Theoretical study of a catalytic mechanism using cyclic and derivative chronopotentiometric techniques with spherical electrodes

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Abstract

A general analytical solution for a pseudo-first order catalytic process in chronopotentiometric techniques (reversal chronopotentiometry, cyclic chronopotentiometry and reciprocal derivative chronopotentiometry) when using spherical electrodes of any size is presented. The evolution from transient to stationary potential–time responses, characterized by the disappearance of the periodical signal in the neighbourhood of the steady state, is analyzed in cyclic and reversal chronopotentiometry. From reversal potential–time responses, the reciprocal derivative d\(t^{1/2}/dE\)–E curves – which are more sensitive than traditional d\(t/dE\)–E curves – have been obtained. The characteristic peaks presented by the d\(t^{1/2}/dE\)–E curves are quantitatively related to the rate constants of the chemical reaction and show a very different behaviour in catalytic and EC processes, allowing the easy discrimination between both mechanisms. Several types of working curves have been proposed to obtain the rate constants of the chemical reaction in a catalytic process.

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1. Introduction

The study of a catalytic mechanism in which the charge transfer reaction is followed (or preceded) by a homogeneous chemical reaction that regenerates the electroactive species is of great interest [1–4]. Elsewhere, chronopotentiometric techniques have been shown to be very useful in studying electrochemical processes with coupled homogeneous kinetics [2–11].

With such a scenario we have developed in this paper the theory for a pseudo-first order catalytic mechanism in several chronopotentiometric techniques like chronopotentiometry with current reversal, cyclic chronopotentiometry and reciprocal derivative chronopotentiometry. The compact and easy-to-manage equations obtained are valid for spherical electrodes of any radius, \(r_0\), including planar electrodes (\(r_0 \rightarrow \infty\)) and spherical ultramicroelectrodes (\(r_0 \rightarrow 0\)) as limit cases. From the analysis of such equations it is deduced that the attainment of the true steady state (i.e. independent of time surface concentrations) do not depend on the electrode size, and the only condition is that the values of the rate constants are sufficiently high.

Taking as our basis the above result, we have analyzed the evolution from transient to stationary potential–time responses in cyclic chronopotentiometry, something which can be achieved by varying the applied current. This study allows us to explain the behaviour of responses in every situation, like the fact that the periodicity characteristic of transient signals tends to disappear in the neighbourhood of the steady state. Moreover, constancy is observed in the periodical responses, which, although it makes cyclic chronopotentiometry a very suitable technique for identifying a catalytic process, justifies the use of two current steps only (reversal chronopotentiometry) in order to obtain quantitative information.

We have analyzed the transient reversal potential–time (E–t) curves and we have proposed working curves based on the measurements of direct and reversal transition times in order to obtain the information concerning the homogeneous chemical reaction in the catalytic process. From the E–t curves, the corresponding reciprocal derivative d\(t^{1/2}/dE\)–E curves have been obtained. This peaked output technique was introduced by Jagner and co-workers [12,13] and has enjoyed wide use in recent years in the study of different electrode processes. This is because the peaks are quantitatively related to the kinetic
and thermodynamic parameters of the electrode process and are scarcely affected by the capacitative effects, since they have been obtained from the central zone of the chronopotentiograms [14,15]. At present, this technique, also known as potentiometric stripping analysis (PSA) [16,17], is widely used in the collection of analytically useful data and in the diagnosis of electrochemical reactions [14,15,17–19]. However, in this work it is pointed out that the reciprocal derivative chronopotentiograms $d\eta/dE-E-I$ obtained from the $E-I$ response are more sensitive and therefore more suitable in obtaining accurate values for the kinetic and thermodynamic parameters of a catalytic process. This technique is very simple to apply and it presents high reproducibility in the measure of the peak potentials and peak heights [15]. Thus, working curves based on the dependence of peak parameters on the rate constants of the chemical reaction have been proposed.

Finally, we have compared the $d\eta/dE-E-I$ curves for a catalytic and an EC[11] mechanism, and these show a very different behaviour, which allows us to propose a simple way to discriminate between both mechanisms.

2. Theory

The reaction scheme for the catalytic mechanism can be written as:

$$C + ne^− \rightarrow B; \quad B + Z\overset{\chi}{\rightarrow} C + Y$$

where B and C are the electroactive species and Z and Y are electroinactive species in the whole range of measured potentials. Assuming that the bulk concentrations of species Z and Y ($C^Z, C^Y$) are much larger than those for B and C ($C^B, C^C$), we define the pseudo-first order rate constants $k_1 = k_1^C \mu C$ and $k_2 = k_2^C \mu C$, and subsequently:

$$K = \frac{k_2}{k_1} = \frac{c^C}{C^Z}$$

where $K$ is the equilibrium constant. Moreover, $k_1$ and $k_2$ in scheme (I) are the rate constants of forward (reduction) and backward (oxidation) heterogeneous processes, respectively.

In this paper, we analyze the response of a catalytic process when different sequences of currents are applied to a spherical electrode of any radius, $r_0$. Indeed, the theoretical bases associated to process (I) have been developed in Appendix for the following techniques:

1. Single-step chronopotentiometry ($I_1$).
2. Reversal chronopotentiometry ($I_1$ and $-I_2$).
3. Cyclic chronopotentiometry ($I_1, I_2$ and $-I_2$, $J_1, J_2, J_3$).
4. Reciprocal derivative chronopotentiometry.

