The pathways towards the steady state $E/t$ and $I/E$ responses when using an alternating current

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Abstract

Equations corresponding to the application of an alternating current to spherical electrodes, including as limit cases planar electrodes and spherical microelectrodes have been deduced. We have also analyzed the evolution from transient to stationary potential–time and current–potential responses. This technique is particularly interesting when the reduction transition time does not exist since, when only the oxidized species is initially present, the reoxidation transition time for a transfer charge reaction under steady state conditions is only dependent on the frequency of the alternating current applied and, therefore, it is possible to detect any kinetic complication relating to the behaviour of the reduced species. We also propose methods for the accurate determination of thermodynamic and kinetic parameters of the charge transfer process from the analysis of the broad central zone of transient and stationary $E/t$ and $I/E$ curves, a region which is barely affected by capacitative distortion. The validity of the theoretical predictions has been experimentally tested with different reversible and irreversible systems.

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1. Introduction

In recent papers [1,2], we have analysed the application of Chronopotentiometry and Reciprocal Derivative Chronopotentiometry with programmed current at microelectrodes, since these present great advantages for carrying out electrochemical measurements and allow the rapid establishment of steady state signals, due to the enhancement of mass transport [3–10].

As has been previously pointed out, the use of programmed (time variable) currents at microelectrodes is needed in order to obtain a time dependent potential since, when a constant current is applied to an electrode of very small size, a constant, and therefore useless, potential is obtained [11–14]. Moreover, the application of programmed currents allows us to obtain $I(t)/E$ responses (with $I(t)$ being the applied current and $E$ the measured potential), which are independent of the particular form of the current applied and also identical to that obtained when any time variable potential $E(t)$ is applied (voltammetric steady state $I/E$ curve) [1]. This curves behaviour is observed independently of the degree of reversibility of the electrode process.

In this paper, we present the theory corresponding to the application of an alternating current of the form $I(t) = I_0 \sin(\omega t)$ to spherical electrodes of any size, including as limiting cases those corresponding to planar electrodes and to spherical microelectrodes. The theoretical treatment of spherical and sphere-cap microelectrodes under conditions of voltammetric steady state diffusion limited current has been previously reported by Oldham et al. [13–15] but in these references the application of programmed currents has not been considered. The analytical solutions obtained by us in this paper present great interest since they allow us to deduce
compact and easily programmable expressions for the potential–time and current–potential curves corresponding to the following cases: (a) there is depletion of the oxidised species at the electrode surface and its reduction transition time is observed; (b) the surface concentration of the oxidised species does not become null and the depletion of the reduced species takes place, so that the reoxidation transition time is reached; (c) neither oxidised nor reduced species are depleted in the electrode surface and as a consequence, an oscillating potential–time curve is obtained.

The use of an alternating current at spherical microelectrodes is particularly interesting when the reduction transition time does not exist because: (a) it is possible to determine the behaviour of the reduced species by applying a single current, whereas when other programmed currents are used, this information cannot be obtained under steady state conditions unless both electroactive species are initially present [1]; (b) when only the oxidized species is initially present, the reoxidation transition time under steady state conditions is only dependent on the frequency of the alternating current applied and, therefore, its measurement leads to the detection of any kinetic complication relating to the behaviour of the reduced species; (c) the potential–time ($E/t$) curves obtained in this case present a broad central zone, barely affected by capacitative distortion, which leads to an accurate determination of thermodynamic and kinetic parameters of the electrode process.

Given that the expressions for the surface concentrations have been obtained in a compact form which is valid for any value of the electrode radius, we have also analysed the evolution from “transient” to “steady state” of the $E/t$ and $I/E$ responses for any degree of reversibility of the electrode process, deducing the limit electrode radius ($r_0$) and frequency ($\omega$) values for which these curves can be considered as practically identical to those corresponding to stationary conditions. Moreover, easy criteria to determine kinetic and thermodynamic parameters of the process from the analysis of the stationary and transient $E/t$ and $I/E$ curves are presented.

Equations deduced in this paper have been tested with different well known experimental systems at different gold disc microelectrodes in order to show qualitatively the conditions under which the steady state can be reached. We have also studied the electrochemical behaviour of two experimental systems at a static mercury drop electrode (SMDE), in order to show how the electrode sphericity affects the response of the different electrode processes, and also to determine kinetic and thermodynamic parameters of the same systems from the analysis of their transient responses. The values obtained are in good agreement with those in the literature.

