Discrimination between CEC, CE and EC mechanisms by using a sinusoidal current–time function

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Abstract—A theoretical treatment corresponding to a CEC process when a sinusoidal current is applied to static and dynamic electrodes is presented. The general equations obtained allow us to deduce as particular cases those corresponding to CE and EC mechanisms. The conditions under which the response of a CEC process may be discriminated from CE and EC mechanisms are discussed. Methods for determining heterogeneous and homogeneous kinetic parameters are also proposed. © 1997 Elsevier Science Ltd. All rights reserved.

Key words: Chronopotentiometry, sinusoidal current, homogeneous kinetics, diagnostic criteria.

INTRODUCTION

As is known [1, 2], the usefulness of the chronopotentiometric techniques in mechanistic investigations is greatly increased when the potential–time curve is recorded for the reverse reaction, corresponding to the reoxidation process. In contrast to several types of programmed current [3, 4] in which the sign of the current does not change during the experiment, the use of perturbations with change in sign, as is the case of alternating current, seems more appropriate for the study of chemical reactions subsequent to the charge transfer, because the relevant kinetic information may be obtained from the transition time corresponding to the reoxidation process instead of from the complete potential–time curve as with the above-mentioned perturbations. This fact is relevant and allows us to distinguish easily for example between CE and CEC mechanisms, whose discrimination was seriously hindered when using other electrochemical techniques [5, 6].

In this work we carry out a general study of a CEC mechanism when an alternating current of the form \( I(t) = I_0 \sin(\omega t) \) [7, 8] is applied to a dropping mercury electrode (dme), taking the more rigorous model of an expanding sphere and assuming, for convenience, the existence of a blank period \( t_0 \geq 0 \).

The general equations deduced in this paper are of great interest since they allow us, on one hand, to deduce as particular cases those corresponding to CE and EC mechanisms and, on the other hand, to obtain the equations corresponding to a static mercury drop electrode (smde) and to a static plane electrode, through elementary transformations.

The response of a CE mechanism by applying a sinusoidal current is also analyzed and compared with that obtained for CEC and EC processes. Moreover, the guides for application of sinusoidal current for discriminating between CEC, CE and EC mechanisms are set.

In spite of the equations obtained in this paper being valid for any numbers of cycles of the alternating current, the most interesting situation is achieved when only the first cycle is considered, since the transition time of oxidized or reduced species is always reached during the first cycle of the current (before or after its change in charge, respectively).

Finally, we propose methods to calculate the rate constants of the precedent and subsequent chemical reactions and also for determining kinetic parameters of the heterogeneous step.

THEORY

Let us consider a CEC process, whose scheme may be represented by the following one

\[
\begin{align*}
B \overset{\alpha_1}{\rightarrow} C + n e^- \overset{\alpha_2}{\rightarrow} D \overset{\alpha_3}{\rightarrow} E.
\end{align*}
\]
The boundary value problem associated with this process is given by,

\[
\begin{align*}
\delta \delta x C_a &= -\delta C_C = -k_1 C_a + k_3 C_C, \\
\delta \delta x C_D &= -\delta C_C = -k_3 C_D + k_4 C_C,
\end{align*}
\]

(1)

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

\[
C_B = C_B^\infty; \quad C_C = C_C^\infty; \quad C_D = C_D^\infty; \quad C_E = C_E^\infty.
\]

(2)

\[
\begin{align*}
t &> 0, \quad r = r_0: \\
\frac{D_C}{nF} \frac{\partial C_C}{\partial r} &= -\frac{D_D}{nF} \frac{\partial C_D}{\partial r} = \frac{I(t)}{nF A(t)},
\end{align*}
\]

(3)

\[
\begin{align*}
\frac{D_C}{nF} \frac{\partial C_B}{\partial r} &= 0,
\end{align*}
\]

(4)

\[
\begin{align*}
\frac{D_D}{nF} \frac{\partial C_E}{\partial r} &= 0,
\end{align*}
\]

(5)

\[
\frac{I(t)}{nF A(t)} = k_1 C_C(r_0, t) - k_3 C_D(r_0, t),
\]

(6)

with \( \delta \) being the operator corresponding to the expanding sphere [9].

