Chronopotentiometry with several types of programmed current at most usual electrodes: general study of systems with coupled first-order chemical reactions

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Abstract

The general equations corresponding to CEC and catalytic processes when current–time functions of the forms \( I(t) = I_0 e^{-t^p} \) and \( I(t) = I_0 f(t) t^p \) are applied to a DME were deduced taking into account the electrode sphericity and using a blank period \( t_1 \). From these expressions we deduce as particular cases those corresponding to other types of electrodes (for example, expanding plane electrode, static mercury dropping electrode and stationary plane electrode), other well-known current–time functions (power current, exponential current and step current), other reaction schemes (CE, EC and E mechanisms) and those cases in which the blank period is zero. Moreover, methods for determining heterogeneous and homogeneous kinetic parameters are proposed in each reaction scheme.

INTRODUCTION

In this work we carry out a general study of the CEC and catalytic mechanisms in chronopotentiometry with several types of programmed current at a DME. We have taken the more rigorous model of an expanding sphere, and assumed the existence of a previous blank period.

The equations corresponding to the \( E/t \) response for a CEC mechanism are of great interest for several reasons. First, the equations for catalytic, CE, EC, and E mechanisms can be obtained as particular cases of the CEC equations. Furthermore, by elementary transformations the equations corresponding to expanding plane electrodes, stationary spherical electrodes (SMDE) and stationary plane electrodes can be deduced from the equations for a DME. Second, many current–time functions (cfts) of interest can be obtained from the general results for a power exponential law \( I(t) = I_0 t^p e^{-t^q} \) \((\alpha = -1/2 \text{ and any value of } w)\) or a power...
law of the total time \(I(t) = I_0(t_1 + t)^n\) (for any value of \(n\)), both applied to non-stationary electrodes after a blank period \(t_1\) [1]. Finally, the case \(t_1 = 0\) can also be obtained easily from our general expressions. In this situation the cts which can be applied to the DME are considerably restricted, so only eulf of the form \(I(t) = I_0 r^n e^{-w t}\) with \(u \geq 1/6\) can be used. In this case, when \(w = 0\) our equations are identical with those obtained by Gálvez and coworkers for catalytic, CE, EEC and E mechanisms [2–5].

We have also obtained asymptotic solutions which are applicable when the chemical reactions proceed so fast that the steady state is attained in the reaction layer [6].

Finally, we also propose methods to calculate equilibrium and rate constants of chemical processes preceding and following the charge transfer reaction (ctr), as well as kinetic parameters of the heterogeneous step.

**THEORY**

The respective schemes corresponding to the CEC and catalytic mechanisms are

\[
\begin{align*}
\text{B} & \xrightarrow{k_1} \text{C} + n e^- \xrightarrow{k_2} \text{D} \xrightarrow{k_3} \text{E} \\
\text{D} & \xrightarrow{k_4} \text{C} + n e^- \xrightarrow{k_5} \text{D} \xrightarrow{k_6} \text{C}
\end{align*}
\]

A catalytic process can be represented by scheme II if both species C and D are initially present in the solution, and under these conditions it can be considered as a particular case of a CEC mechanism. Thus, we shall develop the theory for the CEC process at a DME, and search for the conditions under which the general response of process I reduces to that corresponding to process II.

The boundary value problem associated with process I is given by

\[
\begin{align*}
\delta_c c_B &= -\delta_c c_C = -k_1 c_B + k_2 c_C \\
\delta_D c_D &= -\delta_D c_E = -k_3 c_D + k_4 c_E
\end{align*}
\]

and for

\[
\begin{align*}
t = 0, \quad & r > r_0 \quad c_B = c_B^*, \quad c_C = c_C^*, \quad c_D = c_D^*, \quad c_E = c_E^* \\
t > 0, \quad & r \to \infty \quad c_B = c_C = c_D = c_E = c^*
\end{align*}
\]

for

\[
\begin{align*}
t > 0, \quad & r = r_0 \\
D_c \left( \frac{\partial c_c}{\partial r} \right)_{r = r_0} &= -D_D \left( \frac{\partial c_D}{\partial r} \right)_{r = r_0} = \frac{I(t)}{n \text{FAT}(t)} \\
D_D \left( \frac{\partial c_B}{\partial r} \right)_{r = r_0} &= 0
\end{align*}
\]

\[
D_E \left( \frac{\partial c_E}{\partial r} \right)_{r = r_0} = 0
\]

\[
\frac{I(t)}{n \text{FAT}(t)} = k_1 e_c(r_0, t) - k_3 e_D(r_0, t)
\]

\[
\begin{align*}
\delta_i &= \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{a_i^2}{3r^2} \frac{\partial}{\partial r} \\
\text{and } D_i &= \text{the diffusion coefficient of species } i \quad (i = B, C, D \text{ or } E). \quad \text{In this work, we assume that}
\end{align*}
\]

\[
D_B = D_C = D_D = D_E
\]

and we shall consider for the current applied to the DME, after a blank period \(t_1\), a power-exponential law of the form

\[
I(t) = I_0 t^n e^{-w t} \quad u \geq -1/2, \forall u \in \mathbb{R}
\]