Below are given the expressions for transition times and potential–time ($E-t$) responses for the above techniques. These general equations include those for planar electrodes ($r_0 \rightarrow \infty$) and spherical ultramicroelectrodes ($r_0 \rightarrow 0$) as limit cases. In reciprocal derivative chronopotentiometry the $E-t$ curves are differentiated and the response is obtained in the form of peaks which are quantitatively related to the kinetic parameters of the chemical reaction (see Section 3).

2.1. Single-step chronopotentiometry

When only one current step $I_1$ is applied to the electrode, the expressions for the surface concentrations of electroactive species B and C are given in Appendix by Eqs. (A.10) and (A.11), respectively. Thus, by making $C^C = 0$ in Eq. (A.11), the following non-explicit expression for transition time, $\tau_1$, is obtained:

$$T(\xi_1, \chi_1) = \frac{L_d(\infty)}{I_1}$$

where $T(\xi_1, \chi_1)$ is given by Eq. (A.8) for $t = \tau_1$ (see Eqs. (A.6) and (A.9)) and $L_d(\infty)$ is defined by Eq. (A.12).

It is interesting to note that for the specific case of spherical ultramicroelectrodes ($r_0 \rightarrow 0$), no transition time is obtained when a constant current is applied (see Eqs. (3) and (A.13)).

For a reversible charge transfer reaction, the following expression is obtained from Eq. (A.18) with $\lambda \rightarrow \infty$:

$$E(t) = E^0 + \frac{R T}{n F} \ln \frac{T(\xi(t), \chi(t)) - T(\xi, \chi)}{T(\xi_1, \chi_1) K + T(\xi, \chi)}$$

which can also be written in the form:

$$\frac{T(\xi, \chi)}{T(\xi_1, \chi_1)} = \frac{1 - Ke^{\alpha t}}{1 + e^{\alpha t}}$$

where $T(\xi, \chi)$ and $\eta(t)$ are given by Eqs. (A.8) and (A.19), respectively.

The above equations, in the limit case of a planar electrode ($r_0 \rightarrow \infty$) (Eqs. (A.14) and (A.17)), coincide with those obtained by Delahay et al. [5] and Koutecký and Cizek [6].

2.2. Current reversal chronopotentiometry

In this technique, two successive steps of different sign ($I_1$ and $-I_2$) are applied to a spherical electrode of any size. At time $\tau_1$, the current is reversed and the species B (scheme (I)) is oxidized at the electrode surface. The transition time $\tau_2$ can be obtained by making $C^C = 0$ in Eq. (A.31) and thus, the following equation needs to be solved:

$$T(\xi_1, \chi_1) = \frac{-L_1 + L_2}{L_4} T(\xi_1, \chi_1) = -K \frac{L_d(\infty)}{L_1}$$

where $\xi_1$, $\xi_2$, $\xi_2$, and $\chi$ are given by Eqs. (A.26), (A.28), (A.30), respectively, for $\tau_2 = \tau_2$, and function $T$, for the corresponding variables, is given by Eq. (A.8).
For the particular case when $K = 0$, Eq. (6) takes the following simpler form:

$$
\frac{\eta(T_j; \chi, \xi)}{\eta(T_{\infty}; \chi, \xi)} = \frac{I_j + I_1}{I_1}
$$

and for a planar electrode (Eqs. (A.14) and (A.17)), this equation is written as:

$$
\frac{\eta(T_j; \chi, \xi)}{\eta(T_{\infty}; \chi, \xi)} = \frac{I_j + I_1}{I_1}
$$

which is coincident with that deduced by Furlani and Morpurgo (Eq. (10) in ref. [7]).

On inserting Eqs. (A.31) and (A.32) in the Nernst’s equation, and taking into account Eq. (6) with $I_j = I_1$, the potential–time response corresponding to a reversible charge transfer reaction can be written as:

$$
\frac{\eta(T_j; \chi, \xi)}{\eta(T_{\infty}; \chi, \xi)} = \frac{1}{K} \frac{1 - \frac{1}{1 + e^{\eta(T_j)}}}{1 + \frac{1}{1 + e^{\eta(\infty)}}}
$$

where $\chi$, $\xi$, and $\eta$ are given by Eqs. (A.8) and (A.19), respectively.

2.5. Cyclic chronopotentiometry

In cyclic chronopotentiometry, $n$ successive, alternating sign current steps are applied to the electrode without the balance being recovered in the electrode–solution interphase. The expression for the transition time corresponding to the $j$th current step, $(+\Delta I_j; j = 1, 2, \ldots, n)$, can be obtained by making $c_{\pm}(\eta_j, \tau_j) = 0$ for $j$ even (oxidation), or $c_{\mp}(\eta_j, \tau_j) = 0$ for $j$ odd (reduction), in Eqs. (A.46) and (A.47), respectively.

In this way, the expressions for transition times fulfill (see Eqs. (3) and (6)):

$$
L_j(\tau_j)_{\text{odd}} = \frac{I_j(\infty)}{I_j}
$$

$$
L_j(\tau_j)_{\text{even}} = -\frac{K}{2} \frac{I_j(\infty)}{I_j}
$$

where $L_j(\tau_j)$ for $j$ odd or even is given by Eq. (A.48) for $\tau_j = \tau_j^0$.

