

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/222682805>

Theory for cyclic reciprocal derivative chronopotentiometry with power and exponential programmed currents applied to electrodes coated with reversible electroactive molecular film...

ARTICLE *in* JOURNAL OF ELECTROANALYTICAL CHEMISTRY · NOVEMBER 2000

Impact Factor: 2.87 · DOI: 10.1016/S0022-0728(00)00288-6

CITATIONS

18

READS

11

2 AUTHORS, INCLUDING:



Angela Molina

University of Murcia

210 PUBLICATIONS 1,775 CITATIONS

SEE PROFILE



ELSEVIER

Theory for cyclic reciprocal derivative chronopotentiometry with power and exponential programmed currents applied to electrodes coated with reversible electroactive molecular films

Angela Molina *, Joaquín González

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

Received 25 July 2000; received in revised form 25 July 2000; accepted 25 July 2000

Abstract

Theoretical expressions corresponding to the responses of adsorbed redox molecules exhibiting reversible charge transfer in cyclic reciprocal derivative chronopotentiometry with programmed currents of the form $I(t) = (-1)^{i+1} I_0 t_i^u$ and $I(t) = (-1)^{i+1} I_0 e^{\omega t_i}$ are presented. The effects of the interfacial potential distribution are considered in both cases by using the Smith and White model (Anal. Chem. 64 (1992) 2398). These equations become those previously deduced by Honeychurch (J. Electroanal. Chem. 445 (1998) 63) in reciprocal derivative chronopotentiometry with constant current on making $u = 0$ and $\omega = 0$. The total analogy between the reciprocal derivative chronopotentiograms (dt_i^{u+1}/dE versus E or $d e^{\omega t_i}/dE$ versus E curves) and the cyclic voltammograms (I/E curves) is proved. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Cyclic reciprocal derivative chronopotentiometry; Programmed currents; Interfacial potential distribution; Adsorption

1. Introduction

In recent papers we have demonstrated the total analogy between reciprocal derivative chronopotentiometry with a programmed current variable with any power of time and derivative and differential pulse voltammeteries for a reversible charge transfer reaction with both electroactive species soluble in the electrolytic solution [1,2].

The main aim of this paper is to demonstrate the total analogy between the curves dt_i^{u+1}/dE versus E or $d e^{\omega t_i}/dE$ versus E (when programmed currents of the form $I(t) = (-1)^{i+1} I_0 t_i^u$ or $I(t) = (-1)^{i+1} I_0 e^{\omega t_i}$, respectively, are applied), and the I/E wave shape obtained in cyclic voltammetry (CV), for the case of an electrode coated with a molecular film of a reversible electroactive couple. This analogy is also fulfilled in the more complex case in which the capacitance of adsorbate covered electrodes is considered. To obtain the analytical expressions of the t_i^{u+1}/E and the $e^{\omega t_i}/E$

curves and their derivatives in this last case, we have applied the theory of the interfacial potential distribution deduced by Smith and White for CV [3], when one or several currents successive and alternating in sign and variable with a power of time or exponentially with time, respectively, are applied. The results obtained by Honeychurch in reciprocal derivative chronopotentiometry with constant current coincide with those deduced in this work in the particular case in which $u = 0$ (power time current) and $\omega = 0$ (exponential current) [4].

Cyclic reciprocal derivative chronopotentiometry (CRDCP) with constant current at present enjoys extensive use in the elucidation of electrode processes [5–7], in analytical chemistry and biochemistry [8–13], and in the study of adsorbate covered electrodes [4,14–16]. Although this chronopotentiometric technique presents a similar response to that corresponding to CV, as is demonstrated in this work, the analytical advantages obtained thereby are greater than those obtained in CV [8–11]. This is fundamentally due to the need to work at high sweep rates to improve the peak height in CV, which leads to an increase in the distortion of the I/E curve on account of the increase of the ohmic drop

* Corresponding author. Tel.: +34-968-367524; fax: +34-968-364148.

E-mail address: amolina@fcu.um.es (A. Molina).

effects [9,17]. However, in CRDCP the peak height of the curves dt_i^{u+1}/dE versus E or $d e^{\omega t_i}/dE$ versus E (analytical sensitivity) increases when the applied current decreases and therefore the ohmic drop effects may be negligible.

