Full Paper


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Received: November 27, 2007
Accepted: January 17, 2008

Abstract
This paper develops the theory for a pseudo-first order catalytic mechanism in chronopotentiometry with a power time current, \( I(t) = I_0 u^{\alpha} (u \geq -1/2) \), applied to a spherical electrode of any size, and the advantages of the use of small electrodes and ultramicroelectrodes are discussed. The advantages of using a cyclic power time current to reach a stationary response suitable for characterizing a catalytic mechanism easily and accurately are reported. The reciprocal derivative \((d\eta/dE = E)\) curves, which present peaks quantitatively related to the kinetic parameters of the chemical reaction, have been obtained from the potential-time responses. The influence of the homogeneous kinetic, the electrode radius and the power of time current in the achievement of a stationary response is analyzed. Methods for determining thermodynamic and kinetic parameters of the chemical reaction are proposed.

Keywords: Catalytic mechanism, Power time current, Reciprocal derivative chronopotentiometry, Spherical electrodes, Steady state

DOI: 10.1002/elan.200704143

1. Introduction

In a previous paper we discussed the different behavior shown by a pseudo-first order catalytic process compared with other electrochemical processes which are complicated by chemical reactions as are CE, EC, CEC, ..., mechanisms [1]. The characteristic behavior of a catalytic process is due to the fact that the reaction product is simultaneously required for both the chemical and electrochemical reactions in order to regenerate and transform the depolarizer, respectively. This study is of great importance when the redox mediator is soluble in the electrolytic solution and when it is immobilized at the electrode surface, as in the case of certain enzymes. Indeed, the catalytic action is very frequent in many reactions in Biochemistry, Biology and Pharmacy, and in industrial and environmental processes [2, 3].

In recent papers, the study of the behavior of a pseudo-first order catalytic process when a constant current is applied to a spherical electrode of any size has been carried out [1, 4]. The aim of the present work is to extend our knowledge of such a process by analysis of the potential–time \((E \sim t)\) and reciprocal derivative \((d\eta/dE = E)\) curves in chronopotentiometry with a programmed current of the form \( I(t) = I_0 u^{\alpha} (u \geq -1/2) \), since the use of a power time current presents important advantages over the application of a current step.

On the one hand, the possibility of varying the values of \( I_0 \) and/or \( u \) allow us to change the scan rate easily such that a suitable \( E \sim t \) response can be obtained in a wide range of concentrations. Moreover, by changing these parameters we can find the propitious conditions to obtain a transient or a stationary response. In general, a stationary response is simpler and easier to analyze and hence, it is desirable, if possible, to work under steady state conditions.

It is precisely under these conditions that the use of a power time current assumes greater importance since when a current step is applied, the stationary \( E \sim t \) response gives rise to a constant potential and so no information of the process is obtained. In contrast, the use of a power time current always leads to a typical chronopotentiogram with transition time, from which thermodynamic and kinetic information of the catalytic process can be easily obtained both from the experimental \( E \sim t \) response or, more accurately, from the peaked response in reciprocal derivative chronopotentiometry \((d\eta/dE = E)\) curves. In this technique, the peaks are obtained from the central zone of the chronopotentiogram and thus they are scarcely affected by capacitative effects [4 – 7]. Furthermore, the use of a cyclic power time current under stationary conditions allows the easy characterization of a catalytic process since for the most usual case of an irreversible chemical reaction, identical responses are obtained for all odd currents whereas no response is obtained for the even applied currents.
A similar behavior to that above explained is observed when a variable time current is used to study a simple \( E \) mechanism in microelectrodes, that is, in this case it is necessary to use very small electrodes to attain the steady state conditions \([6, 8]\). However, for a catalytic process the desirable stationary response can be obtained for spherical electrodes of any size, even for planar electrodes, if the homogeneous kinetic is sufficiently fast, something which is frequent in practical cases \([1]\). Furthermore, despite the well-known advantages that the use of microelectrodes offers, they can lead to the loss of the kinetic information in the study of kinetic processes \([1, 9 – 13]\).

Previous studies of this process with chronopotentiometric techniques have been made by using planar electrodes \([14]\) or a DME \([15, 16]\), in such a way the behavior of this process in small sized electrodes or under steady state conditions is much larger than those for \( C \) and \( B \) species \( Z \) and \( Y \) (\( c_{Z*}, c_{Y*} \)) are much larger than those for \( C \) and \( B \) (\( c_{c*}, c_{b*} \)), we define the pseudo-first order rate constants \( k_1 = k_1' c_{Z*} \) and \( k_2 = k_2' c_{Y*} \) and consequently:

\[
K = k_2/k_1 = c_{b*}/c_{c*}
\]

\[
\kappa = k_1 + k_2
\]

where \( K \) is the equilibrium constant and \( k_1 \) and \( k_0 \) in Scheme 1 are the rate constants of forward (reduction) and backward (oxidation) heterogeneous processes, respectively.

In the Appendix (Sec. 5) we have deduced the expressions corresponding to the concentration profiles for a pseudo-first order catalytic mechanism (Scheme 1), when a programmed current of the form \( I(t) = I(t^*) (u > 1/2) \) is applied to a spherical electrode of any radius, \( r_0 \), including as limit cases a planar electrode \( (r_0 \to \infty) \) and an ultramicrospherical electrode \( (r_0 \to 0) \), Tables 1 (transient response) and 2 (stationary response) give the expressions for the surface concentrations and the \(-t\) response in nernstian conditions.