On the other hand, the potential–time response for the $j$th current step can be deduced by substituting the expressions of the surface concentrations of the reduced and the oxidized species (Eqs. (A.46) and (A.47), respectively) in the Butler–Volmer equation. For the particular case of a catalytic mechanism with a reversible charge transfer process:

$$
L_j(\tau_j)_{\text{odd}} = \frac{1 - K e^{-\eta_j\chi}}{1 + e^{\eta_j\chi}}
$$

$$
L_j(\tau_j)_{\text{even}} = -\frac{1}{K} \frac{1 - K e^{-\eta_j\chi}}{1 + e^{\eta_j\chi}}
$$

is obtained (see Eqs. (5) and (9)), where $L_j(\tau_j)$ for $j$ odd or even is defined by Eq. (A.48) and the potential appears in the expression of $\eta_j(\chi)$, given by Eq. (A.19).

From Eqs. (10)–(13) it is easily deduced, for any (odd or even) $j$th step that:

$$
L_j(\tau_j) = \frac{1}{1 + e^{\eta_j(\infty)}} I_j(\infty)
$$

This expression permits us to calculate the $j$th potential–time response, since the potential depends on time through the function $L_j(\tau_j)$. Thus, for any time $\tau_j$, there exists a correspondence between the function $L_j$ and the potential, in such a way that plotting $L_j(\tau_j)$ versus $E(\tau_j)$ the same sigmoidal curve is obtained whatever the current step, $j$, in agreement with the right hand side of Eq. (14).

All the above equations for a catalytic mechanism transform into those corresponding to a simple E mechanism when $\chi_j \rightarrow 0$ (Eqs. (A.45) and (A.42)).

3. Results and discussion

3.1. Catalytic mechanism and stationary state

The compact form of function $T(\xi, \chi)$ given in this paper (Eq. (A.8)), makes the general equations obtained for a catalytic process in cyclic chronopotentiometry applicable to spherical electrodes of any size, including planar electrodes ($r_0 \rightarrow \infty$) and spherical ultramicroelectrodes ($r_0 \rightarrow 0$) as limit cases. Spherical electrodes of small sizes cannot be described from other treatments with series expansion developments [10].

Thus, in Fig. 1 the behaviour of function $T(\xi, \chi) = T(\xi, \chi) \chi^2 / \xi$ versus $\chi$ is shown for different values of the electrode radius, from planar to microspherical electrodes (see Eqs. (A.13)–(A.17)), revealing the peculiar characteristics of this function, which governs the catalytic mechanism. As observed in figure, in the limit case of a planar electrode ($r_0 \rightarrow \infty$), the $T(\xi, \chi)$ function remains practically constant for $\chi \geq 2$ with an error of less than 5% with respect to the limiting value 0.5 (Eq. (A.17)). Indeed, from Fig. 1 it is clear that, in the case of a catalytic mechanism, a steady state dependent on $\xi$ (see Eqs. (A.10)–(A.11), (A.15) and (A.17)) can be reached in a planar...
Fig. 2. Variation with time of the surface concentrations of B (dashed line) and C (solid line) species ((a) Eqs. (A.46)–(A.47)) and reversible potential–time curves ((b) Eqs. (12)–(13)) for a catalytic mechanism in cyclic chronopotentiometry ($j = 1, 2, \ldots, 10$) when a planar electrode ($r \to \infty$) is used (see Eqs. (A.14) and (A.17)).

$N_s = 5s^{-1/2}$ (Eq. (A.16)), $I_1 = I_2 = \ldots = I_{10}$, $K = 0$, $k_1 = 5s^{-1}$, $n = 1$, $T = 298.15$ K. Dotted lines correspond to the transition times. Other conditions are as in Fig. 1.

electrode at relatively short times. Fig. 1 also shows for spherical electrodes that as the electrode radius, $r_0$, decreases, the $T'(\xi, \chi)$ function tends to become independent of the kinetic of the process, i.e. independent of $\chi$, and a different steady state (non-dependent on $\kappa$, see Eqs. (A.10)-(A.13)) is reached [21], which, obviously, is not useful to study the kinetic of the process.

The consequences of the above results on the behaviour of surface concentrations and on the $E$–$t$ response for a cyclic experiment are illustrated in Figs. 2 and 3.

Fig. 2 shows the response for a catalytic mechanism, when ten consecutive current steps are applied to a planar electrode, for $K = 0$ and $k_1 = 5s^{-1}$. Fig. 2a shows the variation of the surface concentrations of species B and C (Eqs. (A.46) and (A.47)) and the fulfilment of the fundamental condition (A.4) is clearly noted. On the other hand, Fig. 2b exhibits the corresponding potential–time response (Eq. (14)), which is the information experimentally available. In both figures, the values of the transition times (dotted lines) can be observed (reduction transition times $\tau_1$, $\tau_3$, $\ldots$ and oxidation transition times $\tau_2$, $\tau_4$, $\ldots$ reached when surface concentration of species C and B, respectively, becomes zero). Note that for the value of current $I_1$ applied, the transition time $\tau_1$ obtained fulfills that $x_{\tau_1} (= k_1 \tau_1) < 2$ and in agreement with the comments in Fig. 1, a transient response has been obtained. It is also interesting to note that, in this figure, even transition times are practically equal, and the same can be said for odd transition times, except for that corresponding to the first current step applied, $\tau_1$.