By defining the variables

\[
\begin{align*}
\varepsilon_1 &= c_B + c_C \\
\phi_1 &= (c_B - K_1 c_C) e^{u t'} \\
\varepsilon_2 &= c_B + c_D \\
\phi_2 &= (c_D - K_2 c_E) e^{u t'}
\end{align*}
\]

eqn. (1) transforms to

\[
\delta_c \varepsilon_1 = \delta_D \varepsilon_2 = \delta_D \phi_1 = \delta_D \phi_2 = 0
\]

With the aid of the dimensionless parameters

\[
\begin{align*}
\delta_c &= \frac{r - r_0}{2(D ft)^{1/2}} \\
\varepsilon_1 &= \frac{2(D ft)^{1/2}}{a_1^{3/2}} \\
\beta &= \frac{t_1}{t_0} \left( \frac{t}{t_0} \right)^{1/3} \\
\chi_1 &= \kappa_1 t \\
\chi_2 &= \kappa_2 t \\
\Omega &= w t
\end{align*}
\]
we can deduce the expressions for the concentration profiles (eqns. (A1), (A19) and (A20)), and also those of the surface concentrations, which are

\[
\frac{c_C(r_0, t)}{c_i^*} = \frac{1}{1 + K_1} \left\{ 1 - \frac{N_i t^{m+2/3}}{t_i^{2/3}} \left[ S_m(\xi_C, \beta, \Omega) + K_1 T_m(\xi_C, \beta, \chi_1, \Omega) \right] \right\} \tag{18}
\]

\[
\frac{c_D(r_0, t)}{c_i^*} = \frac{1}{1 + K_2} \left\{ K_2 \mu_{\text{CEC}} + \frac{\gamma N_i t^{m+2/3}}{t_i^{2/3}} \left[ K_2 S_m(\xi_D, \beta, \Omega) + T_m(\xi_D, \beta, \chi_2, \Omega) \right] \right\} \tag{19}
\]

where

\[m = u - 1/6\] \hspace{1cm} \tag{20}

\[N_i = \frac{2l_0}{nF \epsilon_0 D_C^{3/2} \epsilon_i^*} \tag{21}\]

\[\mu_{\text{CEC}} = \frac{\epsilon_D^*}{\epsilon_i^*} \tag{22}\]

\[\gamma = \left( \frac{D_C}{D_D} \right)^{1/2} \tag{23}\]

and the series \(S_m\) and \(T_m\) are defined in Appendix A (eqns. (A22) and (A23)).

From eqns. (18) and (19) we see that the surface concentration of species C for a CEC mechanism is the same as the concentration of the oxidized species for a CE process [1]. The surface concentration of species D is similar to that corresponding to the reduced species in an EC process if we assume that the initial concentration of the oxidized species is \(c_i^*\) [1]. The transition time \(\tau\) has, therefore, the same value as in a CE mechanism (eqn. (24) in ref. 1).

Inserting eqns. (18) and (19) in eqn. (6), we arrive at the expression for the potential–time function

\[
N_i \frac{D_C^{3/2}}{2k_s} t^{m+1/6} e^{\Omega(t) \Omega(0)} = \frac{1}{1 + K_1} \left[ t_i^{2/3} - \frac{N_i t^{m+2/3}}{t_i^{2/3}} \left[ S_m(\xi_C, \beta, \Omega) + K_1 T_m(\xi_C, \beta, \chi_1, \Omega) \right] \right] \]

\[= \frac{10^{\Omega(t)}}{1 + K_1} \left\{ K_2 \mu_{\text{CEC}} t_i^{2/3} + \frac{\gamma N_i t^{m+2/3}}{t_i^{2/3}} \left[ K_2 S_m(\xi_D, \beta, \Omega) + T_m(\xi_D, \beta, \chi_2, \Omega) \right] \right\} \tag{24}\]

\[\eta(t) = \frac{nF}{RT} \ln \frac{1}{10} \left( E(t) - E^0 \right) \tag{25}\]

Equation (24) is greatly simplified for reversible (\(k_1 \to \infty\)) and totally irreversible (\(k_1 \to 1 \text{ cm s}^{-1}\)) cases (see eqns. (34) and (42) in Results and Discussion).