Moreover, CRDCP with programmed current offers the further advantages:

- The use of programmed current instead of constant current enable us to change the scan rate easily by using different exponents u and ω in the applied programmed currents $I(t) = (-1)^{i+1} I_0 t_i^u$ or $I(t) = (-1)^{i+1} I_0 e^{\omega t_i}$, respectively.
- The possibility of selecting a wide range of values of u and ω exponents of the power and the exponential currents, respectively, allows a suitable selection of transition times in a wider range of concentration than does a constant current [6].
- This versatility is also very desirable when quasireversible processes are analysed since these can be treated as more reversible (by increasing the values of u and ω) or as totally irreversible (by decreasing the values of u and ω) [6].
- The use of derivative chronopotentiometry with constant current is not suitable in the analysis of a totally irreversible charge transfer reaction of the adsorbed species due to the $(dt/dE)/E$ response not presenting any peak, whereas the $(dt_i^{u+1}/dE)/E$ with $u \neq 0$ and the $(d e^{\omega t_i}/dE)/E$ with $\omega \neq 0$ does [18,19].

For the above reasons we think that the use of exponential [20,21] and power currents [1,2] in reciprocal derivative chronopotentiometry may have a promising future in the study of adsorption processes.

2. Cyclic reciprocal derivative chronopotentiometry with power time currents

In a previous paper we have demonstrated that when several successive power currents, cathodic $I(t) = I_0 t_i^u$, with $u > -1$ and $i = 1, 3, 5, \dots$, and anodic $I(t) = -I_0 t_i^u$, with $u > -1$ and $i = 2, 4, 6, \dots$, are applied to a coated electrode with a molecular film of an electroactive reversible couple, the successive potential time responses, supposing that both species are initially adsorbed, are given by [7]:

$$\delta = \frac{\tau_1^{u+1} - t_1^{u+1}}{\Omega \tau_1^{u+1} + t_1^{u+1}} \text{ for } 0 \leq t_1 \leq \tau_1 \quad (1)$$

$$\delta = \frac{\tau_i^{u+1} - t_i^{u+1}}{t_i^{u+1}} \text{ for } 0 \leq t_i \leq \tau_i, i \geq 2 \quad (2)$$

where

$$\delta = \exp\left((-1)^{i+1} \frac{RT}{nF} (E - E^{0'})\right) \quad i = 1, 2, 3 \dots \quad (3)$$

$$\Omega = \frac{\Gamma_{0,B}}{\Gamma_{0,A}} \quad (4)$$

with $\Gamma_{0,A}$ and $\Gamma_{0,B}$ being the initial surface excesses of A and B and $E^{0'}$ being the formal potential of the adsorption reaction.

Eqs. (1) and (2) for the E/t_1^{u+1} and E/t_i^{u+1} responses can also be written as explicit expressions of t_1^{u+1} and t_i^{u+1} , respectively:

$$t_1^{u+1} = \tau_1^{u+1} \left(\frac{1 - \Omega \delta}{1 + \delta} \right) \quad (5)$$

$$t_i^{u+1} = \tau_i^{u+1} \left(\frac{1}{1 + \delta} \right) \quad i \geq 2. \quad (6)$$

where the successive transition times are

$$\tau_1^{u+1} = \frac{(u+1)nFA\Gamma_{0,A}}{I_0} \quad (7)$$

$$\tau_i^{u+1} = (1 + \Omega) \tau_1^{u+1} \quad i \geq 2 \quad (8)$$

By deriving Eqs. (5) and (6) with respect to the potential we obtain:

$$y_i^{\text{power}} = \frac{dt_i^{u+1}}{dE} = (-1)^i \frac{n^2 F^2}{RT} \frac{A(u+1)}{I_0} \Gamma_{0,T} \frac{\delta}{(1 + \delta)^2} \quad (9)$$

$i = 1, 2, 3, \dots$

with

$$\Gamma_{0,T} = \Gamma_{0,A} + \Gamma_{0,B} = \Gamma_{0,A}(1 + \Omega) \quad (10)$$

where $y_i^{\text{power}} = dt_i^{u+1}/dE$ refers to the reciprocal derivative of the E/t_i^{u+1} response which, in contrast to what occurs with the E/t responses, is identical in absolute value when only one or both species are initially adsorbed.