This constancy of transition times, which is characteristic of a catalytic process [2,8], is reached more easily as $x (= k_1 + k_2)$ increases, and barely depends on the electrode radius when conventional spherical electrodes are used. Therefore, cyclic chronopotentiometry is an adequate qualitative technique to identify a catalytic process, but from a quantitative point of view the application of more than two steps does not give additional information.

This peculiar behaviour of a catalytic mechanism is due to the particular dependence of function $T(\xi, \chi)$ on $\chi$, shown in Fig. 1, which manifests that this function reaches a practically constant value for relatively short times if $x (= k_1 + k_2)$ is high enough (see Eqs. (14) and (A.48)).

Fig. 3 illustrates the situation when the stationary state is reached for a planar electrode. Parallel plots like in Fig. 2 have been represented, for the same value of the applied current $I_1$ but for a higher value of $k_1 (= 15s^{-1})$. As can be observed in Fig. 3a, concentrations do not fall to zero and, consequently, no transition times are obtained (see Fig. 3b). For times longer than $0.13s$ concentrations take values practically independent
of time, that is, the stationary state is reached. The response to the application of a constant current is a constant potential, once the stationary state has been attained (Fig. 3b), and therefore, the use of cyclic chronopotentiometry has no sense for a very fast chemical reaction.

It is interesting to note that it is possible to decrease the time scale of the experiment (and hence \( \chi (\omega \times t) \)) by increasing the value of the applied current. Actually, the evolution from stationary (Fig. 3) to transient (Fig. 2) responses can be achieved by increasing the value of the applied current.

### 3.2. Reversal and reciprocal derivative chronopotentiometry

According to the above explanation for Fig. 2, below we will focus our discussion on the application of two current steps (current reversal chronopotentiometry) with the principal aim of proposing methods to obtain the kinetic information of the process. Thus, both the reversal \( E-t \) chronopotentiograms and their derivatives will be studied. Indeed, the response corresponding to a catalytic mechanism in reciprocal derivative chronopotentiometry will be analyzed in its traditional form, i.e. by plotting the reciprocal of the time derivative of the chronopotentiogram versus the measured potential (d\( \delta E/\delta t \)) versus the measured potential (d\( \delta E/\delta t \)).

Fig. 4a shows the direct and reversal \( E-t \) curves corresponding to a planar electrode for \( K=0 \) and different values of the rate constant, \( k_1 \) (Eqs. (4), (9), (A.14) and (A.17)), whereas in Fig. 4b the corresponding reciprocal derivative chronopotentiograms (d\( \delta E/\delta t \)-\( E \) curves) have been plotted. As observed in Fig. 4a, the curves are shifted to more negative potentials as \( k_1 \) decreases, tending logically to the behaviour expected for a reversible process without kinetic complications (E mechanism) when \( k_1 \rightarrow 0 \). Indeed, for low values of \( k_1 \) we can expand the error function according to erf(\( \sqrt{x} \)) \( \approx (2/\sqrt{\pi x}) \) \( \sqrt{x} \) and for \( k_1 \rightarrow 0 \), from Eqs. (4) and (9) (with (A.14) and (A.17)) we get that \( E_{\text{cath}} = E^0 \) for \( t = 0.25t_e \) and \( t_e = 0.215t_e \), which are just the same relations fulfilled in the case of a simple charge transfer reaction [2,23]. As observed in the figure, the transition times \( t_e \) and \( t_1 \) increase and decrease, respectively, when \( k_1 \) is increased and according to the behaviour shown in Fig. 3, for high enough values of \( k_1 \), the stationary state is reached (see curve for \( k_1 = 10^{-3} \) for which no transition time is obtained).

Fig. 4b (d\( \delta E/\delta t \)-\( E \) curves) shows the typical peak-shaped output in reciprocal derivative chronopotentiometry. As can be observed, the cathodic peak parameters are highly affected by the kinetic of the chemical reaction in such a way that as \( k_1 \) increases, cathodic peaks move towards more negative potentials, and their heights \( (h_{\text{cath}}) \) increase, until the peak tends to disappear when \( k_1 \) increases sufficiently and no transition time is observed in the \( E-t \) curve (for \( k_1 = 10 \times 10^{-4} \), stationary state). However, the position of the anodic peaks and their heights \( (h_{\text{an}}) \) hardly depends on the value of \( k_1 \) (\( h_{\text{an}} \) diminishes when the rate constant increases). For \( k_1 \rightarrow 0 \), the catalytic process approach to the behaviour of a reversible E mechanism for which the relation \( \ln(h_{\text{cath}}/h_{\text{an}}) \) is constant, and its cathodic \( (E_{\text{cath}}) \) and anodic \( (E_{\text{an}}) \) peaks potentials are displaced from the formal potential according to \( E_{\text{cath}} = E^0 - 0.693RT/nF(V) \) and \( E_{\text{an}} = E^0 + 0.838RT/nF(V) \), respectively [18].