CATALYTIC MECHANISM

By comparing schemes I and II we deduce that for a catalytic process the following conditions are fulfilled (see eqns. (8), (10), (23) and Notation and Definitions)

\[\gamma = 1 \tag{26}\]

\[\epsilon_i^* = \epsilon_1^* = \epsilon_2^* = \epsilon_i^* \tag{27}\]

\[K_1 = K_2 \tag{28}\]

\[\kappa_1 = \kappa_2 \tag{29}\]

With the aid of these conditions we can obtain the expressions for the surface concentrations corresponding to a catalytic process

\[
\frac{c_C(r_0, t)}{c_i^*} = \frac{1}{1 + K_1} \left\{ 1 - \frac{N_i t^{m+2/3}}{t_i^{2/3}} \left[ (1 + K_1) T_m(\xi_C, \beta, \chi_1, \Omega) \right] \right\} \tag{30}
\]

\[
\frac{c_D(r_0, t)}{c_i^*} = \frac{1}{1 + K_2} \left\{ K_2 + \frac{\gamma N_i t^{m+2/3}}{t_i^{2/3}} \left[ (1 + K_1) T_m(\xi_D, \beta, \chi_2, \Omega) \right] \right\} \tag{31}\]

From these expressions we conclude that the response for mechanism II can be obtained from that corresponding to process I (see eqns. (18) and (19)) taking into account eqns. (26)-(29), and replacing the series \(S_m(\xi_i, \beta, \Omega)\) (eqn. (A22)) by the series \(T_m(\xi_C, \beta, \chi_1, \Omega)\) (eqn. (A23)).

So far, we have carried out the study corresponding to a cft given by eqn. (9). The application of a cft of type \(I(t) = I_0 t^\alpha \) (\(\forall t \in R\)) at non-stationary electrodes, and other cfts which are particular cases of these, is considered in Appendices B and C.

RESULTS AND DISCUSSION

A study of the series \(T_m(\xi_i, \beta, \chi, \Omega)\) (eqn. (A23)) and \(W_m(\xi_i, \beta', \chi')\) (eqn. (B10)) which take part in the determination of the responses corresponding to CEC and catalytic processes has been carried out in ref. 1. For large values of \(\chi\) and \(\chi'\) (eqns. (15), (16) and (B4), (B5)) both series are slowly convergent and we have applied the steady state approximation [6]. In this way we deduce

\[
T_m(\xi_i, \beta, \chi, \Omega) = \frac{\epsilon_i^*}{2 \chi^{1/2}} \chi \gg 1 \tag{32}\]

\[\chi = \chi_1 \text{ or } \chi_2\]
\[ W_p(\xi^*, \beta^*, \chi^*) = \frac{1}{2\beta'(\chi^*)^{1/2}} \quad \chi^* \gg 1 \]

\( \chi^* = \chi^*_1 \) or \( \chi^*_2 \)

**CEC mechanism**

In Fig. 1 we compare the \( E/t \) curves corresponding to a CE mechanism for a power-exponential cf (eqn. 93) and different values of the equilibrium constant of the chemical step \( K_1 \), with those corresponding to a CEC process. In this figure, the curves (a) were obtained for \( K_1 = 0 \), and correspond therefore to E (continuous curve) and EC (dashed curve) mechanisms (see Appendix C). From these curves it can be deduced that the presence of a following chemical reaction results in a shift of the curves to more positive potentials, \( \tau \) remaining unchanged. The effect of the preceding chemical reaction on these \( E/t \) curves is the opposite.

Figure 2 shows the effects of sphericity on the \( E/t \) curves obtained for a cf of type \( I(t) = I_0 \tau^\alpha \) (see Appendix B). We have included curves corresponding to a highly spherical electrode \( (\xi_{sc} = 0.4 \text{ s}^{-1/2}) \) owing to the fact that we have calculated up to the second order spherical correction in the corresponding differential equations. The influence of electrode curvature is maximal near the transition time \( \tau \), and increases when \( \nu \) decreases. We can conclude that, in most of the cases, the expanding plane model \( (\xi_{sc} = 0) \) is not suitable for describing a DME.

The equilibrium and the rate constants \( K_1, k_1 \) and \( k_2 \) of the preceding chemical reaction can be determined from measurements of \( \tau \) using the method indicated in ref 1 for a CE process. For the subsequent chemical reaction, the determination of \( K_2, k_1 \) and \( k_4 \) depends on the reversibility of the process.

For a reversible cfr (\( k_4 \to \infty \)), eqn. (24) takes the form

\[
E(t) - E^o = \frac{RT}{nF} \ln \frac{(1 + K_2)[I_{2s}^{1/2} - \eta N_{Fe}^{1/2}] + K_1 T_n(\xi_c, \beta, \chi, \Omega)}{(1 + K_2)[K_2 \mu_{CEC} I_{2s}^{1/2} + \gamma N_{Fe}^{1/2} K_2 T_n(\xi_c, \beta, \chi, \Omega)]}
\]

(34)

This equation satisfies

\[
E(t \to 0) - E^o = \frac{RT}{nF} \ln \frac{1 + K_2}{(1 + K_1) K_2 \mu_{CEC}} \quad \text{for } m > -2/3
\]

(35)

\[
E(t \to 0) - E^o = \frac{RT}{nF} \ln \frac{(1 + K_2)[2I_{2s}^{1/2} - \eta N_{Fe}^{1/2}(1 + K_1)]}{(1 + K_2)[K_2 \mu_{CEC} I_{2s}^{1/2} + \gamma N_{Fe}^{1/2}(1 + K_2)]}
\]

for \( m = -2/3 \), \( \mu_{CEC} = 0 \)