\[
\delta t = \frac{\partial}{\partial t} + D \left( \frac{\partial^3}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\partial^2}{\partial r^2}.
\]

(7)

When an alternating current of the form

\[
I(t) = I_0 \sin(\omega t)
\]

is applied to a \( \text{dme} \), the expressions for the surface concentrations of species \( C \) and \( D \) may be deduced by following a procedure similar to that described in [3 and 8] using the power expansion for the sine function. Thus, we obtain

\[
\begin{align*}
\frac{C_B(r_0, t)}{c_C} &= \frac{1}{1 + K_3} \left\{ 1 - N_{aw} t^{1/2} [S_C + K_3 X_C] \right\}, \\
\frac{C_D(r_0, t)}{c_C} &= \frac{1}{1 + K_3} \left\{ K_3 \mu + \gamma N_{aw} t^{1/2} \right\}
\end{align*}
\]

(9)

\[
\left\{ K_3 S_D + X_D \right\},
\]

(10)

where

\[
N_{aw} = \frac{2I_0}{nF A(t) D_C^2 c_C^2}.
\]

(11)

\[
A(t) = A_0 t^2,
\]

(12)

\[
t = t_1 + t,
\]

(13)

\[
\mu = \epsilon t^2, \quad \gamma = (D_C/D_D)^2.
\]

(14)

\[
\epsilon^t = C_B^\infty + C_D^\infty.
\]

(15)

\[
\epsilon^t = C_B^\infty + C_D^\infty.
\]

(16)

\[
t_1 \text{ is a stand time prior to application of the current and } S, \text{ and } X_i (i = C, D) \text{ are functional series defined in the Appendix, which may be transformed into those corresponding to a } \text{smde} \text{ as indicated therein. Moreover, we assume that}
\]

\[
D_B = D_C = D_D = D_E.
\]

(18)

When \( I_0 \) and/or \( \omega \) in equation (8) takes values such that there is depletion of species \( C \) at the electrode surface (before the current changes its sign), the reduction transition time, \( \tau_C \), is reached, and at this moment the experiment must be stopped [7]. In this case, \( \tau_C \) (which depends only on the kinetic parameters of the precedent chemical reaction) is identical to that obtained for a CE mechanism, and is given by the following expression (deduced by setting equation (9) equal to zero):

\[
\tau_C^2 = \frac{I^2}{nF A D_C^2 (C_B^\infty + C_D^\infty)}.
\]

(19)

where \( X_C \) is a functional series of the rate constants of the precedent chemical reaction through the \( \chi \) parameter \((= (k_3 + k_4)y))\). Consequently, from measurements of \( \tau_C \) it is possible to determine \( k_3 \) and \( k_4 \) (see Results and Discussion).

On the other hand, when the depletion of species \( C \) does not occur, the transition time corresponding to the reoxidation of \( D \) species, \( \tau_D \), is always reached (after the current changes its sign) when species \( D \) and \( E \) are initially absent from the solution. (Nevertheless, this transition time can also be reached when \( C_B^\infty + C_D^\infty \neq 0 \) [7]). The general expression for \( \tau_D \) is given by

\[
\tau_D^2 = \frac{K_3 (t_1 + t_0)^{1/2} nF A D_C^2 (C_B^\infty + C_D^\infty)}{2I_0 (K_3 S_D + X_D)}.
\]

(20)

which coincides with that obtained for an EC mechanism.

Equation (20) is simplified to

\[
(K_3 S_D + X_D)_{t = \tau_D} = 0
\]

(21)

when species \( D \) and \( E \) are not initially present in the solution. In equations (20) and (21), the \( S_D \) series depends on the rate constants of the subsequent chemical reaction through the \( \chi \) parameter \((= (k_3 + k_4)y))\), so that under these conditions it is possible to determine \( k_3 \) and \( k_4 \) from measurements of \( \tau_D \). (Note that for the particular case of a \( \text{smde} \), equations (19) and (20) adopt a simpler form (see equations (XIV) and (XV) in the Appendix)).
The general potential-time response can be obtained by inserting equations (9) and (10) in equation (6). Thus, we deduce

\[
\frac{N_{\text{tot}}I}{2k_i \sin(\omega t)e^{n_{\text{rot}}}} = \frac{1}{1 + K_i} \times \left\{ 1 - N_{\text{tot}}I^{2/3}[S_C + K_iX_C] \right\} - \frac{e^{n_{\text{rot}}}}{1 + K_2^{1/3}} \left\{ K_i \mu + \gamma N_{\text{tot}}I^{2/3}[K_2S_D + X_D] \right\},
\] (22)

where

\[
\eta(t) = \frac{nF}{RT}(E(t) - E^0).
\] (23)