Reciprocal derivative curves d\( \delta E/\delta t \)-\( E \) like those shown in Fig. 4b have been used in recent years for the study of different electrode processes [12-19] because of the advantageous characteristics that this technique, also known as potentiometric stripping analysis (PSA), presents [16,17]. However, it has been demonstrated in recent papers [11,15,20] that the reciprocal derivative d\( \delta E/\delta t \)-\( E \) curves are more sensitive than the d\( \delta E/\delta t \)-\( E \) curves and therefore are more suitable to obtain accurate values of the rate constants of the chemical reactions.

Thus, in Fig. 5 we have plotted the direct and reversal \( E-t \) curves (Fig. 5a) and the corresponding more sensitive reciprocal derivative d\( \delta E/\delta t \)-\( E \) curves (Fig. 5b) for a catalytic process with reversible charge transfer for \( K=0.2 \), \( x = 5 \times 10^{-3} \) and different values of the electrode radius (Eqs. (5) and (9)). We observe in Fig. 5a that, as indicated in Section 2.1, no transition time is obtained when electrodes of small radius are used. This is because the
Fig. 5. E–t curves (a) and the corresponding reciprocal derivative dE/dt curves (b) for a catalytic mechanism with K = 0.2 in current reversal chronopotentiometry for electrodes of different radius, r (see Eqs. (5) and (9)). K = 7.1 × 10^{-3} (Eq. (A.16), k = (k_1 + k_2) = 5 × 10^{-3}). The values of τ_1 (cm) are on the curves. Other conditions are as in Fig. 2. The curve with τ_1 → ∞ corresponds to a planar electrode. For r = 5 × 10^{-2} cm the steady state has been reached.

steady state has been reached, according with results shown in Fig. 1. It can also be observed in this figure that, for t → 0, all curves start from the same value of potential (the equilibrium potential, E_{eq}), independently of the electrode radius. Indeed, in line with Eqs. (4) and (A.8) it is fulfilled:

\[ E(t \rightarrow 0) = E^F + \frac{RT}{nF} \ln \frac{1}{K} = E_{eq} \]  

(15)

It can be noted from Fig. 5b that due to the value of K = 0.2, the cathodic curves start at a non-null ordinate value, which corresponds in abscissa to the value of the equilibrium potential (see Eq. (15)). It is also observed in this figure that cathodic curves move towards more negative potentials and increase their heights as the electrode radius diminishes, tending to lose the peak for very small electrode radius (see Fig. 5a). On the other hand, the anodic curves are not visibly affected by the electrode size.

3.2.1. Discrimination between catalytic and EC mechanisms

In Fig. 6, we have represented the E–t curves (Fig. 6a) and their corresponding dE/dt curves (Fig. 6b) for a catalytic and an EC mechanism with K = 0, at a planar electrode and for several values of the rate constant k_1, by using the equations deduced in ref. [11] for an EC mechanism. As can be observed in Fig. 6b for a catalytic process, the behaviour of the curves dE/dt = dE/dt is qualitatively similar to that described for curves dE/dt = E in Fig. 4b, but higher peaks and, therefore more sensitivity, are obtained from the dE/dt = E curves.

It is also very interesting to compare the dE/dt = E curves for the catalytic and the EC mechanisms (Fig. 6b). In both cases, the simple reversible E mechanism (reached when k_1 → 0) appears as dotted lines. It can be noted that, whereas for the catalytic mechanism cathodic peaks move towards more negative potentials and become narrower and more asymmetric as k_1 increases. Moreover, although in both cases the peak heights (|h_{p,cat}|) increase with k_1, the effect is much more pronounced for a catalytic process (compare, for example, the curves for k_1 = 6 s^{-1} in both figures). It can also be noted that in the case of a catalytic process for k_1 = 8 s^{-1} the steady state has been reached (see the corresponding curve in Fig. 6a) and therefore no peak is obtained in Fig. 6b. However, for an EC mechanism at a planar electrode, for k_1 = 100 s^{-1} the dE/dt = E curves present a peak. The behaviour shown in this figure for a catalytic process can be easily observed experimentally by varying the concentration of species Z (scheme (I)), and a similar behaviour can also be observed by varying the applied current.

Thus, we can conclude that the very different behaviour of the dE/dt = E curves allows an easy discrimination between catalytic and EC mechanisms.

On the other hand, from the inspection of the anodic response for a catalytic process in Fig. 6b we note that both the peak heights (|h_{p,an}|) and the peak potentials (E_{p,an}) are barely dependent on k_1. This fact can be used in order to estimate the value of the formal potential (E^F) since for an E mechanism both the cathodic and the anodic peak potentials coincide with E^F [15]. In a catalytic process, the relation |h_{p,cat}/h_{p,an}| is always greater than 1.73, the value for an E mechanism [15].

3.2.2. Determination of kinetic parameters of the chemical reaction

In a catalytic mechanism, transition times τ_1 and τ_2 depend on the kinetic parameters of the chemical reaction (see Eqs. (3) and (6)), and hence both can be used to obtain them. This constitutes an advantage in comparison to CE and EC mechanisms, where only τ_1 or τ_2, respectively, are dependent on the kinetic information [2-4,9-11]. Methods based on transition times have the advantage of being independent of the reversibility of the charge transfer reaction.

When a constant current is applied, the equilibrium and the rate constants of the chemical reaction can be determined from measurements of transition time τ_1, as described in ref. [9]. For a reversible charge transfer reaction, K can also be obtained as indicated by Eq. (15).