(36)
\[ E(t) = E^0 + \frac{RT}{nF} \ln \left( \frac{1}{\gamma} \cdot \frac{1 + K_2}{K_2S_m(\xi_D, \beta, \Omega) + T_m(\xi_D, \beta, \chi_2, \Omega)} \right) \]

where

\[ E_i^{1/2} = E^0 + \frac{RT}{nF} \ln \left( \frac{1}{\gamma} \right) \]

From eqn. (38), and choosing \( t = t' \) where

\[ (t')^{\frac{m+2}{3}} = \frac{(t_1 + t')^{2/3}}{N_s[1 + S_m(\xi_{C,r}, \beta, \Omega, \gamma)] + K_1[T_m(\xi_{C,r}, \beta, \chi_1, \Omega)]} \]

we deduce

\[ E(t') = E_i^{1/2} + \frac{RT}{nF} \ln(1 + K_1) \]

where

\[ E_i^{1/2} = E^0 + \frac{RT}{nF} \ln \left( \frac{1}{\gamma} \right) \]

Fig. 3. Potential-time curves corresponding to a CEC process for a reversible ctr (eqn. (34)); \( u = -1/2, w = -0.1 \text{ s}^{-1}, N_s = 0.2 \text{ s}^{-1/3}, \beta = 1, \xi = 0.15 \text{ s}^{-1/6}, \mu = 0.5 \). The values of \( K_2 \) are (a) 0.0, (b) 0.1, (c) 0.5, (d) 1.0, (e) 2.0, and (f) 7.0. Other conditions as in Fig. 2.

Fig. 4. Dependence of \( \Delta E' \) on \( \ln \chi_{2,r} \) for a CEC process (eqn. (41)); \( u = 1/2, w = 0.5 \text{ s}^{-1}, N_s = 1.7 \text{ s}^{-1/3}, \xi = 15 \text{ s}^{-1}, t_1 = 0.5 \text{ s} \). The values of \( K_2 \) are (a) 0.0, (b) 0.2, (c) 0.6, (d) 1.0, (e) 4.0, and (f) 15.0. Other conditions as in Fig. 3.
where
\[ g(\xi_C, \beta, \chi_1, \Omega) = \frac{e^{-\Omega}}{t^{m+1/6}} \times \left[ t^{1/3} - N_t^{m+2/3} \left[ S_m(\xi_C, \beta, \Omega) + K_t T_m(\xi_C, \beta, \chi_1, \Omega) \right] \right] \]

(43)

According to eqn. (42), the kinetic parameters \( \alpha \) and \( k_2 \) of the charge transfer reaction can be obtained through a linear regression of \( E(t) - E^0 \) vs. \( \ln g(\xi_C, \beta, \chi_1, \Omega) \). Moreover, the equilibrium constant \( K_t \) of the preceding chemical reaction can be determined from eqn. (42) by extrapolation to zero time with \( m = -1/6 \).

**Catalytic mechanism**

The transition time \( \tau_e \) corresponding to a catalytic process (see scheme II) is readily obtained by making \( c_c(t_0, \tau_e) = 0 \) in eqn. (30), so that we find
\[ \tau_e^{m+2/3} = \frac{(t_1 + \tau_e)^{2/3}}{N_t(1 + K_t) T_h(\xi_C, \beta, \chi_1, \Omega)} \]

(44)

From this equation we deduce
\[ \lim_{t_0 \to \infty} N_t \tau_e^{m+2/3} = \frac{P_{2n+4/3}}{1 + K_t} \]

(45)

and following a procedure similar to that described in ref. 9 we can obtain \( K_1 \) independently of the reversibility of the ctr.

Once \( K_1 \) is known, the rate constants \( k_1 \) and \( k_2 \) can be determined as outlined below.

Equation (44), after some manipulations, transforms to
\[ \left( \frac{\tau_e}{\tau_d} \right)^{m+2/3} = \frac{1}{Y} \]

(46)

where \( \tau_d \) is the transition time for an E process [8] and
\[ Y = \frac{\left( t_1 + \tau_d \right)^{2/3}}{t_1 + \tau_e} \times \frac{S_m(\xi_C, \beta, \chi_1, \Omega)}{S_m(\xi_C, \beta, \chi_1, \Omega)} \]

(47)

\[ X_m(\xi_C, \beta, \chi_1, \Omega) = \frac{S_m(\xi_C, \beta, \chi_1, \Omega)}{T_m(\xi_C, \beta, \chi_1, \Omega)} \]

(48)

\( \xi_C, \beta, \chi_1, \Omega \) and \( \chi_1, \beta \) being the values of these variables for \( t = \tau_j \) (j = c or d).

