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RECIPROCAL DERIVATIVE CHRONOPOTENTIOMETRY WITH EXPONENTIAL CURRENTS

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Abstract

Theoretical expressions are presented which correspond to the response of adsorbed molecules which exhibit a reversible or totally irreversible charge transfer in Reciprocal Derivative Chronopotentiometry with constant current (RDC) and Reciprocal Derivative Chronopotentiometry with exponential current (RDCE).

In spite of the fact that RDC enjoys an important role in the elucidation of electrode processes, when this technique is applied to adsorbed molecules exhibiting an irreversible charge transfer, peaks are not observed. Under these conditions RDCE turns out to be more suitable than RDC. Furthermore, the use of programmed currents makes the selection of an appropriate range of transition times easier than does the use of constant currents.

Equations for the peak currents and peak potentials of the $(dt/dE)/E$ and $(de^{\omega t}/dE)/E$ curves for reversible and totally irreversible process are given in order to show the advantages of the use of the $(de^{\omega t}/dE)/E$ curve when an exponential current time function is used.

Keywords: Reciprocal derivative chronopotentiometry, adsorption, programmed current, irreversible processes.

Introduction

In the usual Reciprocal Derivative Chronopotentiometry with constant current (RDC) [1-12], the reciprocal derivative (dt/dE) of the E/t curve obtained when a constant current I_0 is applied is represented versus the potential. In spite of the greater advantages of this technique, a serious disadvantage is observed when this technique is applied to adsorbed redox molecules exhibiting an irreversible behaviour since, in these conditions the reciprocal derivative chronopotentiograms do not present peaks.

The main aim of this paper is to show the advantages of the electrochemical technique Reciprocal Derivative Chronopotentiometry with exponential current (RDCE) [13] in the study of adsorbate covered electrodes and to demonstrate how the experimental E/t curve obtained when an exponential current of the form $I(t) = I_0 e^{\omega t}$ is applied, must be transformed into the $E/e^{\omega t}$ curve in order to calculate its reciprocal derivative with respect to the function $e^{\omega t}$, instead of the variable t. Indeed, contrarily to the $(dt/dE)/E$ curves, the $(d e^{\omega t}/dE)/E$ curves always present peaks, whatever the reversibility degree of the process. Moreover, the expressions corresponding to the peak height and the peak potential are very simple and enable the kinetic and thermodynamic parameters to be determined as well as the surface excesses of the electroactive species of the process analysed.

Finally, this new technique presents the same advantages as RDC over cyclic voltammetry, i. e., the effects of the ohmic drop and the capacitive current can become practically negligible since the sensitivity of RDCE increases when the value of the exponential current applied decreases and the peak in RDCE corresponds to the central zone of the $E/e^{\omega t}$ curve in which the double layer effects are minimal [13-15].

Theory

When a cathodic exponential time current of the form $I(t) = I_0 e^{\omega t}$ is applied to a coated electrode with a molecular film of an electroactive couple, the potential time response is given by:

$$\frac{I(t)}{nFAk^{\prime 0}} = \Gamma_A(t)\eta^{-\alpha} - \Gamma_B(t)\eta^{(1-\alpha)} \quad (1)$$

where

$$\eta = e^{\frac{nF}{RT}(E-E^{\prime 0})} \quad (2)$$

and $\Gamma_A(t)$ and $\Gamma_B(t)$ (in mol cm⁻²) are the surface concentrations of the oxidized (A) and reduced (B) species, whose expressions can be easily deduced by taking into account that they fulfil the conditions [12]:

$$\Gamma_A(t) = \frac{I_0}{nFA} \int_0^t e^{\omega t} dt \quad (3)$$

and,

$$\Gamma_A(t) + \Gamma_B(t) = \Gamma_{A,0} \quad (4)$$

with $\Gamma_{A,0}$ being the initial values of the surface concentrations of the oxidised species.