By imposing $d^2 t_i^{u+1}/dE^2 = 0$ on Eq. (9) we obtain:

$$y_{i,\text{peak}}^{\text{power}} = (-1)^i \frac{n^2 F^2}{4RT} \frac{A(u+1)}{I_0} \Gamma_{0,T} \quad i = 1, 2, 3, \dots \quad (11a)$$

$$E_{\text{peak}} = E^{0'} \quad (11b)$$

From Eqs. (9), (11a) and (11b) it can be seen that superimposable responses with symmetrical shape are obtained for a reversible process.

3. Cyclic reciprocal derivative chronopotentiometry with exponential time currents

By following a substantially similar procedure to that applied in the above case when two or more successive exponential currents alternating in sign of the form $I(t) = (-1)^{i+1} I_0 e^{\omega t_i}$ with any value of ω are applied, the different E/t responses when both species are initially adsorbed are given as:

$$\delta = \frac{e^{\omega \tau_1} - e^{\omega t_1}}{\Omega e^{\omega \tau_1} + e^{\omega t_1} - (1 + \Omega)} \text{ for } 0 \leq t_1 \leq \tau_1 \quad (12)$$

$$\delta = \frac{e^{\omega\tau_i} - e^{\omega t_i}}{e^{\omega\tau_i} - 1} \text{ for } 0 \leq t_i \leq \tau_i, i \geq 2 \quad (13)$$

The values of ω are restricted only for the existence of transition time.

Eqs. (12) and (13) corresponding to the $E/e^{\omega t_i}$ responses can, after some rearrangements be given as explicit functions of $e^{\omega t_i}$ as below:

$$e^{\omega\tau_1} - 1 = (e^{\omega\tau_1} - 1) \frac{1 - \Omega\delta}{1 + \delta} \quad (14)$$

$$e^{\omega t_i} - 1 = (e^{\omega\tau_i} - 1) \frac{1}{1 + \delta} \quad i \geq 2 \quad (15)$$

with the successive transition times being in this case:

$$e^{\omega\tau_1} - 1 = \frac{nFA\omega\Gamma_{0,A}}{I_0} \quad (16)$$

$$e^{\omega\tau_i} - 1 = \frac{nFA\omega\Gamma_{0,A}(1 + \Omega)}{I_0} \quad i \geq 2 \quad (17)$$

By deriving Eqs. (14) and (15) with respect to the potential we deduce:

$$y_i^{\text{exp}} = \frac{d e^{\omega t_i}}{dE} = (-1)^i \frac{n^2 F^2}{RT} \frac{A\omega\Gamma_{0,T}}{I_0} \frac{\delta}{(1 + \delta)^2} \quad (18)$$

$i = 1, 2, 3, \dots$

and the peak values $y_{i,\text{peak}}^{\text{exp}}$ are given by:

$$y_{i,\text{peak}}^{\text{exp}} = (-1)^i \frac{n^2 F^2}{4RT} \frac{A\omega\Gamma_{0,T}}{I_0} \quad i = 1, 2, 3, \dots \quad (19)$$

From Eqs. (18) and (19) it can be seen that, just as with the results corresponding to a power time current, we obtain symmetrical cathodic and anodic peaks with $E_{\text{peak}} = E^{0'}$.

4. Consideration of the Smith and White model for the interfacial potential distribution effect on cyclic reciprocal derivative chronopotentiometry with power and exponential current time functions

In this model, it is assumed that the redox centres of the adsorbate are all located in a plane, referred to as the plane of electron transfer (PET), at a distance d from the electrode surface, with the potential profile being linear in the region $0 \leq x \leq d$ and the potential profile in the solution described by the Gouy-Chapman theory [3]. We will not consider that a portion of the molecules could extend beyond the redox centers or the additional inclusion of a Stern layer.

Since electron transfer reversibility is assumed, cathodic and anodic responses are the mirror image of each other. We will show the treatment for the cathodic response only and we will generalise the response obtained in CRDCP for any number of power time or exponential currents applied.

Under these conditions, the Nernstian response of the system, by supposing that both species are initially adsorbed, can be written as (see eq. (5) in Ref. [3]):

$$E - E^{0'} - (\phi_{\text{PET}} - \phi_s) = \frac{RT}{nF} \ln \frac{f}{1-f} \quad (20)$$

where f is the mole fraction of oxidised adsorbate:

$$f = \frac{\Gamma_A(t)}{\Gamma_{0,T}} \quad (21)$$

ϕ_{PET} and ϕ_s are the electrostatic potentials at the plane of electron transfer and in the bulk solution, respectively.