### 2. Theory: Chronopotentiometry with a Power Time Current \( I(t) = I(t^*) (u \geq 1/2) \)

The reaction scheme for the catalytic mechanism can be written as (Scheme 1):

\[
C + n e^- \overset{i_1}{\rightarrow} B \quad \quad B + Z \overset{i_2}{\rightarrow} C + Y
\]

Scheme 1.

where \( C \) and \( B \) are the electroactive species and \( Z \) and \( Y \) are electroinactive species in the whole range of potentials measured. Assuming that the bulk concentrations of species \( Z \) and \( Y \) \( (c_{Z*}, c_{Y*}) \) are much larger than those for \( C \) and \( B \) \( (c_{c*}, c_{b*}) \), we define the pseudo-

### Table 1. Equations for the surface concentrations and the corresponding transient potential-time response for a catalytic mechanism when a power time current \( I(t) = I(t^*) (u \geq 1/2) \) is applied to spherical and planar electrodes. Functions \( T_u \) and \( T_u^* \) are given by Equations 9 and 10, respectively, and \( I(r_0) \) is given by Equation 2.3 in Table 2 and Equation 14.

<table>
<thead>
<tr>
<th>Surface concentrations</th>
<th>( E - t ) response</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spherical electrode</strong></td>
<td><strong>of radius</strong> ( r_0 )</td>
</tr>
<tr>
<td>( \frac{c_C(r_0, t)}{c_C} )</td>
<td>( \frac{1}{1 + K} \left[ 1 - \frac{I(t)}{I(T_u)} \frac{T_u(\xi, \chi)}{T_u(\xi, \chi)} \right] ) (T1.1)</td>
</tr>
<tr>
<td>( \frac{c_B(r_0, t)}{c_B} )</td>
<td>( \frac{1}{1 + K} \left[ K + \frac{I(t)}{I(T_u)} \frac{T_u(\xi, \chi)}{T_u(\xi, \chi)} \right] ) (T1.2)</td>
</tr>
<tr>
<td><strong>Planar electrode</strong> ( (r_0 \to \infty) )</td>
<td></td>
</tr>
<tr>
<td>( \frac{c_C(0, t)}{c_C} )</td>
<td>( \frac{1}{1 + K} \left[ 1 - \frac{I(t)}{I(T_u)} \frac{T_u^<em>(\chi)}{T_u^</em>(\chi)} \right] ) (T1.3)</td>
</tr>
<tr>
<td>( \frac{c_B(0, t)}{c_B} )</td>
<td>( \frac{1}{1 + K} \left[ K + \frac{I(t)}{I(T_u)} \frac{T_u^<em>(\chi)}{T_u^</em>(\chi)} \right] ) (T1.4)</td>
</tr>
</tbody>
</table>

### 2.1. Transient Response

The expressions for the surface concentrations are given in Table 1 by Equations T1.1 and T1.2 for a spherical electrode, and Equations T1.3 and T1.4 for the limit case of a planar electrode.

In Equations T1.1 – T1.4 \( I(t) = I(t^*) \) is the applied current whereas \( I(r_0) \) is the current corresponding to the transition time in the stationary state (see Eqs. T2.3 in Table 2 and 14).

\( T_u(\xi, \chi) \) is a function which is dependent on the electrode sphericity \( (\xi = 2 \sqrt{D_i/r_0}, \text{Eq. A.16}) \) and the homogeneous kinetic \( (\chi = k_t, \text{Eq. A.17}) \), and also on the power of time, \( u \), in the applied current, according to the expression:

\[
T_u(\xi, \chi) = \xi e^{-\frac{\ln(2)\xi}{\beta}} \sum_{j=0}^{\infty} \left( \frac{(\xi)^j}{\beta} \right)^{\frac{1}{\beta} - 1}
\]

\[
E(t) = E^* + \frac{RT}{nF} \ln \left[ \frac{I(t) T_u(\xi, \chi)}{I(T_u)T_u(\xi, \chi)K + I(t)T_u(\xi, \chi)} \right]
\]

where the exponent $u$ can take any real value $u \geq -1/2$ for the surface concentration to have physical meaning [17].

The transition time, $\tau$, can be deduced by making $c_c(r_0, \tau) = 0$ in Equation T1.1. Thus, we obtain the following nonexplicit expression:

$$r^u T_u(\xi, \chi) = \frac{4\pi \sigma_o \rho FD\varepsilon}{I_o(1 + K)}$$

(4)

where $T_u(\xi, \chi)$ is the value of this function at $t = \tau$ (Eq. 3).

By including the expressions for the surface concentrations in Table 1 in the Butler–Volmer equation, the expression for the $E - t$ response is obtained for any degree of reversibility of the charge transfer. For a reversible reaction, from Nernst equation we obtain directly Equation T1.5 for spherical electrodes and Equation T1.6 for planar electrodes. Equation T1.5 can also be written as:

$$\frac{I(t)/T_u(\xi, \chi)}{I(\tau)/T_u(\xi, \chi)} = \frac{1 - Ke^{\eta(t)}}{1 + e^{\eta(t)}}$$

(5)

where

$$\eta(t) = \frac{nF}{RT} [E(t) - E^\circ]$$

(6)

with $E^\circ$ being the formal potential of the charge transfer and $I(\tau)$ is the current applied at $t = \tau$ ($I(\tau) = I_o \tau^u$).

From Equation 5 it is clear that a plot of $I(t)T_u(\xi, \chi)/I(\tau)T_u(\xi, \chi)$ vs. $E$ for any power time current applied is identical to the cathodic zone of the plot of $III_{lin}$ vs. $E$ in voltammetry (see Eq. 27 in [1]).