We can therefore obtain \( k_1 \) and \( k_2 \) from the working curves plotted in Fig. 5.
The expression of potential–time functions (eqns. (6), (30) and (31)) is the following

\[ N \frac{D^{1/2}}{k_s} t^{-m+1/6} e^{\alpha t} = \frac{1}{1 + K_1} \left[ (t^{2/3} - (1 + K_1) N_2 t^{-2/3} m_0 (\xi_C, \beta, \chi_1, \Omega)) \right] \]

This equation simplifies notably for reversible \((k_s \to \infty)\) and totally irreversible \((k_s \ll 1 \text{ cm s}^{-1})\) cases. In these cases, \(K_1\) can also be estimated from the E/t curve by extrapolation to zero time, as indicated for a CEC mechanism (see previous section). For totally irreversible processes \(a\) and \(k_s\) are obtained in a similar way as for CEC processes.

Figures 6 and 7 show the effects of sphericity on the E/t curves for different values of \(K_1\) and \(k_1\) respectively. In the same way as for a CEC mechanism, these effects cannot be generally neglected when a DME or an SMDE is used.

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REFERENCES


APPENDIX A

By using the transformations given by expressions (12)–(17) and supposing that \(\epsilon_1, \phi_1, \epsilon_2\) and \(\phi_2\) (eqn. (10)) have the following forms

\[ \epsilon_1(r, t) = \epsilon_1^0 + \sum_{f, h, j, d=0}^\infty \delta_{f, h, j, d} (s_{1}) \xi_1^{\delta} \beta_{1}^{\beta} \chi_1^{\chi_1} \Omega^{\Omega} \]

\[ \phi_1(r, t) = \sum_{f, h, j, d=0}^\infty \delta_{f, h, j, d} (s_{1}) \xi_1^{\delta} \beta_{1}^{\beta} \chi_1^{\chi_1} \Omega^{\Omega} \]

\[ \epsilon_2(r, t) = \epsilon_2^0 + \sum_{f, h, j, d=0}^\infty \theta_{f, h, j, d} (s_{1}) \xi_1^{\delta} \beta_{1}^{\beta} \chi_1^{\chi_1} \Omega^{\Omega} \]

\[ \phi_2(r, t) = \sum_{f, h, j, d=0}^\infty \theta_{f, h, j, d} (s_{1}) \xi_1^{\delta} \beta_{1}^{\beta} \chi_1^{\chi_1} \Omega^{\Omega} \]

eqn. (11) is transformed into

\[ \rho_{f, h, j, d} (s_{1}) + 2 \rho_{f, h, j, d} (s_{1}) \]

\[ -2 \left( \frac{3f + 2g + 6m + 6i + 6j}{3} \right) \rho_{f, h, j, d} (s_{1}) \]

\[ = -\left( \sum_{f=1}^\infty \sum_{g=f+1}^\infty \rho_{f, h, j, d} (s_{1}) \right) \]

\[ + \sum_{r=0}^{+\infty} \delta_{r, s, h, j, d} (s_{1}) + \frac{1}{2} \left( f + g - 3 \right) \rho_{f, h, j, d} (s_{1}) \]

(A2)
\[ \delta_{f,s,h,i,j}(s_C) = 2s_C \delta_{f,s,h,i,j}(s_C) - \frac{\left[3f + 2g + 6(m + h) + 6i + 6j\right]}{3} \delta_{f,s,h,i,j}(s_C) \]

\[ = -\left\{ \sum_{l+q+1=f} c_i \delta_{f,s,h,i,j}(s_C) + \sum_{r+y=f} d_i \delta_{r,s-3,h,i,j}(s_C) + \frac{1}{f+g-3} \delta_{f,s-3,h,i,j}(s_C) \right\} \]  

(A3)

\[ \sigma'_{f,s,h,i,j}(s_D) + 2s_D \sigma'_{f,s,h,i,j}(s_D) - \frac{\left[3f + 2g + 6(m + h) + 6i + 6j\right]}{3} \sigma_{f,s,h,i,j}(s_D) \]

\[ = -\left\{ \sum_{l+q+1=f} c_i \sigma'_{f,s,h,i,j}(s_D) + \sum_{r+y=f} d_i \sigma'_{r,s-3,h,i,j}(s_D) + \frac{1}{f+g-3} \sigma_{r,s-3,h,i,j}(s_D) \right\} \]  

(A4)

\[ \theta'_{f,s,h,i,j}(s_D) + 2s_D \theta'_{f,s,h,i,j}(s_D) - \frac{3f + 2g + 6h + 6(m + i) + 6j}{3} \theta_{f,s,h,i,j}(s_D) \]

\[ = -\left\{ \sum_{r+y=f} c_i \theta'_{r,s-3,h,i,j}(s_D) + \sum_{l+q+1=f} d_i \theta'_{r,s-3,h,i,j}(s_D) \right\} \]  

(A5)

where

\[ c_i = 2(-1)^i s_i^j \]

(A6)

\[ d_i = \frac{1}{2} (-1)^i (r + 2) s_i^{j+1} \]