If we apply a power or exponential current time function, designed by $I(t)$, we can assume that the total current applied is the sum of a faradaic current (responsible for the redox change of the oxidised or the reduced adsorbed species), and a charging current as below:

$$\frac{I(t)}{nFA} = -\Gamma_{0,T} \frac{df}{dt} - \frac{C_T}{nF} \frac{dE}{dt} \quad (22)$$

where $I(t) = (-1)^{i+1} I_0 t_i^u$, with $u > -1$, for a power time current and $I(t) = (-1)^{i+1} I_0 e^{\omega t_i}$, for any value of ω , for an exponential one. C_T is the total interfacial capacitance, which is given by (see eqs. (17a) and (18a) in Ref. [3]):

$$C_T = C_1(1 - \partial\phi_{\text{PET}}/\partial E) \quad (23a)$$

$$C_1 = \epsilon_0 \epsilon_1 / d \quad (23b)$$

C_1 is the capacitance of the adsorbed layer and ϵ_0 and ϵ_1 are the permittivity of the free space and the dielectric constant of the adsorbed layer, respectively.

By differentiating Eq. (20) with respect to the time and solving for dE/dt we obtain:

$$\frac{dE}{dt} = \frac{RT}{nF} \frac{1}{f(1-f)} \frac{1}{(1 - \partial\phi_{\text{PET}}/\partial E)} \frac{df}{dt} \quad (24)$$

By substituting Eq. (24) in Eq. (22) we deduce (see also Eq. (23a)):

$$\frac{I(t)}{nFA} = -\left(\Gamma_{0,T} + \frac{C_1 RT}{n^2 F^2} \frac{1}{f(1-f)}\right) \frac{df}{dt} \quad (25)$$

Integrating Eq. (25) for a power time current yields:

$$f + \frac{C_1 RT}{n^2 F^2 \Gamma_{0,T}} \ln \frac{f}{1-f} = f_0 + \frac{C_1 RT}{n^2 F^2 \Gamma_{0,T}} \ln \frac{f_0}{1-f_0} - \frac{I_0 t_1^{u+1}}{(u+1)nFA\Gamma_{0,T}} \quad (26)$$

and for an exponential time current:

$$f + \frac{C_1 RT}{n^2 F^2 \Gamma_{0,T}} \ln \frac{f}{1-f} = f_0 + \frac{C_1 RT}{n^2 F^2 \Gamma_{0,T}} \ln \frac{f_0}{1-f_0} - \frac{I_0 e^{\omega t_1}}{\omega nFA\Gamma_{0,T}} \quad (27)$$

with

$$f_0 = \frac{\Gamma_{0,A}}{\Gamma_{0,T}} \quad (28)$$

It is possible to obtain explicit expressions for t_1^{u+1} and $e^{\omega t_1}$ as functions of the measured potential E . So, by re-writing Eq. (20) as:

$$f = \frac{\delta_{\text{PET}}}{1 + \delta_{\text{PET}}} \quad (29)$$

with

$$\delta_{\text{PET}} = \exp\left(\frac{nF}{RT}(E - E^{0'} - (\phi_{\text{PET}} - \phi_s))\right) \quad (30)$$

and by substituting Eq. (29) in Eqs. (26) and (27) the following is obtained for a power time current:

$$t_1^{u+1} = \frac{nFA(u+1)\Gamma_{0,T}}{I_0} \left(\frac{1 - \Omega\delta_{\text{PET}}}{(1 + \delta_{\text{PET}})(1 + \Omega)} - \frac{C_1RT}{n^2F^2\Gamma_{0,T}}\delta_{\text{PET}} + \frac{C_1RT}{n^2F^2\Gamma_{0,T}} \ln \frac{f_0}{1 + f_0} \right) \quad (31)$$

while for an exponential current

$$e^{\omega t_1} - 1 = \frac{nFA\omega\Gamma_{0,T}}{I_0} \left(\frac{1 - \Omega\delta_{\text{PET}}}{(1 + \delta_{\text{PET}})(1 + \Omega)} - \frac{C_1RT}{n^2F^2\Gamma_{0,T}}\delta_{\text{PET}} + \frac{C_1RT}{n^2F^2\Gamma_{0,T}} \ln \frac{f_0}{1 - f_0} \right) \quad (32)$$