From equations (2) and (3) we deduce,

$$\frac{\Gamma_A(t)}{\Gamma_{A,0}} = 1 - \frac{I_0}{nFA\omega\Gamma_{A,0}} (e^{\omega t} - 1) \quad (5)$$

$$\frac{\Gamma_B(t)}{\Gamma_{A,0}} = -\frac{I_0}{nFA\omega\Gamma_{A,0}} (e^{\omega t} - 1) \quad (6)$$

$E^{\prime 0}$ is the surface standard potential, $k^{\prime 0}$ is the heterogeneous rate constant of the electrochemical reaction (s⁻¹), A is the electrode area (cm²), α and $1-\alpha$ are the charge transfer coefficients of the cathodic and anodic surface reactions, respectively, and n , F , R and T have their usual meanings.

The transition time τ (time for which $\Gamma_A(\tau) = 0$) can be easily deduced by making zero equation (5). So we deduce:

$$e^{\omega\tau} - 1 = \frac{nFA\omega\Gamma_{A,0}}{I_0} \quad (7)$$

or,

$$\tau = \frac{1}{\omega} \ln \left(\frac{nFA\omega\Gamma_{A,0}}{I_0} + 1 \right) \quad (8)$$

By introducing equations (5)-(6) and (7) in equation (1) we obtain the following expression for the E/t response,

$$\frac{\omega}{k^{\prime 0}} e^{\omega t} \eta^{\alpha} = e^{\omega\tau} - e^{\omega t} - \eta(e^{\omega t} - 1) \quad (9)$$

Equation (9), for the particular case of reversible processes ($k^{\prime 0} \rightarrow \infty$) is transformed into,

$$\eta = \frac{e^{\omega\tau} - e^{\omega t}}{e^{\omega t} - 1} \quad (10)$$

and for totally irreversible ones ($k^{\prime 0} \ll 1 \text{ s}^{-1}$), equation (9) becomes,

$$\eta^{\alpha} = \left(e^{-\omega t} e^{\omega\tau} - 1 \right) \frac{k^{\prime 0}}{\omega} \quad (11)$$

Reciprocal Derivative Chronopotentiometry is an electrochemical technique which consists in the plotting of the reciprocal derivative with respect to the time of the

potential time curve versus the potential (i.e., the dt/dE vs. E curve). In most cases it presents a peak which depends on the kinetics and thermodynamics parameters of the electrode process [1-12].

The dt/dE response can be numerically deduced from equation (9) however this leads to an easy analytical expression in the case of a reversible process (equation (10)) or an irreversible one (equation (11)). So, from equations (10) and (11) we obtain:

$$\frac{dt}{dE} = -\frac{nF}{\omega RT} \frac{e^{\omega\tau} - 1}{e^{\omega t}} \frac{\eta}{(1+\eta)^2} \quad \text{reversible process} \quad (12)$$

$$\frac{dt}{dE} = -\frac{\alpha nF}{k^0 RT} \frac{\eta^\alpha}{1 + (\omega/k^0)\eta^\alpha} \quad \text{irreversible process} \quad (13)$$

From equations (12) and (13), which correspond, respectively, to the reciprocal derivative curve corresponding to a reversible and an irreversible process when an exponential current $I(t) = I_0 e^{\omega t}$ is applied, we can calculate the peak parameters in both cases, which are:

Table 1. Peak parameters for reversible and totally irreversible processes obtained in RDC (dt/dE vs. E responses) for the application of a current of the form $I(t) = I_0 e^{\omega t}$.

	Totally reversible process (see equation (12))	Totally irreversible process (see equation (13))
Peak potential	$E^{r0} + \frac{RT}{nF} \ln \frac{e^{\omega\tau} - (e^{\omega\tau} - 1)^{1/2}}{(e^{\omega\tau} - 1)^{1/2} - 1}$	No peak is observed
Peak height	$\frac{nF}{\omega RT} \frac{[(e^{\omega\tau} - 1)^{3/2} + 1 + 2(e^{\omega\tau} - 1)^{1/2}]}{(e^{\omega\tau} - 1)^{3/2}}$	No peak is observed

These results are similar to those deduced in reciprocal derivative chronopotentiometry when a constant current is applied (in the same conditions), again with no peak being observed in the case of a totally irreversible charge transfer reaction.

