \frac{4\sqrt{D_{O_l} t_2}}{\sqrt{\pi} r_0} \left(\frac{1}{2} - \frac{1}{27} (\lambda_2)^6 + \dots \right) \right.$$
$$\left. - \frac{D_{O_l} t_2}{r_0^2} \left(\frac{1}{4} - \frac{1}{48} (\lambda_2)^3 + \dots \right) \right\}, \tag{A.20}$$

$$\lambda_2 = \left(\frac{t_2}{t_{bp} + \tau_{O_1} + t_2} \right)^{1/3}. \tag{A.21}$$

By making $C_{O_2}^2(r_0, \tau_{O_1} + \tau_{O_2}) = 0$ in eq. (A.17) we obtain the expression for the transition time for the second step,

$$\frac{(\tau_{O_1} + \tau_{O_2})^{u+1/2}}{(t_{bp} + \tau_{O_1} + \tau_{O_2})^{2/3}} = \frac{\dfrac{n_1 + n_2}{n_2} G_{O_1,O_2}^2}{N_s \left[\dfrac{n_1 + n_2}{n_2} G_{O_1,O_2}^2 S_{DME,O_1} - S_{DME,O_2} \right]}. \tag{A.22}$$

A.3. STEP j

For step j, the G_{O_i,O_l}^j series in the surface concentrations of the species O_j and O_{j+1}, $C_{O_j}^j(r_0, t)$ and $C_{O_{j+1}}^j(r_0, t)$, is analogous to the series given by eq. (A.20) by changing t_2 and λ_2 to t_j and λ_j, with

$$G_{O_i,O_l}^j = 1 - (1 - \gamma_{i,l}) \left\{ \frac{4\sqrt{D_{O_l} t_j}}{\sqrt{\pi} r_0} \left(\frac{1}{2} - \frac{1}{27} (\lambda_j)^6 + \dots \right) \right.$$
$$\left. - \frac{D_{O_l} t_j}{r_0^2} \left(\frac{1}{4} - \frac{1}{48} (\lambda_j)^3 + \dots \right) \right\}, \quad j \geqslant 2, \tag{A.23}$$

$$\lambda_j = \left(\frac{t_j}{t_{bp} + \tau_{O_1} + \dots + \tau_{O_{j-1}} + t_j} \right)^{1/3}. \tag{A.24}$$

A.3.1. Particular cases of G series

(a) Making $t_{bp} \gg t$ in eq. (A.23) we obtain the expression for the G_{O_i,O_l}^j series corresponding to a stationary sphere electrode model (SMDE) of area $A = A_0 t_{bp}^{2/3}$,

$$G_{O_i,O_l}^j = 1 - (1 - \gamma_{i,l}) \left\{ 1 - \exp \left(\frac{D_{O_l} t_j}{r_0^2} \right) \text{erfc} \left(\frac{\sqrt{D_{O_l} t_j}}{r_0} \right) \right\}. \tag{A.25}$$

(b) For planar electrodes ($r_0 \to \infty$) or for planar and spherical electrodes with $\gamma_{i,l} = 1$ ($D_{O_i} = D_{O_l}$ for any i and l), we obtain

$$G_{O_i,O_l}^j = 1. \tag{A.26}$$

References

[1] D. Dubois, G. Moninot, W. Kutner, M.T.J. Jones and K.M. Kadish, J. Phys. Chem. 96 (1992) 7137.

[2] M.M. Khaled, R.T. Carlin, P.C. Trulove, G.R. Eaton and S.S. Eaton, J. Am. Chem. Soc. 116 (1994) 3465.

[3] A.C. Testa and W.H. Reinmuth, Anal. Chem. 33 (1961) 1320.

[4] D.D. McDonald, *Transient Techniques in Electrochemistry* (Plenum Press, New York, 1977) chap. 5.

[5] Z. Galus, *Fundamentals of Electrochemical Analysis*, 2nd ed. (Ellis Horwood, Chichester, 1994).

[6] F.J. Fritz, *Partial Differential Equations Applied Mathematical Sciences*, Vol. 1 (Springer, New York, 1982).

[7] H.F. Weinberger, *Ecuaciones Diferenciales en Derivadas Parciales* (Reverté, Barcelona, 1992).

[8] J. Heyrovsky and J. Kuta, *Principles of Polarography* (Academic Press, New York, 1966) chap. 2.

[9] J. Koryta, J. Dvorák and L. Kavan, *Principles of Electrochemistry*, 2nd ed. (Wiley, Chichester, 1993) chap. 2.

[10] A.J. Bard and L.R. Faulkner, *Electrochemical Methods* (Wiley, New York, 1980) chap. 5.

[11] A. Molina, C. Serna and M. Lopez-Tenés, J. Electroanal. Chem. 278 (1990) 35.

[12] C. Serna, A. Molina and J. González, J. Electroanal. Chem. 399 (1995) 223.