The derivatives of Eqs. (31) and (32) with respect to the potential, dt_i^{u+1}/dE and $d e^{\omega t_i}/dE$ responses, are given by:

$$\begin{aligned} \frac{I_0}{(u+1)} \left(\frac{dt_i^{u+1}}{dE} \right) &= I_0 t_i^u \left(\frac{dt_i}{dE} \right) \\ &= (-1)^i \\ &\quad \times \frac{n^2F^2A\Gamma_{0,T}}{RT} \left(\frac{\delta_{\text{PET}}}{(1 + \delta_{\text{PET}})^2} + \frac{C_1RT}{n^2F^2\Gamma_{0,T}} \right) \\ &\quad \times (1 - \partial\phi_{\text{PET}}/\partial E) \quad i = 1, 2, 3, \dots \end{aligned} \quad (33)$$

for a power time current and:

$$\begin{aligned} \frac{I_0}{\omega} \left(\frac{d e^{\omega t_i}}{dE} \right) &= I_0 e^{\omega t_i} \left(\frac{dt_i}{dE} \right) \\ &= (-1)^i \frac{n^2F^2A\Gamma_{0,T}}{RT} \left(\frac{\delta_{\text{PET}}}{(1 + \delta_{\text{PET}})^2} + \frac{C_1RT}{n^2F^2\Gamma_{0,T}} \right) \\ &\quad \times (1 - \partial\phi_{\text{PET}}/\partial E) \quad i = 1, 2, 3, \dots \end{aligned} \quad (34)$$

for an exponential one.

Note that Eqs. (31) and (32) transform into Eqs. (5) and (14), respectively, and Eqs. (33) and (34) into Eqs. (9) and (18), respectively, when the capacitance of the adsorbate covered is not considered (i.e. when $C_1 \cong 0$)

5. Results and discussion

5.1. Comparison between cyclic voltammetry and cyclic reciprocal derivative chronopotentiometry with power time and exponential currents

5.1.1. Absence of effects of the interfacial potential distribution

By comparing Eqs. (9) and (11a) corresponding to the dt_i^{u+1}/dE versus E curves and Eqs. (18) and (19) corresponding to the $d e^{\omega t_i}/dE$ versus E ones, with Eqs. (28) and (30) for CV deduced by Laviron in Ref. [22] for a reversible charge transfer, which can be written as:

$$\frac{I^{\text{CV}}}{v} = (-1)^i \frac{n^2F^2}{RT} A\Gamma_{0,T} \frac{\delta}{(1 + \delta)^2} \quad i = 1, 2, 3, \dots \quad (35)$$

$$\frac{I_{\text{peak}}^{\text{CV}}}{v} = (-1)^i \frac{n^2F^2}{4RT} A\Gamma_{0,T} \quad i = 1, 2, 3, \dots \quad (36)$$

with v being the constant sweep rate that is given by $v = |dE/dt|$, it is evident that the following is fulfilled:

$$\frac{I_0}{(u+1)} y_i^{\text{power}} = \frac{I_0}{\omega} y_i^{\text{exp}} = \frac{I^{\text{CV}}}{v} \quad (37)$$

and

$$\frac{y_i^{\text{power}}}{4y_{i,\text{peak}}^{\text{power}}} = \frac{y_i^{\text{exp}}}{4y_{i,\text{peak}}^{\text{exp}}} = \frac{I^{\text{CV}}}{4I_{\text{peak}}^{\text{CV}}} = \frac{\delta}{(1 + \delta)^2} \quad (38)$$

This behaviour is shown in Fig. 1 in which, we have plotted the normalised $(t_i^{u+1}/\tau_i^{u+1})/(E - E^{0'})$ curves (black circles, see Eqs. (5) and (6)), obtained for the application of two successive power time currents of the form $I_0 t_1^u$ and $-I_0 t_2^u$ (with $u = 1$), and also the $((e^{\omega t_i} - 1)/(e^{\omega \tau_i} - 1))/(E - E^{0'})$ curves (white squares, see Eqs. (14) and (15)), obtained for the application of two successive exponential currents of the form $I_0 e^{\omega t_1}$ and $-I_0 e^{\omega t_2}$ (with $\omega = 0.2$). In Fig. 1b the normalised derivatives $(y_i^{\text{power}}/4y_{i,\text{peak}}^{\text{power}})$ and $(y_i^{\text{exp}}/4y_{i,\text{peak}}^{\text{exp}})$ corresponding to the above mentioned programmed currents (see Eqs. (9) and (11a) and Eqs. (18) and (19), respectively), are shown together with the voltammetric curve $I^{\text{CV}}/4I_{\text{peak}}^{\text{CV}}$ given by Eqs. (35) and (36).