For a reversible process, equation (22) is simplified to

\[
E(t) = E^0 + \frac{RT}{nF} \ln \frac{1 + K_i}{1 + K_i^{1/3}} + \frac{RT}{nF} \ln \frac{1 - N_{\text{tot}}I^{2/3}[S_C + K_iX_C]}{N_{\text{tot}}I^{2/3}[K_2S_D + X_D]},
\] (24)

whereas for a totally irreversible process, the following two situations are distinguished (\(\mu = 0\)):

(a) \(I(t) > 0 (\omega t < \pi)\). Equation (22) becomes

\[
E(t) = E^0 + \frac{RT}{2nF} \ln \frac{1 + K_i}{1 + K_i^{1/3}} + \frac{RT}{2nF} \ln g_C,
\] (25)

where

\[
g_C = \frac{1 - N_{\text{tot}}I^{2/3}[S_C + K_iX_C]}{\sin(\omega t)(1 + K_i)}.
\] (26)

(b) \(I(t) < 0 (\pi < \omega t < 2\pi)\). Equation (22) takes the form

\[
E(t) = E^0 - \frac{RT}{(1 - a)nF} \ln \frac{2k_i}{N_{\text{tot}}I^{2/3}} + \frac{RT}{(1 - a)nF} \ln g_s,
\] (27)

where

\[
g_s = \frac{-(1 + K_i)\sin(\omega t)}{\gamma N_{\text{tot}}I^{2/3}[K_2S_D + X_D]}.
\] (28)

As is evident from equations (25) and (26), the potential-time response obtained for a totally irreversible process when the current applied is cathodic (\(I(t) > 0\)) depends only on the kinetic parameters of the preceding chemical step, through the series \(X_C\), and is identical to that corresponding to a CE mechanism. In turn, the potential-time response obtained when the current is anodic (\(I(t) < 0\)) is affected, according to equations (27) and (28), by the kinetics of the subsequent chemical step, and coincides with that corresponding to an EC mechanism.

**RESULTS AND DISCUSSION**

A profound analysis of the \(X_C\) and \(X_D\) series which appear in the expressions for the surface concentra-

trations (equations (9) and (10)) is necessary since they contain all the information about the rate of chemical steps involved in the electrode process. The \(X_C\) series is a function of the rate constants \(k_1\) and \(k_4\) through the \(\chi_1\) parameter and the \(X_D\) series depends on \(k_1\) and \(k_4\) through the \(\chi_2\) parameter.

For large values of \(\chi (\equiv \chi_1, \chi_2)\), the \(X_C\) and \(X_D\) series are simplified to

\[
X_i = \frac{\sin(\omega t)}{2k_i^{1/3}} (i = C, D) \quad (\chi \gg 20)
\] (29)

when the steady-state approximation is applied, independently of the type of electrode considered.

For small values of the argument the following limit is obtained

\[
\lim_{\chi \to \infty} X_i = S_i \quad (i = C, D).
\] (30)

Moreover, equations (9) and (10) allow us to deduce the respective expressions for CE and EC mechanisms (which may be considered as particular cases of CEC process [3, 4]) by proceeding as follows.

**CE mechanism.** For a CE process, whose scheme may be represented by

\[
B = \frac{A}{n_{\text{rot}}} C + ne^{-\frac{\gamma t}{\lambda_s}} D,
\]

we find easily the expressions for the surface concentrations of electroactive species by setting \(K_2 = \infty\), in equations (9) and (10). Thus, we obtain (note that \(\mu = [C][1 + K_i]/[C][K_i(1 + K_i)])

\[
C_C(t, t) = \frac{1}{1 + K_i} \left\{ 1 - N_{\text{tot}}I^{2/3}[S_C + K_iX_C] \right\},
\] (31)

\[
C_D(t, t) = \frac{C_D^0}{e^{\frac{\gamma t}{\lambda_s}}} \left[ K_2S_D + X_D \right].
\] (32)