2. Experimental

The computer driven potentiostat-galvanostat was designed and constructed by QUICELTRON (Spain).

Pulse and waveform generation and data acquisition were performed using i-SBXDD4 and DAS16-330i (ComputerBoards, USA) boards, respectively. All computer programmes were written in our laboratory. Experimental $E/t$ curves were sampled at a frequency 2000 times higher than that of the alternating current and then digitally filtered in order to reduce the noise. The $I/E$ curves were obtained by plotting the alternating applied current, $I_0 \sin(\omega t)$, vs. the measured potential, $E$, in the interval $0 \leq t \leq \tau$, with $\tau$ being the transition time of the process.

A three electrode cell was employed in the experiments. Static mercury-drop electrode (SMDE) and gold disc microelectrodes of different radii served as working electrodes. The SMDE was constructed using a DME, EA 1019-1 (Metrohm) to which a homemade valve was sealed. The electrode radii of the SMDE were determined by weighing a large number of drops (in this case, the errors observed were negligible). The counter electrode was a Pt foil and the reference electrode was a Ag/AgCl|1 M KCl electrode.

All the kinetic and thermodynamic values obtained correspond to series of five replicates. The results obtained are the mean of the five experimental values. The errors correspond to the standard deviation.

Ferrocene, tetrabutylammonium hexafluorophosphate (PF$_6$TBA), CH$_3$CN, FeCl$_3$, K$_2$C$_2$O$_4$, H$_2$C$_2$O$_4$, CrCl$_3$ and NaClO$_4$ were of Aldrich, reagent grade. All chemical reagents were used without further purification.

Nitrogen gas was passed through solutions for deaeration for 15 min prior to measurements.

The diffusion coefficients of Cr$^{3+}$, ferrocene and Fe$^{3+}$ were determined by chronocoulometric measurements of Cr$^{3+}$ in NaClO$_4$ 0.5 M solutions at a SMDE ($r_0 = 1.644 \times 10^{-2}$ cm), and ferrocene 10 mM in CH$_3$CN + 0.25 M PF$_6$TBA and FeCl$_3$ 10 mM + 0.5 M K$_2$C$_2$O$_4$ at a gold electrode ($r_0 = 5 \times 10^{-2}$ cm), obtaining $D_{\text{Cr}^{3+}} = (6.48 \pm 0.06) \times 10^{-6}$ cm$^2$ s$^{-1}$, $D_{\text{ferrocene}} = 2.26 \times 10^{-5}$ cm$^2$ s$^{-1}$ and $D_{\text{Fe}^{3+}} = 7.23 \times 10^{-6}$ cm$^2$ s$^{-1}$. All the values obtained are in agreement with previous results in the literature (see [1,14,16–19]).

3. Theory

We will consider the charge transfer reaction,

$$O + ne^- \overset{k_i}{\underset{k_h}{\rightleftharpoons}} R, \quad (1)$$

which takes place at a stationary spherical electrode of area $A = 4\pi r_0^2$, with $r_0$ being the electrode radius, when
an alternating current of the form \( I(t) = I_0 \sin(\omega t) \) is applied. \( k_f \) and \( k_b \) are the heterogeneous rate constants of reduction (forward) and oxidation (backward) processes, respectively.

The mass transport to/from the electrode surface is described by the following differential equations system and boundary conditions [16,20,21]:

\[
\hat{\rho}_{O\text{-}C}(r,t) = \hat{\rho}_{R\text{-}C}(r,t) = 0,
\]

where \( \hat{\rho}_i \) (i = O or R) is the mass transfer operator.

\[
\hat{\rho}_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) r,
\]

\[
t > 0, r \geq r_0,\]

\[
t > 0, r \rightarrow \infty, c_o(r,t) = c^*_o; c_r(r,t) = c^*_r,
\]

\[
D \left( \frac{\partial c_o(r,t)}{\partial r} \right)_{r=r_0} = 0,
\]

\[
D \left( \frac{\partial c_r(r,t)}{\partial r} \right)_{r=r_0} = \frac{I(t)}{nF},
\]

with \( I(t) \) being an alternating current of the form \( I(t) = I_0 \sin(\omega t) \).

In Eqs. (1)–(4), \( c_o(r,t), c_r(r,t), c^*_o \) and \( D_i \) are the solution of Eq. (1) corresponding to the current applied, the bulk concentration and the diffusion coefficient, respectively, of the i species, with i = O or R.