These results are not desirable since for totally irreversible processes when the peak does not exist, the characterisation of a determined totally irreversible electrode process is not possible with this technique.

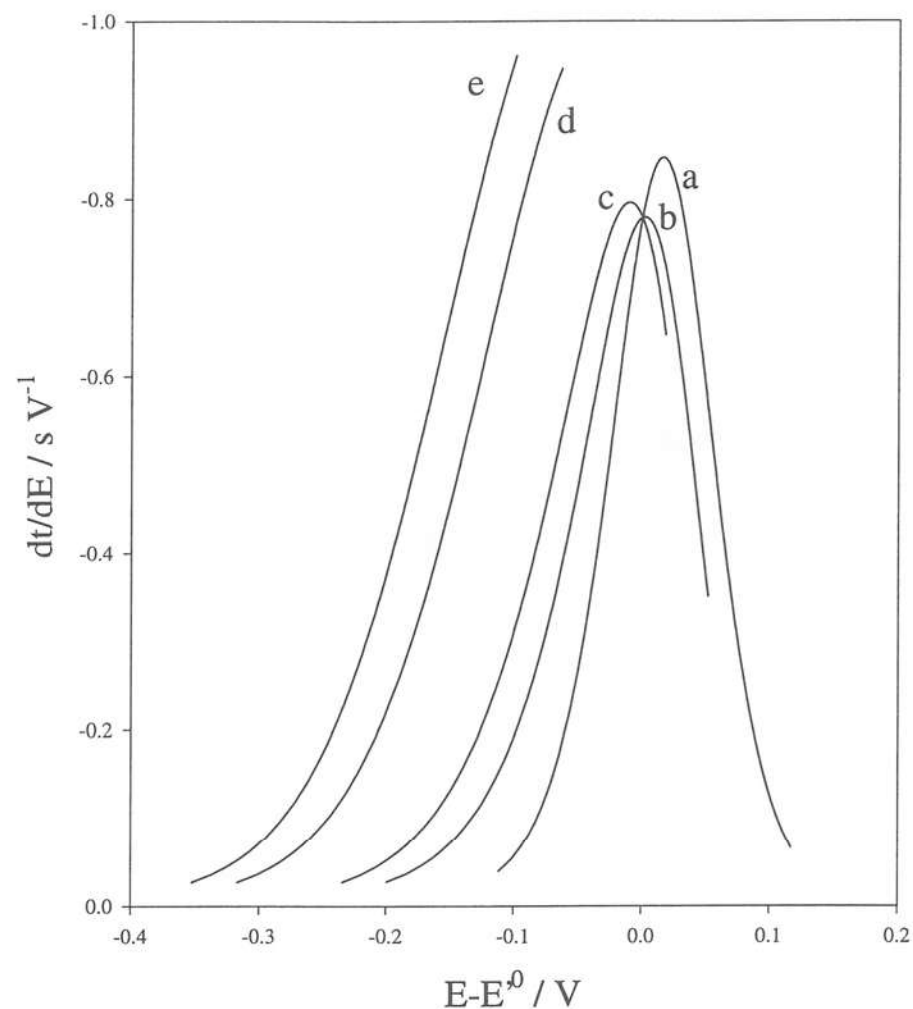


Figure 1. Theoretical RDC curves (dt/dE vs. $E - E^0$ curves, see equations (12) and (13)) corresponding to the application of an exponential current time function $I(t) = I_0 e^{15t}$, $\omega = 15 \text{ s}^{-1}$, $n=1$, $\alpha = 0.5$, $I_0 / (nF\Gamma_{A,0}) = 5 \text{ s}^{-1}$. The values of k^0 (in s^{-1}) are: a) 150, b) 15, c) 7.5, d) 1.50 and e) 0.75.