When two constant currents of contrary sign are applied to the electrode, working curves like those in Fig. 7 can be made from measurements of direct and reversal transition times. In this figure we have plotted (τ_1 + τ_2) for several values of the electrode radius, the
expression for this relationship between the first and second transition times can be deduced from Eq. (7), obtaining:

\[ \frac{(\tau_1 + \tau_2)}{\tau_2}^{1/2} = 2 \sqrt{\frac{k_1 \Delta}{k_2 \Delta}} \tau_2 \left( \frac{X_{\text{cat}}}{X_{\text{an}}} \right) \]  

(16)  

As shown in figure, in the limit case of a planar electrode \((r_0 \to \infty)\) and for \(X_{\text{cat}} \to 0\), the result for a simple E mechanism is obtained \((\tau_2/\tau_1 = 1/3, i.e. (\tau_1 + \tau_2/\tau_2)^{1/2} = 2) [23]\). Furthermore, \(\tau_2\) decreases when \(X_{\text{cat}}\) \((k_1\) or \(\tau_1\)) increases since a higher amount of species B is chemically reconverted to C before reversal of the current and hence the ratio \((\tau_1 + \tau_2)/\tau_2\) increases with \(X_{\text{cat}}\). For spherical electrodes a similar behaviour is observed, with the relationship \(\tau_2/\tau_1\) being smaller as the electrode radius decreases (see Fig. 6). Thus, once the direct and the reverse transition times, \(\tau_1\) and \(\tau_2\), have been measured, the value of \(k_1\) (or \((k_1 + k_2)\) if \(K \neq 0\)) can be immediately determined from the abscissa corresponding to the value of the transition time ratios represented. This abscissa has been represented only as far as \(X_{\text{cat}} = 2\), since as has been seen in Fig. 1, for greater values of \(X_{\text{cat}}\), stationary conditions have been practically reached and greater values of the ratio \((\tau_1 + \tau_2/\tau_2)^{1/2}\) have no physical meaning, although they can be calculated from Eq. (16) [7].

In reciprocal derivative chronopotentiometry, both the peak heights and the peak potentials are dependent on the value of the rate constants of the chemical reaction, as shown in Fig. 5. Hence, this fact allows us to propose several possibilities for working curves to determine these kinetic parameters. The most useful are plotted in Fig. 8 for \(K = 0\) and three values of the electrode radius (see Fig. 6b). Indeed, this figure shows the variation of the cathodic peak height \(|h_{\text{p,cat}}|\) (Fig. 8a) and the cathodic
peak potential (Fig. 8b) with $k_1$ obtained from the corresponding $d^2\delta E/dE^2$ curves, since as has already been mentioned, these curves are considerably more sensitive than $d\delta E/dE$ curves (see Fig. 5). Fig. 8 shows that a maximum value of $k_1$ can be determined, with the maximum being different for each electrode radius. The existence of a maximum value for $k_1$ is due to the fact that $g_{r,1}(=k_1 r_1)$ must be less than 2 (see Fig. 1). A decrease of the radius increases $r_1$ (see Fig. 6a) and hence smaller values of $k_1$ can be determined. Obviously, an increase of the applied current $I_1$ decreases $r_1$ and greater values of $k_1$ could be determined for each radius considered.

4. Conclusions

1. General analytical equations for a pseudo-first order catalytic mechanism in several chronopotentiometric techniques (single-step, reversal, cyclic and reciprocal derivative chronopotentiometry) have been deduced for spherical electrodes of any radius. These general equations include those for planar electrodes and spherical ultramicroelectrodes as limit cases.

2. In a catalytic process, the only condition for obtaining an independent: time response is that the values of the rate constants are sufficiently high, i.e. a true steady state can be reached for electrodes of any size. This behaviour is only shown by a catalytic mechanism.

3. The periodicity characteristic of transient signals in cyclic chronopotentiometry tends to disappear in the neighbourhood of the steady state, in such a way that no transition time is observed.

4. Cyclic chronopotentiometry is an adequate qualitative technique to identify a catalytic process, but from a quantitative point of view the application of more than two steps (reversal chronopotentiometry) does not give additional information.

5. The use of reversal current chronopotentiometry is very useful for the study of the catalytic mechanism since homogeneous kinetic parameters can be obtained by using the working curves given in this paper.

6. The reciprocal derivative curves proceeding from the $E = \pm k_1$ response, $i.e.$ the $d^2\delta E/dE^2$ curves, are more sensitive than the $d\delta E/dE$ curves and therefore are more suitable to obtain accurate values of the rate constants of the chemical reaction in a catalytic process. Thus, working curves based on the $d^2\delta E/dE^2$ versus $E$ curves have been proposed in order to determine these kinetic parameters.

7. The $d^2\delta E/dE^2$ curves for a catalytic and an EC mechanism show a very different behaviour which allows an easy discrimination between both mechanisms.