(A7)

and the boundary problem (eqns. (2)-(5)) is given by the following:

for \( s_i \to \infty \)

\[ \rho_{f,s,h,i,j}(s_C) = \delta_{f,s,h,i,j}(s_C) - \sigma_{f,s,h,i,j}(s_D) = \theta_{f,s,h,i,j}(s_D) = 0 \]  

(A8)

for \( s_i = 0 \)

\[ \rho'_{f,s,h,i,j}(0) = 0 \quad \text{unless } f = 0, g = 2, h = 1, i = 0 \]  

(A9)

\[ \rho'_{0,2,0,0}(0) = \frac{\sigma^* N_i}{k_i^j} \quad j \geq 0 \]  

(A10)

\[ \delta'_{0,2,0,0}(0) = -\frac{k_i}{h_i} \rho'_{0,2,0,0}(0) \quad h,j \geq 0 \]  

(A11)

where

\[ \sigma'^{0,2,0,0}(0) = \frac{\sigma^* N_i}{k_i^j} \quad j \geq 0 \]  

(A13)

\[ \theta'^{0,2,0,0}(0) = \frac{1}{l_i^j} \sigma'^{0,2,0,0}(0) \quad i,j \geq 0 \]  

(A14)

The differential equations (A2)–(A5) with the boundary conditions (A8)–(A14) have the following solutions

\[ \rho_{f,s,h,i,j}(s_C) = 0 \quad \text{unless } g = 3n + 2(n \geq 0), h = 1, i = 0 \]  

(A15)

\[ \sigma_{f,s,h,i,j}(s_D) = 0 \quad \text{unless } g = 3n + 2(n \geq 0), h = 0, i = 1 \]  

(A16)

The form of the functions \( \rho_{f,s,h,i,j}(s_C) \) and \( \sigma_{f,s,h,i,j}(s_D) \) can be obtained from the functions \( \sigma_{f,s,h,i,j}(s_C) \) calculated in ref. 8 for an E process by changing \( C_C \) for \( \sigma'^* N_i / k_i^j \) and \( -\gamma \sigma'^* N_i / k_i^j \) respectively, in eqns. (A10)–(A18) of this reference.

Moreover

\[ \delta_{f,s,h,i,j}(s_C) = -\frac{k_i}{h_i} \rho^{0,2,0,0}(s_C) \]  

(A17)

\[ \theta_{f,s,h,i,j}(s_D) = \frac{1}{l_i^j} \sigma^{0,2,0,0}(s_D) \]  

(A18)

The superscripts \((m + h)\) and \((m + i)\) in these equations indicate that we must also change \( m \) for \((m + h)\) and \((m + i)\) respectively, in the above-mentioned equations in ref. 8 to obtain the functions \( \delta_{f,s,h,i,j}(s_C) \) and \( \theta_{f,s,h,i,j}(s_D) \). In this way, the concentration profiles are totally determined (see eqn. (A1)). Indeed, from eqn. (10) we have

\[ c_C(r,t) = \frac{\epsilon_i(r,t) - e^{-\gamma x_i} \phi_i(r,t)}{1 + K_i} \]  

(A19)

\[ c_D(r,t) = K_i \epsilon_i(r,t) + e^{-\gamma x_i} \phi_i(r,t) \]  

(A20)

These equations are simplified at the electrode surface \( r = r_0 \) (\( s_i = 0 \)), since

\[ \epsilon_i(r_0,t) = \epsilon_i^* N_i \frac{x_1^m}{k_1^j} \beta^2 S_m(\xi_C, \beta, \Omega) \]  

(A21)

\[ \phi_i(r_0,t) = K_i \epsilon_i^* N_i \frac{x_1^m}{k_1^j} \beta^2 T_m(\xi_C, \beta, \xi_1, \Omega) e^{x_1} \]  

\[ \epsilon_i(r_0,t) = \epsilon_i^* N_i \frac{x_2^m}{k_2^j} \beta^2 S_m(\xi_D, \beta, \Omega) \]  

(A21)

\[ \phi_i(r_0,t) = \gamma \epsilon_i^* N_i \frac{x_2^m}{k_2^j} \beta^2 T_m(\xi_D, \beta, \xi_2, \Omega) e^{x_2} \]
where
\[
S_m(\xi, \beta, \Omega) = \sum_{j=0}^{\infty} \frac{J_m(j, \beta)}{p_m(j, \beta)} e^{-x} \sum_{z=0}^{\infty} \xi^z (\beta')^z \frac{\Omega^j}{j!}
\]
(A22)

and
\[
T_m(\xi, \beta, \chi, \Omega) = \sum_{z=0}^{\infty} \frac{s_{m+z} (\xi, \beta, \Omega)}{e^{-x} \sum_{z=0}^{\infty} \xi^z (\beta')^z} \frac{\Omega^j}{j!}
\]
(A23)

where
\[
\xi = \xi_C, \beta, \chi = \chi_C, \xi = \xi_D, \beta = \beta_C, \chi = \chi_D
\]
and
\[
p_m(j, \beta) = J_m(j, \beta), J_m(j, \beta), J_2(m, j, \beta)
\]
are defined by expressions (25) and (26) in ref. 8.