Figure 1 shows the dt/dE vs. E curves for a charge transfer reaction with different values of k^0 (in s^{-1}) for the application of an exponential current

$I(t) = I_0 e^{15t}$, $\omega = 15 \text{ s}^{-1}$ and $I_0 / (nFA\Gamma_{A,0}) = 5 \text{ s}^{-1}$. As can be seen, the peak potential is shifted towards more cathodic values when k'^0 decreases. Moreover, the peak disappears for values of the rate constant $k'^0 \leq 5.0 \text{ s}^{-1}$, in these conditions (i. e. the process behaves as totally irreversible).

The above behaviour can be notably improved if we take into account that the chronopotentiograms (E/t responses, see equations (9), (10) and (11)) show that the potential function η ($= \exp\left(\frac{nF}{RT}(E - E'^0)\right)$) depends on t through the function $e^{\omega t}$. This fact suggests that in order to obtain a simpler and more useful reciprocal derivative response the experimental E/t response should first be transformed into the $E/e^{\omega t}$ response and then the reciprocal derivative of this curve should be determined with respect to the function $e^{\omega t}$ instead of the variable t .

Indeed, by determining this reciprocal derivative of equations (10) and (11) we deduce for a totally reversible process,

$$\frac{de^{\omega t}}{dE} = \frac{n^2 F^2 A \omega \Gamma_{0,A}}{RT I_0} \frac{\eta}{(1+\eta)^2} \quad \text{reversible process} \quad (14)$$

whereas for a totally irreversible one we obtain,

$$\frac{de^{\omega t}}{dE} = -\frac{cnF}{RT} \frac{(\omega / k'^0) \eta^\alpha}{(1 + (\omega / k'^0) \eta^\alpha)^2} \left(1 + \frac{nFA\omega\Gamma_T}{I_0} \right) \quad \text{irreversible process} \quad (15)$$

From equations (14) and (15) we obtain the following expressions for the peak potentials and the peak heights in the case of reversible and irreversible processes:

Table II. Peak parameters for reversible and totally irreversible processes obtained in RDCE ($de^{\omega t}/dE$ vs. E responses) for the application of a current of the form $I(t) = I_0 e^{\omega t}$.

	Totally reversible process (see equation (14))	Totally irreversible process (see equation (15))
Peak potential	E'^0	$E'^0 + \frac{RT}{cnF} \ln\left(\frac{k'^0}{\omega}\right)$
Peak height	$\frac{nF}{4RT} (e^{\omega\tau} - 1)$	$\frac{cnF}{4RT} e^{\omega\tau}$