### 2.1.1. Particular Cases

#### a) Current Step at Spherical Electrodes

For the particular case of a current step, $u = 0$, Equation 3 can be written in a compact form [1, 4]

$$T_0(\xi, \chi) = \frac{\xi^2}{4\chi} \frac{e^{-\chi}}{\int \{ \exp(\xi/2)^2 \text{erf}(\xi/2) - \exp(\chi) \left(1 - \frac{2\sqrt{\chi}}{\xi} \text{erf}(\sqrt{\chi}) \right) \}}$$

(7)

#### b) Planar Electrode

For a planar electrode $r_0 \to \infty$, function $T_u^{lin}(\chi)$ in Table 1 has the following form:

$$T_u^{lin}(\chi) = \tau^u e^{-\chi} \sum_{j=0}^{\infty} \frac{1}{P_{2j+1+1}} \frac{\chi^j}{\beta^j}$$

(8)

This expression can be written in the form of Bessel functions [14].

### 2.2. Stationary Response

The stationary response can be obtained from transient one under the condition $\chi \gg 1$ (i.e., for a fast chemical reaction). Under this condition the general functions $T_u(\xi, \chi)$ (Eqs. 3 and 7) and $T_u^{lin}(\chi)$ (Eq. 8) notably simplify to functions $T_u$ and $T_u^{lin}$, respectively, given by

$$T_u = \frac{\sqrt{D}}{\sqrt{D + r_0 \sqrt{\kappa}}} = \frac{\delta_r}{r_0}$$

$$T_u^{lin} = \frac{1}{(2\kappa^{1/2})^{-1}}$$

(9)

(10)

which are independent of the value of exponent $u$ in the applied current.

Note that the only requirement, $\chi \gg 1$, makes it possible for the stationary state to be attained in a planar electrode. This behavior is characteristic of a catalytic mechanism [1].

In Equation 9 $\delta_r$ is the thickness of the linear reaction layer in spherical diffusion, whose expression is given by [12, 13]

$$\delta_r = \frac{1}{r_0 + \sqrt{\beta}}$$

(11)

In the limit case $r_0 \to \infty$, from Equation 11 we obtain:

$$\delta_r^{lin} = \frac{\sqrt{D}}{\kappa}$$

(12)

which is the classical expression of the thickness of the linear reaction layer in planar diffusion [18].

In the limit case of an ultramicroelectrode ($r_0 \to 0$), from Equation 11 we have [12, 13]

$$\delta_r^{u-micro} = r_0$$

(13)

Note that the Equations T2.1 and T2.2 point out that the dependence of the surface concentrations with the time under steady state conditions is only due to the applied current time function ($I_d^u$).

The transition time under steady state conditions, $\tau_{ss}$, can be obtained by making $c_c(r_0, \tau) = 0$ in Equation T2.1 of Table 2:

$$\tau_{ss}^u = \frac{nFAD\varepsilon}{I_o(1 + K)\delta_r}$$

(14)

Note that the current necessary for reaching the transition time in chronopotentiometry, $I(t_u)$ (Eq. T2.3 in Table 2), is
identical to the voltammetric cathodic limit current under steady state conditions, that is \( I(t_w) = I_{\text{lim}} \) [1].

In the limit case of an ultramicroelectrode \((r_0 \to 0)\), from Equations 13 and 14 we have:

\[
e^s_{\text{ul}} = \frac{4\pi r_dRD^2e^s}{I_0(1 + K)} = I_0(\infty) \]

(15)

where \( I_0(\infty) \) is the voltammetric steady-state limiting current for a simple charge transfer process [1]. Therefore, no kinetic information can be obtained for the catalytic process when using very small electrodes [1, 9–11].

The \( E - t \) response for a reversible process is given by Equation T2.4 in Table 2. This equation can be rewritten in the form (see Eq. 5):

\[
E(t) = E^* + \frac{RT}{nF} \ln \frac{1 - I(t)}{I(t_{\text{ss}})}
\]

(16)

which implies that the relation between current and potential at the steady state is unique, that is, one value of current corresponds to one value of potential and vice-versa. Thus, it is clear that the stationary II/E response is common for any applied power time current or any variable with time potential.

The expressions obtained for the \( E - t \) response, be it transient or stationary (see Tables 1 and 2), are valid in a range of potentials which depends on the value of equilibrium constant, \( K \). Thus,

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

(17)

In other words, if a cathodic current is applied, the response develops only for \( E \leq E_{eq} \). For the most usual value of equilibrium constant, \( K = 0 \), the \( E - t \) response develops in the whole range of potential values [1, 4]. The starting potential, according to Equation 17, is independent of exponent \( n \) and \( r_0 \). Note that this equation can be used to determine the value of \( K \) from the experimental \( E - t \) curve.

2.3. Reciprocal Derivative Chronopotentiometry

The reciprocal derivative chronopotentiometry technique, also known as potentiometric stripping analysis (PSA) [19, 20], consists of plotting the \( dI/dE \) versus \( E \) curves, which present characteristic peaks that are related to the kinetic parameters of the chemical reaction. These peaks are barely affected by capacitative effects since they are obtained from the central zone of the \( E - t \) curves. This fact, together with a high reproducibility in the measure of peak parameters, among other advantages, makes this technique a powerful tool in the study of electrochemical processes [4–7, 20–22].