By combining eqns. (A19)–(A21), we have deduced the expressions (18) and (19)
for surface concentrations.

**APPENDIX B: POWER LAW CURRENT OF THE TOTAL TIME I(t) = I_d t^\alpha \forall t < R**

In order to obtain the response corresponding to a CEC mechanism (scheme I)
for this current we must replace \(\phi_1\) and \(\phi_2\) in eqn. (10) by the new variables
\[
\phi_1' = (c_C - K_1 c_C) e^{\xi t};
\]
\[
\phi_2' = (c_D - K_2 c_D) e^{\xi t};
\]
and instead of the variables defined by eqns. (14)–(16) we introduce
\[
\beta' = \left(\frac{t}{t_s}\right)^{1/2}
\]
(B3)

\[
\chi_1' = \kappa_1 t_s
\]

\[
\chi_2' = \kappa_2 t_s
\]

Furthermore, the dimensionless parameter \(\Omega\) (eqn. (17)) disappears.

In this way, and following a similar procedure to that indicated in Appendix A
and in ref. 10, we have obtained the following expressions for the surface
concentrations of the species C and D
\[
\frac{c_C(t_0, t)}{\epsilon_i(t_0)} = \frac{1}{1 + K_1} \left(1 - \frac{N_1 t^{1/2}}{t_s^{1/2 - m}} \left[V_m(\xi_C, \beta') + K_1 W_m(\xi_C, \beta', \chi_1)\right]\right)
\]

(B6)

\[
\frac{c_D(t_0, t)}{\epsilon_i(t_0)} = \frac{1}{1 + K_2} \left[K_2 \mu_{\text{CEC}} + \frac{\chi N_2 t^{1/2}}{t_s^{1/2 - m}} \left[K_2 V_m(\xi_D, \beta') + W_m(\xi_D, \beta', \chi_2)\right]\right]
\]

(B7)

with
\[
m = v = 1/6
\]

\[
V_m(\xi, \beta') = F(m, \beta') - \xi_1 F_1(m, \beta') - \xi_2^2 F_2(m, \beta')
\]

(B8)

\[
W_m(\xi, \beta', \chi' = e^{-x} \sum_{z=0}^{\infty} V_m^{m+z}(\xi, \beta') (\chi')^z z！
\]

(B10)

\[
\xi_i = \xi_C, \beta, \chi = \chi_C, \xi = \xi_D, \beta = \beta_C, \chi = \chi_D
\]

where \(F(m, \beta')\), \(F_1(m, \beta')\) and \(F_2(m, \beta')\) are defined in refs. 1 and 10.

The response corresponding to a catalytic process (scheme II) can be obtained
from eqns. (B6) and (B7), calculated for a CEC mechanism, taking into account
eqns. (26)–(29) and substituting the series \(V_m\) (eqn. (B9)) for the series \(W_m\) (eqn.
(B10)).

**APPENDIX C**

The general equations obtained in previous sections for CEC and catalytic
mechanisms have been calculated for a DME and for applied cts of types
\(I(t) = I_d e^{\xi t}\) and \(I(t) = I_d t^\alpha\). From these expressions it is possible to deduce
those corresponding to a great variety of special situations, as is described in the
following.

**Other mechanisms**

The response corresponding to EC, CE and E mechanisms can be deduced
from eqns. (18) and (19) for a power-exponential ctf and eqns. (B6) and (B7) for a
power law current of the total time \(t_s\), if we make in these equations the following
substitutions.

**EC mechanism**

In this case, the condition \(K_1 = 0\) must be fulfilled in order to obtain the
response for an EC mechanism when the concentration of oxidized species is \(\epsilon_i(t_0)\).

**CE mechanism**

The equations corresponding to this process are obtained by making \(K_2 \to \infty\)
and replacing \(\mu_{\text{CEC}}\) by \(\mu\) (see Notation) in the above-mentioned expressions [1].

**E mechanism**

If we write \(\mu\) instead of \(\mu_{\text{CEC}}\) (see Notation), and the conditions \(K_1 = 0\) and
\(K_2 \to \infty\) are fulfilled simultaneously, from the above-mentioned expressions we
obtain the equations corresponding to a simple ctf for a concentration of oxidized
species equal to \(\epsilon_i(t_0)\). [8,10].

**Other forms for the applied ctf**

After a blank period \(t_s\)

The potential–time response corresponding to mechanisms I and II for a
power-exponential ctf reduce to those corresponding to a power ctf of the form
\( I(t) = I_0 e^{\alpha t} \) \((u \geq -1/2)\), an exponential ctf of the form \( I_0 e^{\alpha t} \) \((\forall \omega \in R)\) and a current step, by making \( j = 0\), \( m = -1/6\) and both conditions \((j = 0, m = -1/6)\) respectively, in the series \( S_m \) and \( T_m \) (eqns. (A22) and (A23)). For a power law current of the total time \( t_1\), the response corresponding to a current step can also be obtained by making \( m = -1/6\) \((\omega = 0)\) in the series \( V_m \) and \( W_m \) (eqns. (B9) and (B10)).