As noted, the expression for surface concentration of species \(D\) coincides with that obtained for a CEC process (equation (9)), whereas the one corresponding to species \(D\) is simplified to that of an EC mechanism [8]. Consequently, the reoxidation transition time (\(\tau_D\)) for a CE process, which is always reached when there is no reduction transition time (\(\tau_C\)), is identical to that obtained for an EC mechanism. In turn, \(\tau_D\) depends on the rate constants \(k_3\) and \(k_4\) (see equations (10) and (21)) for a CEC process. This fact is relevant and allows us to discriminate easily between CE and CEC mechanisms from measurements of transition times corresponding to the electrooxidation of species \(D\) (see below for further discussion).

**EC mechanism.** Let us consider an EC process, whose scheme is given by

\[
C + ne^{-\frac{\gamma t}{\lambda_s}} D = \frac{A}{n_{\text{rot}}} E.
\]

The expressions for the surface concentrations of electroactive species for this mechanism can be
deduced by setting \( K_i = 0 \) in equations (9) and (10), so we obtain:

\[
\frac{C_C(t_C, t)}{t_C} = 1 - N_w t_C^{1/2} S_C, \tag{33}
\]

\[
\frac{C_D(t_D, t)}{t_D^{1/2}} = \frac{1}{1 + K_i} \left( \frac{K_i \mu_{EC} + \gamma N_w t_C^{1/2}}{K_i S_0 + X_0} \right). \tag{34}
\]

By comparing equations (33) and (34) with equations (9) and (10), it can be deduced that, whereas the values of the reoxidation transition time \( t_D \) are coincident for CEC and EC mechanisms, the reduction transition time \( t_C \) does not depend on the kinetic parameters in the case of an EC process, being dependent on \( k_1 \) and \( k_2 \) in a CEC mechanism. Therefore, it is possible to discriminate between CEC and EC mechanisms by measurements of \( t_C \). (This fact will be discussed below when the potential-time response is analyzed).

**Kinetic information obtained from transition times**

As mentioned above, \( t_C \) and \( t_D \) contain kinetic information about the precedent and subsequent chemical reactions, respectively. In order to determine the rate constants of the two chemical steps involved in the electrode process, it is necessary firstly to know the equilibrium constants \( K_i \) and \( K_j \). By proceeding as in [3], \( K_i \) can be determined. Once \( K_i \) is known, by extrapolation of the transient response (potential-time curve) to equilibrium response (near zero time) when species \( D \) or \( E \) are initially present in the solution, \( K_j \) can be obtained. So, by setting \( t \to 0 \) in equation (22), we obtain,

\[
E(t \to 0) - E_n = \frac{R T}{n F} \ln \frac{1 + \frac{K_j}{(1 + K_i) K_j \mu}}{1 + K_j}. \tag{35}
\]

Subsequently, it is possible to determine kinetic parameters of the chemical steps by using the working curves plotted in Fig. 1(A) and (B). Thus, the rate constants corresponding to the precedent chemical reaction \(( I ) k_1 \) and \( k_2 \) can be easily deduced from Fig. 1(A), in which we have plotted \( Y(t_C/\tau_C(t_C))^{1/2} \) vs \( \tau_C(t_C) \) (see Notation) for several values of the equilibrium constant \( K_i \). These working curves correspond to the instant when the transition time of species \( C \) is reached and the condition \( C_C(t_C, t_C) = 0 \) is fulfilled. In order to verify this condition it is necessary that \( N_w t_C^{1/2} = (2nF A_i D_C^{1/2} e^* \tau_C(t_C)) \) is higher than a fixed minimum value \( N_{\text{min}} \) given by (see equations (9), (11) and (12)):

\[
N_{\text{min}} = \left[ \frac{2nF A_i D_C^{1/2} e^*}{(nF A_i D_C^{1/2} e^*)_{\text{min}}} \right]^{1/2} = \frac{1}{H_{\text{max}}}, \tag{36}
\]

where \( H_{\text{max}} \) is the absolute maximum of the \( H \) function vs time defined as

\[
H = (S_C + K_j X_C)^{1/2} \tau_C(t_C). \tag{37}
\]