It is clear that the response in CV is identical to the responses in CRDCP. Indeed, for a reversible process under these conditions it is fulfilled that:

$$\text{current} \times \frac{dt}{dE} = \frac{n^2F^2}{RT} A\Gamma_{0,T} \frac{\delta}{(1 + \delta)^2} \quad (39)$$

where *current* refers to any current, measured in voltammetry or applied ($I_0 t_i^u$ or $I_0 e^{\omega t_i}$) in chronopotentiometry, and $(dE/dt)^{-1}$ refers to the inverse of the imposed sweep rate in voltammetry or to the inverse of the calculated dE/dt value in chronopotentiometry.

Eq. (39) is fulfilled in CV and also in CRDCP with power current and with exponential current since it can be clearly demonstrated that Eqs. (9), (18) and (35) can be written, respectively, like Eq. (39):

$$I_0 t_i^u \frac{dt_i}{dE} = I_{\text{applied}} \frac{dt_i}{dE} = (-1)^i \frac{n^2 F^2}{RT} A \Gamma_{0,T} \frac{\delta}{(1+\delta)^2} \quad (40)$$

$$I_0 e^{\omega t_i} \frac{dt_i}{dE} = I_{\text{applied}} \frac{dt_i}{dE} = (-1)^i \frac{n^2 F^2}{RT} A \Gamma_{0,T} \frac{\delta}{(1+\delta)^2} \quad (41)$$

$$I^{\text{CV}} \frac{dt}{dE} = I_{\text{measured}} \frac{dt}{dE} = (-1)^i \frac{n^2 F^2}{RT} A \Gamma_{0,T} \frac{\delta}{(1+\delta)^2} \quad (42)$$

Note that Eqs. (40) and (41), corresponding to the chronopotentiometric response, and Eq. (42), corresponding to the voltammetric one, are identical.

In spite of the total analogy between the responses in CRDCP with programmed current and CV, it is interesting to point out that CRDCP with programmed current presents more analytical sensitivity than CV. This can be proved by taking into account that to increase the peak height in CRDCP for a fixed value of the exponents of time in the programmed currents, u or ω , the amplitude of the programmed current applied I_0 must be diminished (see Eqs. (11a) and (19)), by which it is accomplished that the ohmic drop effects become