**Vanishing blank period**

If the preceding blank period \( t_1\) vanishes, the power exponential ctf \( I(t) = I_0 t^{\beta} e^{\alpha t} \) cannot be applied in the general form that has been studied in this work, since the exponent \( u \) is restricted to values \( u \geq 1/6\) [11]. The response corresponding to this situation can be deduced by making \( \beta = 1\) in the series \( S_m \) and \( T_m \) (eqns. (A22) and (A23)). In the particular case \( w = 0\), i.e. \( I(t) = I_0 t^{\beta} \) \((\forall \omega \geq 1/6)\), our equations are equivalent to those previously deduced by Gálvez and coworkers for catalytic, CE, EC and E mechanisms [2–5].

**Other electrodes**

The equations for an expanding plane electrode are obtained by making \( \xi_0 = 0\) in all the expressions of this paper. This model has been studied by Kant and Rangarajan for power ctf's only, and with the additional assumption that the diffusion coefficients of all species are equal [12]. We can also deduce the expressions corresponding to a static mercury drop electrode (SMDE) and a stationary plane electrode, both of area \( A = A_0 t^{2/3}\) by making \( t_1 \gg t\), \((\omega = 1)\) and \( \xi_0 = 0\), \( t_1 \gg t\) respectively, in eqns. (18), (19), (B6) and (B7) of this work. In this situation the general response deduced for catalytic, CE, EC and E mechanisms agrees with the results found in the literature [13,14].

**NOTATION AND DEFINITIONS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I(t) )</td>
<td>current–time function</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>charge transfer reaction</td>
</tr>
<tr>
<td>( A_0 )</td>
<td>area of a DME at ( t_1 = 1) s</td>
</tr>
<tr>
<td>( c_i^+ )</td>
<td>bulk concentration of species ( i ) ((i = B, C, D \text{ or } E))</td>
</tr>
<tr>
<td>( \mu )</td>
<td>time-dependent faradaic current ((I_0 t^{\beta} e^{\alpha t}, u \geq -1/2 \text{ and } \forall \omega \in R)) or ( I_0 t^{\beta} ) ((\forall \omega \in R))</td>
</tr>
<tr>
<td>( k_{f, b} )</td>
<td>heterogeneous rate constants of the forward and reverse charge transfer reactions</td>
</tr>
<tr>
<td>( k_s )</td>
<td>apparent heterogeneous rate constant of charge transfer at ( E^0 )</td>
</tr>
<tr>
<td>( k_m, k_2 )</td>
<td>rate constants of the preceding chemical reaction in a CEC process</td>
</tr>
<tr>
<td>( k_3, k_4 )</td>
<td>rate constants of the subsequent chemical reaction in a CEC process</td>
</tr>
<tr>
<td>( K_1 )</td>
<td>equilibrium constant of the preceding chemical reaction in a CEC process ((k_2/k_1))</td>
</tr>
<tr>
<td>( K_2 )</td>
<td>equilibrium constant of the chemical reaction in a catalytic process</td>
</tr>
<tr>
<td>( m )</td>
<td>equilibrium constant of the subsequent chemical reaction in a CEC process ((k_4/k_3))</td>
</tr>
<tr>
<td>( p_j )</td>
<td>(2(1 + j/2)/\Gamma(1 + j/2))</td>
</tr>
<tr>
<td>( r )</td>
<td>distance from the centre of the spherical electrode</td>
</tr>
<tr>
<td>( r_0 )</td>
<td>electrode radius at time ( t_1)</td>
</tr>
<tr>
<td>( t )</td>
<td>time elapsed between current application and measurement of the potential</td>
</tr>
<tr>
<td>( t_1 )</td>
<td>total time ((t_1 + t))</td>
</tr>
<tr>
<td>( t_0 )</td>
<td>blank period</td>
</tr>
</tbody>
</table>

**Greek letters**

- \( \alpha \): electron-transfer coefficient
- \( \varepsilon_i^+ \): \( c_i^+ e^{\kappa_i} \)
- \( \varepsilon_i^- \): \( c_i^- e^{\kappa_i} \)
- \( \kappa_i \): \( k_i + k_2 \)
- \( \kappa_2 \): \( k_3 + k_4 \)
- \( \mu \): \( c_i^+ e^{\kappa_i} / c_i^- e^{\kappa_i} \)
- \( \mu_{CEC} \): dimensionless spherical correction parameter
- \( \xi_0 \): \( 2 - D_i^{1/2}/a \)
- \( \tau \): transition time corresponding to CEC or CE processes
- \( \tau_c \): transition time corresponding to a catalytic process
- \( \tau_d \): transition time corresponding to EC or E processes

Other definitions are conventional.