This minimum value, which was previously deduced in [7] for an E process \(( I ) k_1 \) (when \( K_i = 0 \)), depends on \( K_i \) and the rate constants \( k_1 \) and \( k_2 \) when we consider a CEC mechanism. In this way, the working curves from Fig. 1(A) may be obtained under these conditions from equation (19) after some manipulations. Thus, we find

\[
Y \left( \frac{t_C(t_C)}{\tau_C(t_C)} \right)^{1/2} = \frac{1}{1 + K_j(S_C/X_C)_{\tau_C(t_C)}}, \tag{38}
\]

where

\[
Y = \left( \frac{(S_C)_{\tau_C(t_C)}}{\tau_C(t_C)} \right)^{1/2} \left( \frac{t_C(1 + \tau_C(t_C))}{t_C + \tau_C(t_C)} \right). \tag{39}
\]

For the particular case of a **smde**, equations (XVI), (XVII) and (XVIII) must be used instead of equations (39), (36) and (37).

**Fig. 1.** (A) Dependence of \( Y (t_C/\tau_C(t_C))^{1/2} \) on \( \tau_C(t_C) \) for a smde (equations (38) and (XVI)). \( \tau_C(t_C) = 0.2 \), \( \tau_C(t_C) = 1 \). \( K_i \) values are noted with the curves. (B) Working curves deduced from equation (21) for a dme with the expanding plane electrode model (\( \tau_e = 0 \)) for \( \Omega = 0 \). \( K_i \) values are noted with the curves.
In turn, the rate constants of the subsequent chemical step (i.e., $k_1$ and $k_2$) can only be determined when the depletion of species $C$ has not taken place and the transition time of species $D$ is reached, as shown in Fig. 1(B). In this figure, we have plotted $\tau_0/\tau_0(e)$ vs $\chi_0$ (see Notation) for the case where species $D$ and $E$ are not initially present in the solution (this situation is more usual for a CEC mechanism). Thus, if the electrode sphericity is not taken into account the $S_0$ and $X_0$ series depend only on $\Omega$ and $\chi$ parameters when we work with $\Omega = \omega t$, fixed $\chi$ dependence on $\beta$ parameter disappears, according to equation (IX). Under these conditions,

$$\frac{\tau_0}{\tau_0(e)} = \frac{(\Omega)_{\chi = \chi_0}}{(\Omega)_{\chi = \chi_0(e)}}$$

where $\Omega = \omega t$. Moreover, when species $D$ and $E$ are not initially present in the solution, $\tau_0$ is not a function of $N_{\text{tot}}e^2$ (see equation (21)) and therefore is independent of most of the experimental parameters, such as $I_0$, $C_0^C + C_0^E$, etc., which take part in equation (11).

Comparison of the potential–time response of a CEC process with those corresponding to CE and EC mechanisms

In Fig. 2 we compare the potential–time response for a CEC mechanism (curves a, b, c and d) with that corresponding to a CE process (curve e). This figure shows the influence of the rate constant of the second chemical step on the $E/t$ curves for a CEC mechanism, when the electrochemical step behaves as reversible and the subsequent chemical reaction is irreversible ($K_1 = 0$). As can be seen, $\tau_0$ values corresponding to a CEC mechanism are always smaller than that corresponding to a CE process (curve e) and only in the case in which $k_1 = 0$ (i.e., subsequent chemical reaction does not exist) the respective reoxidation transition times are coincident. This fact allows us to discriminate between CEC and CE processes by using currents which change in sign; as mentioned above, by applying only cathodic currents this is not possible because the transition times corresponding to the reduction of species $C$ are identical for CEC and CE mechanisms.

In Fig. 3, the $E/t$ curves a–f obtained for a CEC process are compared with curve g found for an EC mechanism. This figure shows the response obtained for a CEC process when the transition time of species $C$ is reached, for a fixed value of $K_1$ and different values of $K_i$. As can be noted, the reduction transition time for a CEC process increases as $K_i$ becomes smaller, and only when $K_i = 0$ (i.e., no preceding chemical reaction) the $\tau_0$ values for CEC and EC mechanisms are coincident.