Thus, once the expressions for the \( E - t \) response are available, the corresponding reciprocal derivative response can be obtained. In the case of a transient response (see Table 1), the \( E - t \) curves are numerically differentiated by using a finite-difference formula of the fifth degree [23]. However, in the case of a stationary response, the simple expression obtained for the \( E - t \) response (see Table 2) makes it possible to carry out the analytical derivation \( dI/dE \).

Thus, from Equation 16 it is obtained:

\[
\frac{dt}{dE} = -\frac{nF}{RT \left(u + 1 \right)} \left(1 + K \right) \left(1 - Ke^s\right)^{1 + \frac{n}{2}} \frac{e^{\frac{n}{2} E}}{(1 + e^{\frac{n}{2} E})^{\frac{n}{2}}}
\]

(18)

Alternatively, from Equation 16 we can obtain the expression for \( dI(t)/dE \) in stationary state conditions, which is given by:

\[
\frac{dI(t)}{dE} = -\frac{nF}{RT \left(u + 1 \right)} I_0^s \left(1 + K \right) \frac{e^{\frac{n}{2} E}}{(1 + e^{\frac{n}{2} E})^{\frac{n}{2}}}
\]

(19)

The characteristic peak parameters, peak potential, \( E_{p} \), peak height, \( h_{p} \), and semipavek width, \( \sigma_{1/2} \), corresponding to the \( dI/dE \) and \( dI(t)/dE \) versus \( E \) curves (for the most usual case of \( K = 0 \)), are summarized in Table 3. It is interesting to note that the expressions in Table 3 are valid for any size of the electrode.
2.4. Cyclic Chronopotentiometry with Power Time Cycles

When \( j \) successive and alternating in sing power time currents of the form \((-1)^{j+1}I_{p}t_{j}^{u}, j = 1, 2, 3...\)

are applied, if the catalytic rate constants are higher enough for the steady state to have been reached, the expressions of the surface concentrations corresponding to any \( j \) applied current have an identical form to that in Table 2 for a single power current (see Sect. 5.2):

\[
\frac{c_{\text{p}}(r_{0}, t_{j})}{e^{t}} = \frac{1}{1 + K} \left[ \frac{1}{I(t_{u})} - \frac{(-1)^{j+1}I_{p}t_{j}^{u}}{I(t_{u})} \right]
\]

(20)

and the expression for the \( E - t_{j} \) response for any \( j \) current applied is given by:

\[
E(t_{j}) = E^{r} + \frac{RT}{nF} \ln \frac{I(t_{u}) - I(t_{j})}{I(t_{u})K + I(t_{j})}
\]

(22)

where \( I(t_{u}) \) is given by Equation T2.3 in Table 2 and Equation 14.

3. Results and Discussion

3.1. Study of the Behavior of Function \( T_{u} \)

From the equations of surface concentrations in Tables 1 and 2 we can easily understand the key role of functions \( T_{u}(\xi, \gamma) \) (spherical electrode) and \( T_{u}^{\text{plan}}(\gamma) \) (planar electrode) in the attainment of the stationary state. In this section we study the behaviour of these functions and the influence of the homogeneous kinetic, the electrode sphericity and the power of time in the applied current in attaining the stationary limit.

In Figure 1a the function \( T_{u}^{\text{plan}}(\gamma) (= T_{u}^{\text{plan}}/\gamma^{1/2}) \) planar electrode, Equation 8) is plotted versus \( \gamma (= k/t) \), for three selected values of the exponent \( u \) in the applied current (\( u = 0, 1/2, 1 \)). The dotted line to which the three curves converge corresponds to the function \( T_{u}^{\text{plan}}(\gamma) (= T_{u}^{\text{plan}}/\gamma^{1/2}) \) (Eq. 10) which is independent of exponent \( u \) in the applied current. As can be seen, the function \( T_{u}^{\text{plan}}(\gamma) \) reaches the stationary limit (\( \gamma \gg 1 \)) at relatively small values of \( \chi \), and smaller ones as the exponent \( u \) diminishes. Indeed, as is shown in Figure 1a, for \( u = 0 \), the error of the function \( T_{u}^{\text{plan}}(\gamma) \) with respect to the stationary limit is less than 5% for \( \gamma \geq 2 \), for \( u = 1/2 \) this happens for \( \gamma \geq 5.5 \) and for \( u = 1 \) it must be fulfilled that \( \gamma \geq 10 \).

According to these results, it is possible to obtain a stationary response for a catalytic mechanism in a planar electrode (at short times), provided the homogeneous kinetic constants are sufficiently high [1].

Thus, for very fast catalytic processes, as many in practice are, the response should be stationary for any value of \( u \), but for moderately fast processes, the response would change from stationary to transient by increasing the value of exponent \( u \).

In Figures 1b and 1c the same type of plots as in Figure 1a for a planar electrode are represented, this time for a spherical electrode at different values of the sphericity parameter, \( \xi (= 2\sqrt{D}/r_{0}) \). In these figures, the function \( T_{u}(\xi, \gamma) \) (Eq. 3) is plotted in solid lines versus \( \chi \), for \( u = 1/2 \) (Fig. 1b) and \( u = 1 \) (Fig. 1c). The dotted lines correspond to the function at the stationary state \( T_{u}^{\text{s}} \) (Eq. 9), which is independent of the exponent \( u \) in the applied current. The vertical lines are traced, for each value of \( \xi \), at the value of \( \gamma \) for which the difference between the values of functions \( T_{u}(\xi, \gamma) \) and \( T_{u}^{\text{s}} \) is less than 5%. Furthermore, the limit of the stationary function, \( T_{u}^{\text{s}} \) (Eq. 9), when the homogeneous catalytic reaction does not take place (i.e., \( k = 0, \gamma \rightarrow 0 \)) or for ultramicroelectrodes (\( r_{0} \rightarrow 0, \xi \rightarrow \infty \)) behaves as an \( E \) simple mechanism being in these conditions \( T_{u}^{\text{s}} = 1 \).