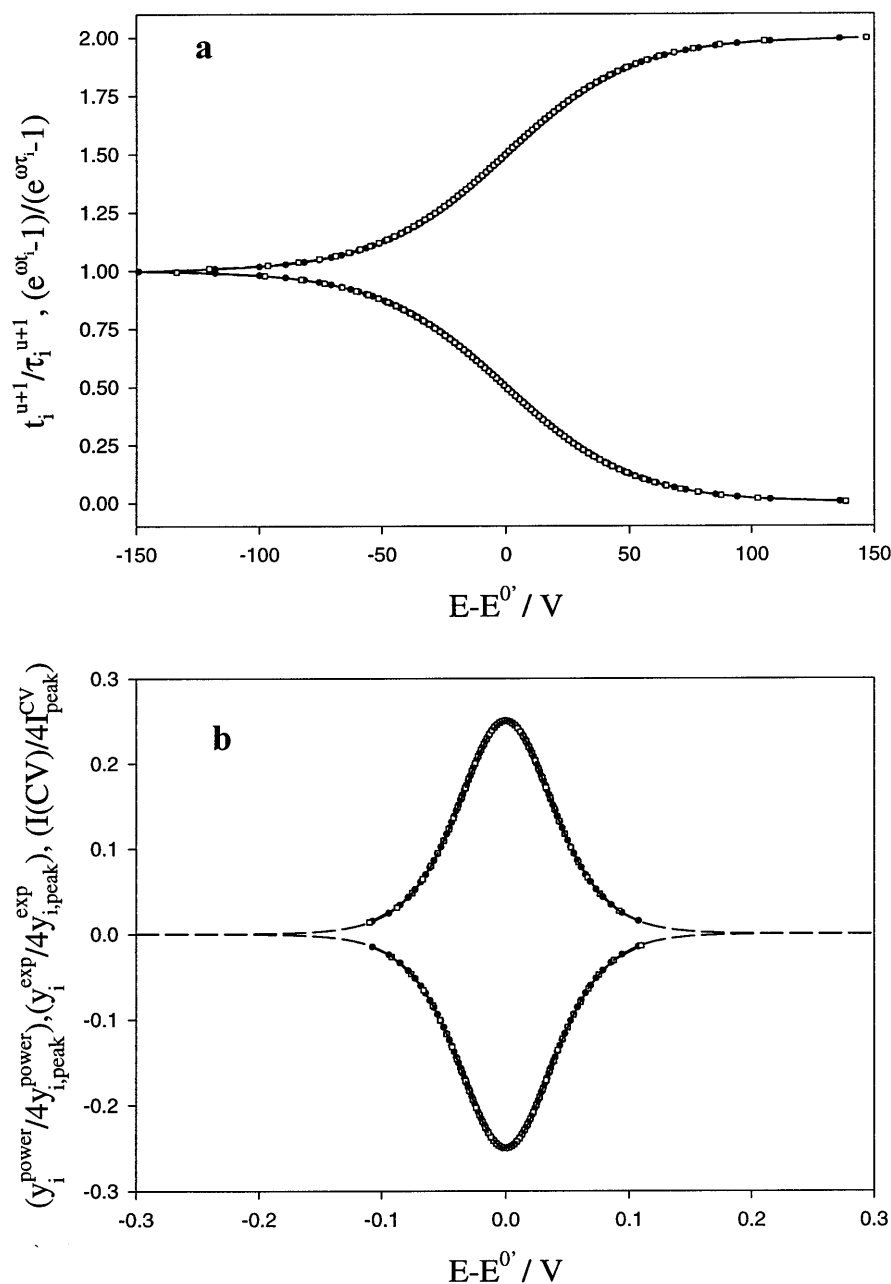


Fig. 1. (Black circles) $(t_i^{u+1}/\tau_i^{u+1})/(E-E^0)$ curves (a, see Eqs. (5) and (6)) and $y_i^{\text{power}}/(4y_{i,\text{peak}}^{\text{power}})/(E-E^0)$ curves (b, see Eqs. (9) and (11a)), corresponding to the application of two successive power time currents of the form $I_0 t_i^u$ and $-I_0 t_i^u$, $u=1$. (White squares) $((e^{\omega t_i}-1)/(e^{\omega \tau_i}-1))/(E-E^0)$ curves (a, see Eqs. (14) and (15)) and $y_i^{\text{exp}}/(4y_{i,\text{peak}}^{\text{exp}})/(E-E^0)$ curves (b, see Eqs. (18) and (19)), corresponding to the application of two successive exponential currents of the form $I_0 e^{\omega t_i}$ and $-I_0 e^{\omega t_i}$, $\omega=0.2$. (---) $I(\text{CV})/4I_{\text{peak}}^{\text{CV}}$ obtained in CV (b, see Eqs. (35) and (36)).

negligible, whereas to increase the peak current in CV the sweep rate v must be increased (see Eq. (36)), which leads to an increase of the ohmic drop, which distorts the I/E curve [9–17].

5.2. Effect of the interfacial potential distribution

Eqs. (33) and (34) can also be written as a function of the mole fraction of the oxidised adsorbate f . So, by taking into account Eqs. (23a) and (30) we deduce:

$$I_0 t_i^u \frac{dt_i}{dE} = (-1)^i \times \left(\frac{n^2 F^2 A \Gamma_{0,T}}{RT} f(1-f)(1 - \partial \phi_{\text{PET}} / \partial E) + C_T A \right) \quad (43)$$

for a power time current and:

$$I_0 e^{\omega t_i} \frac{dt_i}{dE} = (-1)^i \times \left(\frac{n^2 F^2 A \Gamma_{0,T}}{RT} f(1-f)(1 - \partial \phi_{\text{PET}} / \partial E) + C_T A \right) \quad (44)$$

for an exponential one.