This problem can be solved by using the dimensionless parameters method [22], in a similar way to that followed in [16]. So, we have deduced the following general expressions for the surface concentrations of O and R:

\[
c^*_o(r_0,t) = 1 - \frac{I_0}{I_d(\infty)} Y(\xi_o, \Omega),
\]

\[
c^*_r(r_0,t) = \mu + \gamma^2 \frac{I_0}{I_d(\infty)} Y(\xi_r, \Omega),
\]

\[
\mu = \frac{c^*_r}{c^*_o},
\]

\[
\gamma = \left( \frac{D_0}{D_k} \right)^{1/2},
\]

\[
\xi = \frac{2\sqrt{D_0 t}}{r_0} \quad \text{for} \quad i = O, R,
\]

\[
\Omega = \omega t
\]

and \( I_d(\infty) \) is the diffusion steady-state limiting current for ultramicrospheres [14],

\[
I_d(\infty) = nFAD_o c^*_o / r_0 = 4\pi r_0 nF D_o c^*_o.
\]

The \( Y(\xi, \Omega) \) function, with \( i = O \) or \( R \), is a double sum given by

\[
Y(\xi, \Omega) = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)!} \sum_{m=0}^{\infty} \frac{(-1)^m \xi^{2m+1}}{\Pi P_{4n+3+m}},
\]

with

\[
P_x = \frac{2\Gamma(1+x/2)}{\Gamma(1/2)}
\]

\[
\Gamma = \text{Euler Gamma function}
\]

According to Eqs. (A.1)–(A.11) from the Appendix A, the above expression for the \( Y(\xi, \Omega) \) function can be rewritten in the following compact function of \( \xi \) and \( \Omega \) variables, which refer to the electrode sphericity and to the dimensionless frequency of the alternating current applied, respectively (see Eqs. (9) and (10)),

\[
Y(\xi, \Omega) = \frac{1}{1 + \phi_i^2} \left[ -\phi_i \exp \left( \frac{\xi^2}{4} \right) \text{erfc} \left( \frac{\xi}{2} \right) + \sin(\Omega) \right]
\]

\[
+ \phi_i \cos(\Omega) - \xi \phi_i G_c(\Omega) + \xi \phi_i^2 G_s(\Omega),
\]

with

\[
\phi_i = \frac{4\Omega}{\xi^2},
\]

and

\[
G_c(\Omega) = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n}}{(2n)! P_{4n+1}},
\]

\[
G_s(\Omega) = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n + 1)! P_{4n+3}}.
\]

The expressions obtained for the surface concentrations of both electroactive species are valid for any value of the electrode radius, i.e., for any value of \( \xi \) (see Eq. (9)) and, therefore, they allow us to analyze the behaviour of the system when an alternating current is applied to electrodes of any size, from \( r_0 \rightarrow \infty \) (planar electrodes) to \( r_0 \rightarrow 0 \) (spherical ultramicroelectrodes). The surface concentrations in both limits can be easily deduced from Eqs. (5), (6), and (14).

Thus, for planar electrodes, by making \( r_0 \rightarrow \infty \), i.e., \( \phi_i \rightarrow \infty \) in Eq. (14), we obtain (see Eqs. (9) and (15)),

\[
\lim_{\phi_i \rightarrow \infty} \left[ \frac{I_0}{I_d(\infty)} Y(\xi, \Omega) \right] = \chi G_s(\Omega),
\]

where

\[
\chi = \frac{2I_0^{1/2}}{nF \sqrt{D_0 c^*_o}}.
\]

By taking into account Eq. (18), the expressions for both surface concentrations (Eqs. (5) and (6)), become:
with \( x = 0 \) referring to the electrode surface. Eqs. (20) and (21) coincide with those previously obtained by us for a stationary planar electrode (Eqs. (3) and (4)) in [20].