However, if the species $C$ is not depleted at the electrode surface the transition times corresponding to the electrooxidation of species $D$ do not differ for CEC and EC mechanisms. This fact is illustrated in Fig. 4, where curves a, b and c correspond to a CEC process and curve d to an EC mechanism. (Note that these curves are shifted to more negative potentials as $K_i$ becomes higher). As is evident, according to Figs 3 and 4, it is necessary to use cathodic currents for discriminating between CEC and EC mechanisms, as discussed above with Fig. 3.

The situation corresponding to a rapid chemical kinetics is shown in Fig. 5, in which we have plotted the $E/t$ curves for high values of the rate constants of
the precedent and subsequent chemical steps. Note that when $K_2 \neq 0$ these curves show a cross point which corresponds to the value of the time $t_c = \pi/\omega$, for which the $X_c$ and $X_d$ series are annulled. Under these conditions (if $(k_1 + k_2)t \geq 20$ and $(k_1 + k_3)t \geq 20$) the steady-state approximation (equation (29)) can be applied, this cross point is independent of the chemical rate constants $k_1$, $k_2$, $k_3$ and $k_4$, and therefore may be used for determining the equilibrium constant $K_2$ or $K_1$ if $K_1$ or $K_2$ value is known. Thus, if we substitute $t_c = \pi/\omega$, $X_c = 0$ and $X_d = 0$ in equation (22), we find ($\mu = 0$)

$$E_c = E^0 + \frac{RT}{nF} \ln \frac{1 + K_1}{(1 + K_1)K_1} +$$

$$\times \frac{RT}{nF} \ln \frac{L_{12} - N_{anodic}S_c}{N_{anodic}S_d}.$$  \hspace{1cm} (41)

On the other hand, when $K_1 = 0$ note that the potential–time curves from Fig. 5 show a common asymptote instead of a cross point for $t_c = \pi/\omega$, which is always coincident with the reoxidation transition time value $t_d$.

The influence of chemical kinetics when the electrochemical step behaves as totally irreversible is shown in Figs 6 and 7, where the $E(t)$ curves obtained for a CEC process are compared with those found for a CE mechanism (Fig. 6) and an EC mechanism (Fig. 7). As can be deduced from equations (25)–(28), in order to discriminate between CEC (curves a, b, c in Fig. 6) and CE mechanisms (curve d) we must use the anodic region of these curves, since the cathodic regions coincide for the above-mentioned mechanisms. On the contrary, according to equations (25)–(28) and Fig. 7 (where curves a, b and c correspond to a CEC and curve d to an EC mechanism), we must use the cathodic region of these curves for discriminating between CEC and EC processes, because the anodic regions for both mechanisms mentioned are coincident. Moreover, as can be seen from Fig. 6 (curve a), the characteristic shoulder which appears on the potential–time curves when the electrochemical step behaves as irreversible

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**Fig. 4.** Potential–time curves at a scan corresponding to a CEC mechanism when the electrochemical step behaves as reversible. $N_{anodic} = 1.0 \text{s}^{-1}$, $\zeta_{anodic} = \zeta_c = 0.1 \text{s}^{-1}$. The values of $K_i$ are: (a) 1.5, (b) 1.0, (c) 0.5. The curve corresponding to an EC mechanism (curve d) is also included. Other conditions as in Fig. 3.

**Fig. 5.** Potential–time curves at a scan corresponding to a CEC mechanism with fast both precedent and subsequent chemical steps when the charge transfer reaction behaves as reversible. $\omega = 0.5 \text{s}^{-1}$, $t_c = 0.5 \text{s}$, $N_{anodic} = 1.2 \text{s}^{-1}$, $\zeta_{anodic} = \zeta_c = 0.1 \text{s}^{-1}$. $K_i = 0.5$, $k_1 + k_2 = 100 \text{s}^{-1}$. The values of $K_2$ are noted with the curves. The values of $k_3 + k_4$ (s$^{-1}$) are: (---) 20, (--) 50, (--) 100. Other conditions as in Fig. 2.