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Appendix A

A.1. Application of a constant current, $I_1$

To obtain the expressions for the concentration profiles of the electroactive species involved in a catalytic process represented by scheme (1) ($c_{i,1}(r,t)$, $i=B, C$), when a current step $I_1$ is applied to a spherical electrode of any size, the following equation system must be solved:

$$
\begin{align*}
\frac{d}{dt} c_{B,1}(r,t) &= D \left( \frac{\partial^2 c_{B,1}(r,t)}{\partial r^2} - \frac{2}{r} \frac{\partial c_{B,1}(r,t)}{\partial r} \right) - k_1 c_{B,1}(r,t) + k_2 c_{C,1}(r,t) \\
\frac{d}{dt} c_{C,1}(r,t) &= D \left( \frac{\partial^2 c_{C,1}(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c_{C,1}(r,t)}{\partial r} \right) + k_1 c_{B,1}(r,t) - k_2 c_{C,1}(r,t)
\end{align*}
$$

(A.1)

where $D$ is the diffusion coefficient, assumed equal for species B and C; and $r$ the distance from the centre of the electrode to any point in the solution.

The boundary value problem is given by:

$$
\begin{align*}
t &= 0, \quad r \geq r_0 \\
\quad t > 0, \quad r \to \infty
\end{align*}
\Rightarrow c_{B,1}(r,t) = c_0^B, \quad c_{C,1}(r,t) = c_0^C
$$

(A.2)
expression of $\phi$ be solved by following the procedure indicated in ref. [11]. The constant current considered (1, 2, ...), scheme (I) it is always fulfilled that [21, 24, 25]:

$$c = 1(1,2,\ldots) \Rightarrow 0$$

$\phi$ from Eqs. (A.4), (A.5) and (A.7) we obtain the following differential equation in the variable $\chi$ with $A$ the area of the stationary spherical electrode ($A = 4\pi r_0^2$, with $r_0$ being the electrode radius) and $c_B^0$ and $c_C^0$ are the bulk concentrations of B and C species. In Eqs. (A.1)–(A.3), subscript 1 in $c_{B1}(r, t)$ and $c_{C1}(r, t)$ refers to the fact that a constant current $I_1$ is being applied to the electrode. In this sense, in all expressions appearing in this work the subscript refers to the current step considered (1, 2, ...).

Taking into account that in a catalytic system following scheme (I) it is always fulfilled that [21, 24, 25]:

$$c_{B1}(r, t) + c_{C1}(r, t) = c_B^0 + c_C^0 \quad \forall r \geq r_0, t \quad (A.4)$$

where $j = 1$ for this first step current applied, and introducing the variable:

$$\phi_1(r, t) = [c_{B1}(r, t) - Kc_{C1}(r, t)]e^t$$

with $c = k \times t \quad (A.6)$

the differential equation system (A.1) is simplified to a single differential equation in the variable $\phi_1(r, t)$. This equation can be solved by following the procedure indicated in ref. [11]. The expression of $\phi_1(r, t)$ at the electrode surface ($r = r_0$) is:

$$\phi_1(r_0, t) = I_1[1 + (1 + K) e^{\tau T(\xi, \chi)}]$$

where

$$T(\xi, \chi) = \underbrace{\frac{\xi^2}{4} - \frac{\xi^2}{2}}_{\xi} e^{-\xi^2} \left[ e^{\xi^2} \operatorname{erfc} \left( \frac{\xi}{2} \right) \right]$$

$$\xi = \frac{2\sqrt{D} t}{r_0} \quad (A.9)$$

and from Eqs. (A.4), (A.5) and (A.7) we obtain the following expressions for the surface concentrations of species B and C:

$$c_{B1}(r_0, t) = \frac{1}{1 + K} \left[ I_1 - \frac{I_1}{I_{D(\infty)}} T(\xi, \chi) \right] \quad (A.10)$$

$$c_{C1}(r_0, t) = \frac{1}{1 + K} \left[ I_1 + \frac{I_1}{I_{D(\infty)}} T(\xi, \chi) \right] \quad (A.11)$$

where

$$I_{D(\infty)} = \frac{4\pi r_0^2 D (c_B^0 + c_C^0)}{(1 + K)} \quad (A.12)$$

$\phi$ are the voltammetric steady state limiting current for a simple charge transfer process [26].

Eqs. (A.10) and (A.11) are valid for spherical electrodes of any radius, including planar electrodes ($r_0 \to \infty$) and spherical microelectrodes ($r_0 \to 0$) as limit cases. For microspherical electrodes ($\xi \gg 1$) it is fulfilled that:

$$T(\xi \gg 1, \chi) = 1 \quad (A.13)$$

and to compare with planar electrodes we define the function $T(\xi, \chi)$ as

$$T(\xi, \chi) = \frac{\sqrt{\xi}}{4} T(\xi, \chi) \quad (A.14)$$

in such a way that

$$I_1 \frac{I_{D(\infty)}}{I_{D(\infty)I}} T(\xi, \chi) = \frac{I_1}{I_{D(\infty)}} T(\xi, \chi) \quad (A.15)$$

and, thus, for the case of planar electrodes ($\xi \to 0$) we have

$$T(\xi \to 0, \chi) = \frac{\sqrt{\xi}}{2} \quad (A.17)$$

The potential–time response corresponding to the application of $I_1$ is obtained by substituting (A.10) and (A.11) in the Butler–Volmer equation:

$$I_1 \frac{I_{D(\infty)}}{I_{D(\infty)I}} e^{\phi(\xi, t)} = \left[ 1 - \frac{I_1}{I_{D(\infty)}} T(\xi, \chi) \right] - e^{\phi(\xi, t)} \left[ K + \frac{I_1}{I_{D(\infty)}} T(\xi, \chi) \right] \quad (A.18)$$

where

$$\eta(t) = \frac{nF}{RT} [E(t) - E^0] \quad (A.19)$$

with $E^0$ being the formal potential of the charge transfer and $K$ the apparent rate constant of the heterogeneous reaction at $E^0$.