As can be seen, the kinetic stationary limit is reached (with an error of less than 5%) at smaller values of \( \chi \), when \( \xi \) increases (i.e., \( r_{0} \) decreases).

The series in function \( T_{u}(\xi, \gamma) \) (Eq. 3) is slowly convergent for \( \xi > 17 \) in such a way that the function \( T_{u}^{\text{s}} \) (Eq. 9) can be used under these conditions if \( \chi > 0.6 \) for the values of the exponent \( u \) considered. Thus, for \( \xi > 17 \) and \( \chi < 0.6 \) an asymptotic solution should be used, and \( T_{u}^{\text{s}}(\xi, \gamma) \) is calculated from the following expression (see Eq. 3):

\[
T_{u}^{\text{s}}(\xi, \gamma) = \sum_{n=0}^{\infty} \frac{(-1)^{n}}{n!} \frac{1}{(1 + u)^{n+1}}
\]
obtained at a spherical electrode of radius 

In Figures 2a – c we have plotted the 

3.2. Potential–Time Curves

In Figures 2a – c we have plotted the E – t response for a reversible catalytic process with K = 0 (Eq. T1.5 in Table 1), obtained at a spherical electrode of radius \( r_0 = 0.01 \) cm when varying the value of the kinetic constant \( k_r \). Figures 2a – c correspond, respectively, to values \( u = 0 \) (current step), \( u = 1/2 \) (square root time current) and \( u = 1 \) (linear time current), in the applied current, \( I(t) = I_0 e^t \).

From Figure 1 it can be noticed that by increasing the value of \( k_r \) sufficiently (that is, increasing \( \chi \)) the function \( T_u \) reaches the stationary limit (i.e., a stationary response is obtained), for any value of \( u \). However, Figures 2a – c show that an increase of \( k_r \) has a very different effect on the E – t curves for a current step (Fig. 2a) and a variable-with-time current (Figs. 2b and 2c).

For a current step, \( I_0 \), the transient curve (with transition time) and the stationary one (constant potential) can be detected at sight [1, 4]. The condition for no transition time to be obtained is \( I_0 < nFADc_0 a((1/r_0) + \sqrt{k_r/D}) \) (see Eq. T2.3 in Table 2 and Eq. 14) and therefore, the steady state will be more easily reached the higher the \( k_r \) and the smaller the \( r_0 \) values are.

For a power time current, a typical chronopotentiogram with transition time is always obtained, regardless of whether the steady state has been attained or not. In fact, curves for \( k_r = 10 \) s\(^{-1} \) and \( k_r = 20 \) s\(^{-1} \) in Figures 2b and 2c correspond to stationary responses. In this case, from Equation T2.4 in Table 2, it is possible to detect that the steady state has been reached by using a plot of \( E \) vs. \( (t_{SS}^{2/3} - r_{0}^{2/3})/r_{0}^{2/3} \), which must be linear for a stationary curve. The formal potential \( E^* \) can be obtained from the ordinate of this plot, and the slope corresponds to RT/nF. The value of the rate constant \( k_r \) can be obtained from the value of \( t_{SS} \) (Eqs. 11 and 14). This is valid for planar and spherical electrodes provided the electrode radius is not too small, in which case the kinetic of the process can not be detected (see Sec. 2.2).

Thus, the use of a power current time function \( (u \neq 0) \) is of special interest in order to obtain kinetic information in this technique (and also in reciprocal derivative chronopotentiometry, see below), since a stationary response showing transition time is obtained.

3.2.2 Reciprocal Derivative Curves

Figures 2d – f show the reciprocal derivative curves \( (dt/dE) \) corresponding to the E – t responses in Figures 2a – c. Hence, the curves have been plotted at several values of the kinetic constant \( k_r \) and the same values of exponent \( u \) in the applied current: \( u = 0, 1/2 \) and 1 in Figures 2d, 2e and 2f, respectively.

As can be seen in these figures, for any value of exponent \( u \), when the steady state has not been reached both the peak potentials and the peak heights depend on the rate constant \( k_r \) in such a way that the peak heights increase as higher the value of \( k_r \) is.

In contrast, under steady state conditions the behavior of the derivative curves obtained with a power time current differs from that observed for a current step. Indeed, whereas in the last case these curves do not present a peak (curves for \( k_r = 10 \) s\(^{-1} \) and \( k_r = 20 \) s\(^{-1} \) in Fig. 2d) and hence they are not suitable to obtain kinetic information, the stationary curves corresponding to a square root time current (curves for \( k_r = 7 \) s\(^{-1} \), \( k_r = 10 \) s\(^{-1} \) and \( k_r = 20 \) s\(^{-1} \) in

Fig. 1. Dependence of the functions a) \( T_u^\text{plan}(\chi) = T_u^\text{plan}/r_{0}^{1/2} \), Eq 8, b) and c) \( T_u^\text{ss}(\chi,u) \) (Eq. 3), on the kinetic parameter \( \chi \) (\( = k t \)), in solid lines. In (b) \( (u = 1/2) \) and (c) \( (u = 1) \), the values of the sphericity parameter \( \xi = \sqrt{D t/r_{0}} \) are also on the curves. The corresponding stationary functions a) \( T_u^\text{ss} = T_u^\text{ss}/r_{0}^{1/2} \), Eq. 10), b) and c) \( T_u^\text{ss} \) (Eq. 9) are plotted in dotted lines. Dashed lines indicate the values of \( \chi \) for which the error of function \( T_u^\text{plan}(\chi) \) and \( T_u^\text{ss}(\chi,u) \) with respect to the stationary limit is less than 5%.