**Fig. 6.** Effects of rate constant of the subsequent chemical step on the potential–time curves at a scan corresponding to a CEC process when the electrochemical step behaves as totally irreversible. $\omega = 1 \text{s}^{-1}$, $N_{anodic} = 0.8 \text{s}^{-1}$, $\zeta_{anodic} = \zeta_c = 0.15 \text{s}^{-1}$. $k_1 = 10^{-3} \text{cm} \text{s}^{-1}$, $z = 0.5$, $K_i = 1$, $k_1 + k_3 = 1 \text{s}^{-1}$, $K_2 = 0$. The values of $k_3$ (s$^{-1}$) are: (a) 10, (b) 1, (c) $10^{-3}$. The curve corresponding to a CE mechanism (curve d) is also included. Other conditions as in Fig. 2.
Discrimination between CEC, CE and EC mechanisms

By evaluating potential–time curves, the cathodic and anodic regions obtained when the charge transfer reaction is totally irreversible may be used for discriminating between CEC and CE mechanisms. Thus, the cathodic region of E(t) curves allows CEC and CE processes to be distinguished whereas the anodic region may be used for discriminating between CEC and CE processes.

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NOTATION

- \( a \) radius of dme for \( t = 1/s = (3m_{\text{dme}}/4\pi)^{1/3} \)
- \( A(t) \) time-dependent area for a dme \((= A_s t^{1/3}) \)
- \( A_s \) electrode area for \( t = 1/s = (4\pi)^{1/3} (3m_{\text{dme}}/d)^{1/3} \)
- \( d_{\text{dme}} \) dropping mercury electrode
- \( k_{j_1}, k_{j_2} \) heterogeneous rate constants of the forward and reverse charge transfer reactions
- \( k_c \) apparent heterogeneous rate constant of charge transfer at \( t^* \)
- \( k_{j_1}, k_{j_2} \) homogeneous rate constants corresponding to the forward and reverse of the preceding chemical reaction
- \( k_{j_1}, k_{j_2} \) homogeneous rate constants corresponding to the forward and reverse of the subsequent chemical reaction
- \( K_j \) equilibrium constant of the preceding chemical reaction \((= k_{j_1}/k_{j_2}) \)
- \( K_k \) equilibrium constant of the subsequent chemical reaction \((= k_{j_2}/k_{j_1}) \)
- \( m_{\text{dme}}, d \) rate of flow and density of mercury
- \( p \) \( 2f(1 + r^2)/f(1 + r) \) rate of flow and density of mercury
- \( r \) distance from the center of the electrode
- \( t \) electrode radius at time \( t \) for a dme \((-dt^3) \) or fixed electrode radius for a smde
- \( t_0 \) static mercury drop electrode
- \( t_{\text{c}} \) time elapsed between the application of the alternating current and the potential measurement
- \( t_0 \) blank period used, optionally, only with non stationary electrodes (dme)

Greek letters

- \( \alpha \) electron transfer coefficient
- \( \beta = t/(n + 1) = \Omega/\Omega + \Omega \)
- \( \Gamma \) Euler Gamma function
- \( \gamma = (D_e / D_0)^{1/2} \)
- \( \epsilon_{\text{c}} = C_{\text{c}} + C_{\text{e}} \)
- \( \epsilon = C_{\text{e}} + C_{\text{f}} \)
- \( \mu = \epsilon_{\text{f}}/\epsilon_{\text{c}} \)
- \( \xi \) dimensionless parameter \((=2(D_e t_{\text{d}}^{1/2})/r_0) \)
- \( \xi_0 = \xi_{\text{c}}^{1/3} \) for a smde and \( = \xi_{\text{f}}^{1/3} \) for a dme
- \( \tau_{\text{C}} \) reduction transition time of species \( C \) for a CEC mechanism
- \( \tau_{\text{D}} \) oxidation transition time of species \( D \) for a CEC mechanism