If the charge transfer reaction is totally irreversible ($\xi^2 \ll 1$), the general Eq. (A.18) simplifies to:

$$E(t) = E^0 + \frac{RT}{nF} \ln \left( \frac{I_1}{I_{D(\infty)}} + \frac{RT}{nF} \left[ K + \frac{I_1}{I_{D(\infty)}} T(\xi, \chi) \right] \right) \quad (A.20)$$

where $T(\xi, \chi)$ is given by Eq. (3).

A.2. Application of a second constant current, $I_2$

In current reversal chronopotentiometry, we apply a second constant current of the opposite sign, $-I_2$, consecutively to the first current $I_1$, in such a way that the electrode process does not start from equilibrium conditions. This second current is applied in the time interval $0 \leq t_2 \leq t_3$, with $t_3$ being the transition time corresponding to the oxidation of species B (see scheme (II)). If
the current is reversed at the transition time \(t_1\), the total time is given by
\[
t = t_1 + t_2
\]
and the differential equation system (A.1) must be solved again, this time with their solutions being the functions \(c_{2,i}(t, \theta), i = B, C\), where subscript 2 refers to the second applied current. Due to the linearity of the equation system, the solutions \(c_{2,i}(r,t)\) can be expressed in the following manner:
\[
c_{2,i}(r,t) = c_{1,i}(r,t) + \tilde{c}_{2,i}(r,t)
\]
where \(c_{1,i}(r,t), i = B, C\), are the solutions found for the application of the first constant current and \(\tilde{c}_{2,i}(r,t), i = B, C\), are new unknown functions to be determined.

In this case, Eq. (A.4) remains valid (with \(j = 2\) and by analogy with Eq. (A.5) we define the variable:
\[
\phi_j(r,t) = [\rho]_j(r,t) - Kc_{2,i}(r,t)e^{\xi_j} = \tilde{\phi}_j(r,t) + \tilde{\phi}_2(r,t)
\]
where according with Eqs. (A.5), (A.22) and (A.23):
\[
\tilde{\phi}_2(r,t) = [\rho]_2(r,t) - Kc_{2,i}(r,t)e^{\xi_1}
\]
being
\[
\xi_2 = \kappa(t_1 + t_2)
\]
Consequently with the above comments for application of \(I_2\), we have only one differential equation to solve for \(\tilde{\phi}_2(r,t)\), with the boundary value problem also depending on this variable. By following the procedures indicated in ref. [11] we deduce that:
\[
\phi_2(r_0,t) = \frac{I_1(1 + K)}{4\pi r_0 FD} e^{\xi_1} [T(\xi_1, 2, \chi_2) - \frac{I_2 + I_3}{I_1} T(\xi_2, 2)]
\]
where
\[
\xi_1 = \frac{2\sqrt{AK(t_1 + t_2)}}{r_0}
\]
\[
\xi_2 = \frac{2\sqrt{AKt_2}}{r_0}
\]
\[
\chi_2 = x \times t_2
\]
From Eqs. (A.4), (A.24) and (A.27) we deduce the surface concentrations of species B and C corresponding to the application of the second current step, \(t_2\):
\[
\frac{c_{2,i}(r_0,t)}{c_{B}^0 + c_{C}^0} = \frac{1}{1 + K} \left\{ \frac{K + I_1}{I_1} T(\xi_1, 2, \chi_2) - \frac{I_2 + I_3}{I_1} T(\xi_2, 2) \right\}
\]
where

\[ I_0 = 0 \]  \hspace{1cm} (A.41)

\[ t_{m,j} = \tau_m + \tau_{m+1} + \cdots + \tau_j \]  \hspace{1cm} (A.42)

\[ t_{j,j} = \tau_j \]  \hspace{1cm} (A.43)

\[ \xi_{m,j} = 2 \sqrt{D \tau_m r_0} \]  \hspace{1cm} (A.44)

\[ \chi_{m,j} = \kappa \tau_{m,j} \]  \hspace{1cm} (A.45)

From Eqs. (A.4), (A.33) and (A.40) we deduce the surface concentrations of both species, B and C:

\[ c_B^*(r_0, t) + c_C^*(r_0, t) = \frac{1}{1 + K \left\{ K + \frac{I_1}{I_d(\infty)} L_j(t_j) \right\}} \]  \hspace{1cm} (A.46)

\[ c_C^*(r_0, t) = 1 - c_B^*(r_0, t) \]  \hspace{1cm} (A.47)

where

\[ L_j(t_j) = T(\xi_1, x_1, \cdot \cdot \cdot, \xi_j, x_j) + \sum_{m=2}^{j} \left( \frac{i_{m+1} + i_{m-1}}{I_1} \right) T(\xi_m, x_m, \cdot \cdot \cdot, \xi_j, x_j) \]  \hspace{1cm} (A.48)

Eqs. (A.46) and (A.47) show that the surface concentrations of species B and C 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 [10].

References