By comparing Eqs. (43) and (44) with the results obtained by Smith and White (see eqs. (15) and (23) in Ref. [3]) for CV, and which can be written in the following way:

$$\frac{I^{\text{CV}}}{v} = \frac{n^2 F^2 A \Gamma_{0,T}}{RT} f(1-f)(1 - \partial \phi_{\text{PET}} / \partial E) + C_T A \quad (45)$$

it is evident that the above three equations are identical. Therefore, the effects of the interfacial potential distribution on the $(dt_i^{u+1}/dE)/E$ and the $(de^{\omega t_i}/dE)/E$ curves are the same as those shown in Ref. [3]. So for example, Eqs. (43) and (44) are greatly simplified when the condition $\partial \phi_{\text{PET}} / \partial E \ll 1$ is fulfilled (i.e. the total interfacial capacitance is relatively independent of the electrode potential during the reduction/oxidation of the film). According to Smith and White the condition $C_T \cong C_1$ yields to the following requirements:

$$\left. \begin{aligned} \frac{F^2 \Gamma_{0,T}}{(2000 \varepsilon_0 \varepsilon_3 R T c_s)^{1/2}} &\ll 1 \\ \frac{C_1}{\left(\frac{2000 \varepsilon_0 \varepsilon_3 c_s}{RT} \right)^{1/2}} &\ll 1 \end{aligned} \right\} \quad (46)$$

with c_s being the molar concentration of the supporting electrolyte and ε_3 the dielectric constant of the solvent. Eq. (46) is fulfilled when the covering of electroactive species is small and the supporting electrolyte concentration is high.

Eqs. (43) and (44) convert to that deduced by Honeychurch (see eq. (24) in Ref. [4]) when a constant current I_0 is applied by making $u = 0$ in Eq. (43) and $\omega = 0$ in Eq. (44).

Acknowledgements

The authors greatly appreciate the financial support provided by the Dirección General Científica y Técnica (Project number PB96-1095) and to the Fundación SENECA (Expedient number 00696/CV/99). Also J.G. thanks CajaMurcia for the grant received.

References

- [1] A. Molina, J. Gonzalez, *Electrochem. Commun.* 1 (1999) 477.
- [2] J. Gonzalez, A. Molina, M. Lopez-Tenes, C. Serna, *J. Electrochem. Soc.* 147 (2000) 3429.
- [3] C.P. Smith, H.S. White, *Anal. Chem.* 64 (1992) 2398.
- [4] M.J. Honeychurch, *J. Electroanal. Chem.* 445 (1998) 63.
- [5] S. Bi, J. Yu, *J. Electroanal. Chem.* 405 (1996) 51.
- [6] L.M. Abrantes, A. Molina, J. Gonzalez, F. Saavedra, *Electrochim. Acta* 45 (1999) 457.
- [7] A. Molina, J. Gonzalez, F. Saavedra, L.M. Abrantes, *Electrochim. Acta* 45 (1999) 761.
- [8] M. Tomschik, F. Jelen, L. Havran, L. Trnková, P.E. Nielsen, E. Palecek, *J. Electroanal. Chem.* 476 (1999) 71.
- [9] J. Wang, X. Cai, J. Wang, C. Jonsson, E. Palecek, *Anal. Chem.* 67 (1995) 4065.
- [10] E. Palecek, *Electroanalysis* 8 (1996) 7.
- [11] J. Wang, E. Palecek, P.E. Nielsen, G. Rivas, X. Cai, H. Shiraishi, N. Dontha, D. Luo, P.A.M. Farias, *J. Am. Chem. Soc.* 118 (1996) 7667.
- [12] J. Wang, X. Cai, J.R. Frenades, D.H. Grant, M. Ozsoz, *J. Electroanal. Chem.* 441 (1998) 167.
- [13] J. Wang, X. Cai, G. Rivas, H. Shiraishi, N. Dontha, *Biosensors Bioelectr.* 12 (1997) 587.
- [14] M.J. Honeychurch, M.J. Ridd, *Electroanalysis* 7 (1995) 1041.
- [15] M.J. Honeychurch, M.J. Ridd, *Electroanalysis* 8 (1996) 49.
- [16] S. Komorsky-Lovric, F. Scholz, *J. Electroanal. Chem.* 445 (1998) 81.
- [17] D.F. Milner, M.J. Weaver, *Anal. Chim. Acta* 198 (1987) 245.
- [18] A. Molina, J. Gonzalez, C. Serna, 50th ISE Meeting, Abstract Number 1112, Pavia, Italy, 1999.
- [19] A. Molina, J. Gonzalez, unpublished results.
- [20] R.W. Murray, *Anal. Chem.* 35 (1963) 1784.
- [21] J. Albaladejo, A. Molina, D. Ruiz-Hernandez, *Chem. Phys. Lett.* 152 (1988) 519.
- [22] E. Laviron, *J. Electroanal. Chem.* 52 (1974) 355.