\[
T_u^\text{mon}(\xi,u) = \xi e^{-\sum_{j=0}^{\infty} \left( \sum_{l=j}^{\infty} (-1)^{l-j} l^{l-j} \prod_{k=0}^{l-j} \frac{1}{k!} \right) \left( \xi^{j} - \xi^{j+l} \right)} \quad (23)
\]

3.2. Influence of the Applied Current on the Responses Obtained

3.2.1. Potential–Time Curves

In Figures 2a – c we have plotted the E – t response for a reversible catalytic process with K = 0 (Eq. T1.5 in Table 1), obtained at a spherical electrode of radius \( r_0 = 0.01 \) cm when varying the value of the kinetic constant \( k_r \). Figures 2a – c correspond, respectively, to values \( u = 0 \) (current step), \( u = 1/2 \) (square root time current) and \( u = 1 \) (linear time current), in the applied current, \( I(t) = I_0 e^t \).
Fig. 2. Reversible potential–time curves (a–c) (Eq. T1.5 in Table 1) and reciprocal derivative curves (d–f) obtained for a catalytic process with $K = 0$ when a power time current $I(t) = I_F t^u$ is applied to a spherical electrode of radius $r_0 = 0.01$ cm. The values of exponent $u$ are indicated in the figures. The influence of the catalytic rate constant $k_1$ on $E - t$ and $dI/dE - E$ curves is shown. $D = 10^{-5}$ cm$^2$/s, $n = 1$, $T = 298$ K, $\varepsilon^* = 1$ mM, $I_F/A = 10^3$ $\mu$A/cm$^2$. The values of $k_1(s^{-1})$ are on the curves.

Fig. 2e) and a linear time current (curves for $k_1 = 10$ s$^{-1}$ and $k_1 = 20$ s$^{-1}$ in Fig. 2f) present well defined peaks, whose height increases with the catalytic kinetic constant $k_1$. However, the position of peaks remains unchanged, independently of the value of $k_1$. According to the equations in Table 3, this behavior informs us that the stationary state has been reached, since in these conditions the peak potential, $E_p$, does not depend on $k_1$.

Similar plots, with the same qualitative behavior, as those in Figure 2 (which have been obtained by increasing the value of the homogeneous rate constant), can be registered in Figure 3d. In these conditions, from this plot the value of $k_1$ can be accurately obtained, for planar and spherical electrodes. These parameters can be also obtained from the $dI(t)/dE$ vs. $E$ curves (see Table 3) [24].

To illustrate the above results, in Figure 3 the variation of the peak potential (Figs. 3a and 3b) and the peak height (Figs. 3c and 3d) with the catalytic kinetic constant has been plotted for $K = 0$ and three values of the electrode radius, when power currents of the form $I(t) = I_F t^u$ and $I(t) = I_F$ (the values of $u$ are shown in the figures) are used. It is observed in Figures 3a and 3b that the peak potential changes with $k_1$ and $r_0$ until a value $k_1 \approx 10$ s$^{-1}$ (for the specific conditions of Fig. 2). From this value, the peak potential does not change either with $k_1$ or $r_0$, which indicates that the steady state has been reached. Thus, as explained above, the formal potential $E^\circ$ and the number of electrons transferred can be determined.

From the equation for the peak height in the $dI/dE - E$ curves, $|h_p|$, in Table 3 and Eqs. 11 and 14, we can write:

$$|h_p|_{\text{SS}} = \frac{u}{4\pi F} (nF\sqrt{Dc_c})^{1/4} (1 + u)^{1/u} = \left( \frac{\sqrt{D}}{r_0} + \sqrt{\kappa} \right)^{1/u}$$

Thus, it is clear that for a linear time current ($u = 1$), a plot of $|h_p|_{\text{SS}}$ vs. $\sqrt{\kappa}$ will be linear with the ordinate given by $D^{1/2}/r_0$ and, hence, parallel lines are obtained at different values of the electrode radius once the steady state is reached, as seen in Figure 3d. In these conditions, from this plot the value of the homogeneous kinetic constant can be accurately obtained. Once more it can be noticed that the steady state is reached at smaller values of $k_1$ when the electrode radius decreases.

Similar plots are obtained for a square root time current (Fig. 3c). In this case a plot of $|h_p|_{\text{SS}}$ vs. $\kappa$ is linear when the steady state is reached.

3.2.3 Cyclic Curves

Figure 4 shows the stationary $E-t$ response for a catalytic mechanism, when ten consecutive and alternating in sign square root time currents are applied to a spherical electrode of radius $r_0 = 0.01$ cm, for two values of equilibrium constant
K (Figs. 4a and 4b) and the corresponding reciprocal derivative curves (Figs. 4c and 4d). As can be seen, and according to Equations 20–22, when $K = 0$ (Fig. 4a), identical responses are obtained for all odd currents applied ($j = 1, 3, 5, ...$), with the transition time given by Equation 14, whereas no response is obtained for the even applied currents ($j = 2, 4, 6, ...$), as expected for an irreversible chemical reaction. In contrast, for $K = 0.5$ (Fig. 4b), the initial presence of species B in solution gives rise to a reversal response, which is identical for all even currents, with the transition time, $t_{ss}'$, given by ($c_B, j_r(0, t_{ss}') = 0$, see Equation 21):

$$t_{ss}' = \frac{K}{1 - u} t_{ss}$$  \hspace{1cm} (25)

where $t_{ss}$ is the transition time for the odd responses, given by Equation 14.