CONCLUSIONS

We have analyzed the responses corresponding to CEC and CE mechanisms when an alternating current is applied to spherical electrodes. This technique is very powerful to characterize a CEC process and allows us to discriminate between this mechanism and CE and EC processes, according to whether the transition time of the oxidized species, \( \tau_{\text{c}} \), is reached or not. If species \( C \) is depleted at the electrode surface, the transition time of \( C \), \( \tau_{\text{c}} \), which contains interesting homogeneous kinetic information about the precedent chemical step, may be used for discriminating between CEC and CE mechanisms. On the other hand, if we work under conditions in which the transition time of the species \( C \), \( \tau_{\text{c}} \), is not reached, the reoxidation transition time of the reduced species, \( \tau_D \), allows CEC and CE mechanisms to be distinguished. In this case, \( \tau_D \) contains kinetic information about the subsequent chemical reaction and allows us to determine the rate constants corresponding to this step.
\[ \tau_c(\epsilon) = \text{reduction transition time of species } C \text{ for an } E \text{ mechanism} \]
\[ \tau_o(\epsilon) = \text{oxidation transition time of species } D \text{ for an } E \text{ mechanism} \]
\[ \chi = \text{x or } \chi \]
\[ \chi_1 = (k_1 + k_2) \]
\[ \chi_2 = (k_1 + k_3) \]
\[ \Omega = \omega \]
\[ \Omega_0 = \omega_0 \]
\[ \omega = \text{angular frequency of alternating current } (2\pi \text{ times the conventional frequency in hertz}) \]

Other symbols are conventional.

**REFERENCES**


**APPENDIX**

The \( S \) and \( X_i \) \((i = C, D)\) series, which take part in the expressions for surface concentrations, have been deduced for a *dune* adopting the expanding sphere electrode model. These series allow us, nevertheless, to deduce those corresponding to a static spherical electrode (smde) and to a planar electrode (pe) through simple transformations, as shown below.

The \( S \) and \( X \) series are defined as

\[
S = S_i(\xi_i, \beta, \Omega) = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)!} J_{2n}(\xi_i, \beta), \quad (I)
\]

\[
X_i = X_i(\chi_i, \beta, \chi, \Omega) = \exp(-\chi) \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)!} \chi^n J_{2n}(\xi_i, \beta), \quad (II)
\]

where \( J_{2n}(\xi_i, \beta) \) may be considered as a particular case of \( J_{2n}(\xi, \beta) \) \((n = 0)\), whose general expression is given by

\[
J_{2n}(\xi, \beta) = \frac{1}{P_{2n+1} + \alpha} \left\{ 1 + \frac{\beta^2}{3(2n+1)!} + \frac{7}{18} \right\} \left( \frac{\beta}{(2j + 4n + 5)(2j + 4n + 7)} + \frac{20}{27} \right), \quad (III)
\]

The \( S \) and \( X \) series for a *smde* are simplified to

\[
S_{smde} = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)!} \frac{1}{P_{2n+1} + \alpha} \left\{ 1 + \frac{\beta^2}{3(2n+1)!} - \frac{1}{4(2n+2)} \right\} \left( \frac{\xi^2}{2n+1} \right), \quad (XII)
\]
\[ X_{\text{comb}} = \exp(-\gamma) \sum_{n=1}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)!} \]

\[ \times \left[ \frac{1}{p_{2n+4} \zeta} - \frac{1}{4(2n+2)} \zeta^2 \right. \]

\[ \left. + \frac{1}{2p_{2n+4} + \lambda(2n+4) \zeta^2} + \cdots \right] \]  

By respecting the transition times of electroactive species, equations (19) and (20) for a stationary electrode are simplified to

\[ \tau_s^{(i)} = \frac{nFAD_i}{2\eta_i(C_s + C^*_s)} \] (XIV)

\[ \tau_s^{(b)} = \frac{-K_s nFAD_i}{2\eta_i(K_sC_s + X_s)} \] (XV)

and \( Y \) in equation (38) is simplified to

\[ Y = \frac{(\overline{S}_C) - \tau_C}{(\overline{S}_C) + \tau_C} \] (XVI)

The condition \( C_C (\eta, \tau_C) = 0 \) is then verified when \( N_{\text{comb}} \) is higher than a fixed minimum value \( N_{\text{min}} \) given by (see equations (9) and (XI))

\[ N_{\text{min}} = \left[ \frac{2\eta_i}{nFAD_i^2} \right]_{\text{min}} = \frac{1}{H_{\text{max}}} \] (XVII)

where \( H_{\text{max}} \) is the absolute maximum of the \( H \) function vs time defined as

\[ H = (S_C + K_sX_s)^{1/2} \] (XVIII)

**Stationary plane electrode.** In this case we have \( \xi = 0 \) and \( \beta = 0 \), and the response for this electrode of area \( A = A_0 \tau_s^{(i)} \) may be obtained from that deduced for a stationary spherical electrode by setting \( \xi = 0 \).