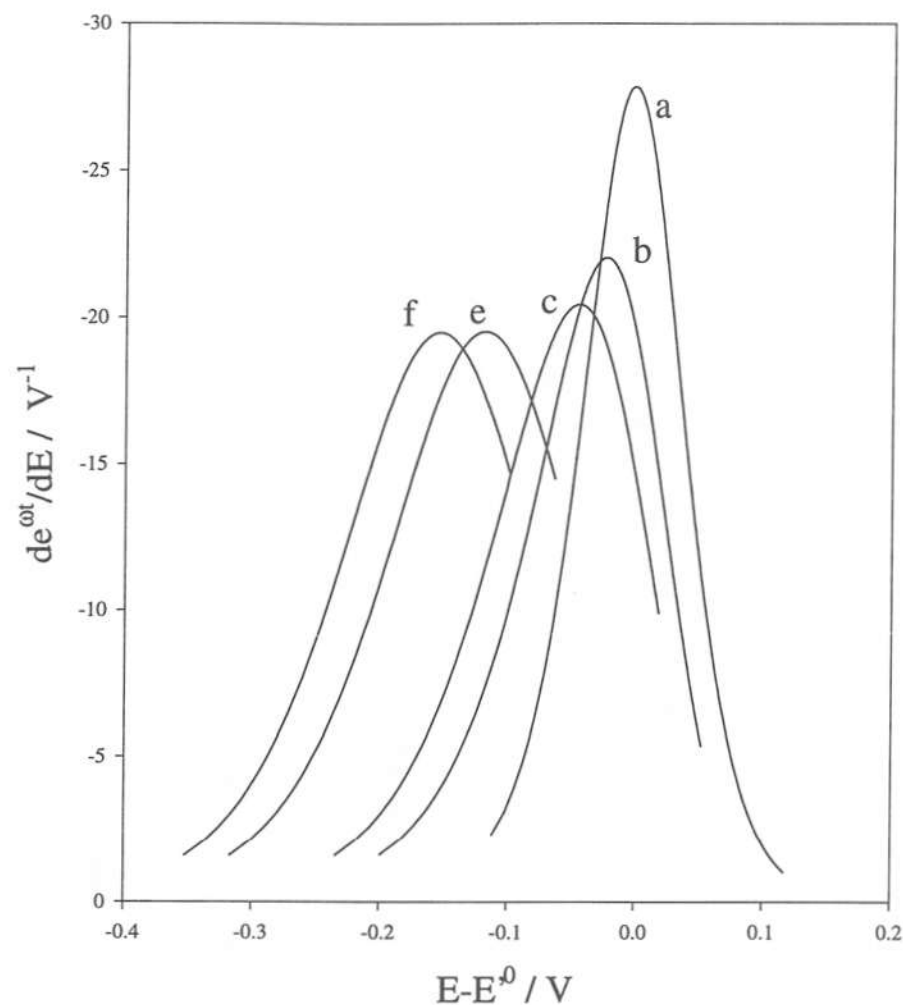


Figure 2. Theoretical RDCE curves ($de^{\omega t}/dE$ vs. $E - E'^0$ curves, see equations (14) and (15)) corresponding to the application of an exponential current time function $I(t) = I_0 e^{15t}$, $\omega = 15 \text{ s}^{-1}$. Other conditions as in Figure 1.

In Figure 2 we have plotted the $de^{\omega t}/dE$ vs. E curves for the same values of the surface constant k^0 than those used in Figure 1. In this case ($\alpha = 0.5$) the peak height for a reversible process (curve a) coincides with the surface standard potential E^0 . These curves always present a peak independently of the value of k^0 , which is shifted towards negative potentials as k^0 decreases. The peak height decreases with k^0 until reach its limit value (given in Table (2)) for $k^0 \leq 5.0 \text{ s}^{-1}$.

Final comments

As can be seen, the use of the $de^{\omega t}/dE$ curves instead of the dt/dE curves in this case presents the following, very interesting advantages:

1. The peak parameters are quantified in both cases (reversible and totally irreversible processes), and they are given by very easy mathematical relationships from which the deduction of thermodynamic (E^0) and kinetic (k^0 and α) parameters are immediate. The surface excesses are also easily determined from the peak height since in both cases this height depends on $e^{\omega\tau}$ (i. e., on $(nFA\omega\Gamma_{A,0})/I_0$).

2. Unlike what occurs in RDC, the $de^{\omega t}/dE$ response presents a peak whatever the degree of reversibility of the process. Thus the kinetic parameters of an irreversible process can be easily determined from expressions in Table II.

3. The signals corresponding to the $de^{\omega t}/dE$ vs. E curves have been compared with those obtained in CV and show that the use of RDCE technique, just like the use of RDC, minimizes the effects of the ohmic drop and of the charge current [3, 12, 15].

4. The value of ω can be selected, which leads to the following advantages:

a) A suitable selection of transition times in a wider range than with a constant current.

b) A quasireversible charge transfer reaction can be treated as more reversible (by increasing the value of ω) or as totally irreversible (by decreasing the value of ω).

5. The expressions of the peak heights and the peak potentials are also simpler than those obtained when CV is used.

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