According to the above results, the derivative responses will give rise to an unique curve (in reality five curves superposed) for $K = 0$ (Fig. 4c), whose peak height is given in Table 3. If $K \neq 0$ (Fig. 4d) an only cathodic-anodic response (due to the odd ($j = 1, 3, ...$) and even ($j = 2, 4, ...$) currents respectively) will be obtained, with the cathodic, $h_{p,c}$, and anodic, $h_{p,a}$, peak heights given, respectively, by:

$$h_{p,c} = \frac{dt}{dE} = -\frac{nF}{RT} u \frac{\tau_{ss}(1 + K)(1 - Ka') \alpha}{(1 + \alpha)^{\frac{2}{2}}}$$  \hspace{1cm} (26)

and

$$h_{p,a} = \frac{dt}{dE} = \frac{nF}{RT} u \frac{\tau_{ss}}{(1 + K) (K\alpha' - 1)^{\frac{2}{2}}} \frac{\alpha'}{(1 + \alpha)^{\frac{2}{2}}}$$  \hspace{1cm} (27)

where

$$\alpha = e^{\eta_{pc} - \eta_{pa} - \frac{1}{4} (1 + K)^2 - 4Ku^2}$$  \hspace{1cm} (28)

$$\alpha' = e^{\eta_{pa} - \eta_{pc} - \frac{1}{4} (1 + K)^2 - 4Ku^2}$$  \hspace{1cm} (29)

and

$$\eta_{pc} = \frac{nF}{RT} (E_{pc} - E^0)$$  \hspace{1cm} (30)

$$\eta_{pa} = \frac{nF}{RT} (E_{pa} - E^0)$$  \hspace{1cm} (31)

with $E_{pc}$ and $E_{pa}$ being the cathodic and anodic peak potential values, respectively.

For the particular case of a linear time current ($u = 1$), Equations 26 and 27 are notably simplified and the relation between the peak heights is given by:

$$\eta_{pc} = \frac{nF}{RT} (E_{pc} - E^0)$$  \hspace{1cm} (30)

$$\eta_{pa} = \frac{nF}{RT} (E_{pa} - E^0)$$  \hspace{1cm} (31)

where $E_{pc}$ and $E_{pa}$ are the cathodic and anodic peak potential values, respectively.
Thus, the value of $K$ can be determined easily and accurately from the peak height relation. Note that it could also be determined from Equation 25. Nevertheless, the use of Equation 32 allows a more accurate determination of equilibrium constant since the peaks proceed from the central zone of the chronopotentiogram, where the capacitive effects are minima.

For the particular case of a square root time current ($u = 1/2$), the relation between peak heights in Figure 4c, obtained from Equations 26 and 27, is $|h_{p,c}|/h_{p,a} = 3.2$ and cathodic and anodic peak potential values, obtained from Equations 28–31, are $E_{p,c} = E'' = -27.21$ mV and $E_{p,a} = E'' = 36.86$ mV, respectively.

This behavior can be used to detect that the steady state has been attained. Note that under steady state conditions it is necessary to use a power of time $u > 0$ since a current step ($u = 0$) would lead to independent of time responses.

4. Acknowledgements

The authors greatly appreciate the financial support provided by the Dirección General de Investigación Científica y Técnica (Project Number CTQ2006-12552/BQU), and the Fundación SENECA (Project Number 03079/P1/05). C. M. Soto thanks the Ministerio de Educación y Ciencia for the grant received.

5. Appendix

5.1. Transient Conditions

In order to obtain the expressions for the concentration profiles of the electroactive species involved in a catalytic process represented by Scheme 1, when a current of the form $I(t) = I_0 u(t)$ is applied to a spherical electrode of any size, the following equation system must be solved:

$$
\frac{[c_i]}{[c_j]} = D \left[ \frac{\partial [c_i]}{\partial r} + \frac{r}{D} \frac{\partial [c_i]}{\partial t} \right] + k_1 c_i(r, t) - k_2 c_i(r, t) + k_3 c_i(r, t) - k_4 c_i(r, t) + k_5 c_i(r, t)
$$

(A.1)

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

The boundary value problem is given by:

\[\begin{align*}
& t = 0; \quad r \geq r_0 \\
& t > 0; \quad r \to \infty \\
& t > 0; \quad r = r_0
\end{align*}\]

\[c_{c}(r, t) = c_{c}^{n} \quad (A.2)\]

\[c_{b}(r, t) = c_{b}^{n} \quad (A.3)\]

\[D \left[ \frac{\partial c_{c}(r, t)}{\partial r} \right]_{r=r_0} \equiv \frac{I_{d}^{n}}{nF \alpha A} \quad (A.4)\]

where \( A \) is the area of the stationary spherical electrode \((A = 4\pi r_0^2, \) with \( r_0 \) being the electrode radius) and \( c_{c}^{n} \) and \( c_{b}^{n} \) are the bulk concentrations of C and B species.

On inserting the variable:

\[u_{i}(r, t) = \frac{c_{i}(r, t)}{\varepsilon^{c}} \]  

\[i = C, B \quad (A.5)\]

where

\[\varepsilon^{c} = c_{c}^{c} + c_{b}^{c} \quad (A.6)\]

the system (A.1) is simplified to the following:

\[\hat{D}u_{c}(r, t) = \hat{D}u_{b}(r, t) = k_{1i}u_{b}(r, t) - k_{2i}u_{c}(r, t) \quad (A.7)\]

where:

\[\hat{D} = \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial r^2} \quad (A.8)\]

Taking into account that in a catalytic process following Scheme 1 it is always fulfilled that [1, 25–27]

\[u_{c}(r, t) + u_{b}(r, t) = \frac{r}{r_0} \quad \forall \quad r, t \quad (A.9)\]

and defining the function

\[\phi(r, t) = (u_{b}(r, t) - K u_{c}(r, t))e^{\epsilon t} \quad (A.10)\]

only one differential equation in the variable \( \phi(r, t) \) needs to be solved:

\[\frac{\partial \phi(r, t)}{\partial t} = D \frac{\partial^2 \phi(r, t)}{\partial r^2} \quad (A.11)\]

with the following boundary conditions:

\[t = 0; \quad r \geq r_0 \quad \phi(r, t) = 0 \quad (A.12)\]

\[t > 0; \quad r \to \infty \quad \phi(r, t) = 0 \quad (A.13)\]

\[t > 0; \quad r = r_0 \quad \phi(r, t) = \frac{I_{d}^{n}}{nF \alpha A e^{\epsilon t}} (1 + K) e^{\epsilon t} \quad (A.14)\]

where \( K \) is the rate constant for the overall reaction.

Equation A.11 can be solved by following the procedure indicated in [28]. The solution is given by the expression:

\[\phi(r, t) = N_{i}(1 + K) e^{\epsilon t} \quad \times \sum_{j=0}^{\infty} \sum_{i=0}^{\infty} \frac{(-1)^j \xi^{i}}{P_{2n+2j+1}} \frac{\psi_{2n+2j+1}(s)}{s^{j+1}} \quad (A.15)\]

\[\xi = 2\sqrt{D\ell} \quad (A.16)\]

\[\chi = k_{1}t \quad (A.17)\]

\[s = \frac{r - r_0}{2\sqrt{D\ell}} \quad (A.18)\]

\[P_{2n+2j+1} = \frac{2I(1 + n)}{I^{(n)}(1 + 2n + 2j + 1)} \quad (A.19)\]

where \( I(\chi) \) is the Euler Gamma function, and \( \psi(s) \) are the Koutecky’s functions [28].

From Equations A.5, A.9, A.10 and A.14 we obtain the following expressions for the concentration profiles of species C and B.

\[c_{c}(r, t) = \frac{1}{(1 + K)} - \frac{r_0^{2} I(t)}{r nF \alpha A e^{\epsilon t}} T_{u}(\xi, \chi) \psi_{2n+2j+1}(s) \quad (A.20)\]

\[c_{b}(r, t) = \frac{K}{(1 + K)} + \frac{r_0^{2} I(t)}{r nF \alpha A e^{\epsilon t}} T_{u}(\xi, \chi) \psi_{2n+2j+1}(s) \quad (A.21)\]

where \( T_{u}(\xi, \chi) \) is defined by Equation 3.
The expressions for the surface concentrations \( (r = r_0) \) of species C and B are in Table 1. Note that \( I(r_0)T_\alpha = I(r)T_\alpha (\varepsilon, \gamma) \), where \( I(r_0) = I_0 \ r_0^\alpha \) and \( I(r) = I_0 \ r^\alpha \) (see Eqs. 4, 9, and 14).

5.2. Cyclic Chronopotentiometry Under Steady State Conditions

To obtain the expressions for the concentration profiles of the electroactive species involved in a catalytic process represented by Scheme 1 under steady conditions, \( c_i, (r,t_j) \), \( i = C, B \), when \( j \) successive currents alternating in sign in the way \( I(t_j) = (-1)^j I_0 \) are applied to a spherical electrode of any size, by proceeding in the same way as in Section 5.1 with the additional assumption \( \partial c_i / \partial r = \partial c_0 / \partial r = 0 \) in Equations A.1, and introducing the function

\[
\phi(r,t_j) = u_0(r,t_j) - K u_i(r,t_j)
\]  

(B.1)

instead of A.10, we must solve the following differential equation:

\[
\frac{\partial^2 \phi(r,t_j)}{\partial r^2} - \frac{\kappa}{D} \phi(r,t_j) = 0
\]  

(B.2)

with the boundary conditions:

\[ r \to \infty \quad \phi(r,t_j) = 0 \]  

(B.3)

\[ r = r_0 \quad \phi(r_0,t_j) = \frac{1}{nFAD} \delta_i(1 + K) e^{-(r-n)/\sqrt{\kappa D}} \]  

(B.4)

Thus, the solution of Equation B.2 is given by the expression:

\[
\phi(r,t_j) = \frac{I(t_j)}{nFADr^\alpha} \delta_i(1 + K) e^{-(r-n)/\sqrt{\kappa D}}
\]  

(B.5)

From Equations A.5, A.9, B.1 and B.5 we obtain the expressions for the concentrations profiles of species C and B:

\[
\frac{c_i(r,t_j)}{r^\alpha} = \frac{1}{(1 + K)} - \frac{r_0}{r} \delta_i \frac{I(t_j)}{nFAD} e^{-(r-n)/\sqrt{\kappa D}}
\]  

(B.6)

where \( \delta_i \) is defined by Equation 11.

The expressions for the surface concentrations are given by Equations 20 and 21 in Section 2.4.

6. References