For spherical ultramicroelectrodes, by making \( r_0 \to 0 \), i.e., \( \phi_i \to 0 \), \( \xi_i \phi_i \to 0 \) and \( \xi_i \phi_i^2 \to 0 \), in Eq. (14), the corresponding limit value for the \( Y(\zeta, \Omega) \) function is given by

\[
\lim_{\phi_i \to 0} Y(\zeta, \Omega) = \sin(\Omega). 
\]

In this case, the surface concentrations of both elect rode species become those corresponding to process (I) under steady-state conditions, which are given by

\[
\frac{c^0_O(r_0, t)}{c^0} = 1 - I_0 \sin(\Omega) I_d(\infty),
\]

\[
\frac{c^0_R(r_0, t)}{c^0} = \mu + \gamma^2 I_0 \sin(\Omega) I_d(\infty). 
\]

The above expressions are those expected when ultramicrospheres are used and they provide proof of the good behaviour of the compact function \( Y(\zeta_i, \Omega) \) for very small values of the electrode radius since, as has been demonstrated in a previous paper [1], under steady state conditions, the input (applied current, \( I(t) \)) and output (surface concentrations) signals are related in the form,

\[
\frac{c^0_O(r_0, t)}{c^0} = 1 - I_0 \sin(\Omega) I_d(\infty),
\]

\[
\frac{c^0_R(r_0, t)}{c^0} = \mu + \gamma^2 I_0 \sin(\Omega) I_d(\infty). 
\]

with \( I(t) \) being any current–time function (i.e., \( I(t) = I_0 f(t) \) with \( f(t) \) being any time dependent function, which in this case is \( f(t) = \sin(\Omega) \)).

Finally, by introducing the expressions for the surface concentration of species O and R into the Butler–Volmer equation, we obtain a general current–potential or current–time function, given by

\[
\frac{I_0 \sin(\text{cot})}{nFk^0e_o^*} = e^{-\frac{nF(\xi(t) - E^o)}{RT}} \left[ 1 - \frac{I_0}{I_d(\infty)} Y(\zeta_i, \Omega) \right]
\]

\[
- e^{\frac{-nF(\xi(t) - E^o)}{RT}} \left[ \mu + \gamma^2 \frac{I_0}{I_d(\infty)} Y(\tilde{\zeta}_i, \Omega) \right].
\]

This expression takes the following simpler form for a reversible electrode process:

\[
E = E^o + \frac{RT}{nF} \ln \left( 1 - \frac{I_0}{I_d(\infty)} Y(\zeta_i, \Omega) \right) + \frac{RT}{nF} \ln \left( \frac{I_0}{I_d(\infty)} \right),
\]

whereas for a totally irreversible one, Eq. (26) becomes:

\[
E = E^o + \frac{RT}{2nF} \ln \left( \frac{k^0}{D_0} \right) + \frac{RT}{2nF} \ln \left( \frac{I_0}{I_d(\infty)} \right) \left( 1 - \frac{I_0}{I_d(\infty)} Y(\zeta_i, \Omega) \right).
\]

Under steady state conditions, Eq. (26), corresponding to the potential–time or current–potential relationship for any degree of the reversibility of the electrode process, can be written in a completely general form, i.e., under these conditions we can obtain a universal \( I(t)/E \) response which is independent of the particular form of the current–time function applied [1]. Indeed, if Eq. (25) are introduced in the Butler–Volmer equation, we obtain:

\[
\frac{I(t)}{nFk^0e_o^*} = e^{-\frac{nF(\xi(t) - E^o)}{RT}} \left( 1 - \frac{I(t)}{I_d(\infty)} \right)
\]

\[
- e^{\frac{-nF(\xi(t) - E^o)}{RT}} \left( \mu + \gamma^2 \frac{I(t)}{I_d(\infty)} \right),
\]

with \( I(t) = I_0 \sin(\text{cot}) \) for this particular case.

In Eqs. (26)–(29), \( k^0 \), \( \gamma \) and \( E^o \) are the apparent heterogeneous rate constant at \( E^o \), the charge transfer coefficient and the formal potential of the charge transfer process, respectively.

4. Results and discussion

4.1. Behaviour of the function \( Y(\zeta, \Omega) \)

Fig. 1 shows the variation of the \( Y(\zeta, \Omega) \) function, with \( i = O \) or \( R \), which appears in the expressions of the surface concentrations of species O and R (see Eqs. (5) and (6)). These expressions, according to the compact form of the \( Y(\zeta, \Omega) \) function (see Eq. (14)), are valid for any value of the radius of the spherical electrode. Fig. 1(a) shows a 3D plot of the function \( Y(\zeta, \Omega) \), which depends on the values of the variables \( \Omega \) and \( \zeta \), from which it is possible to obtain the curves shown in Fig. 1(b) and (c) by plotting the variation of \( Y \) with \( \zeta_i \) for given values of \( \Omega \) (Fig. 1(b)), or by plotting the variation of \( Y \) with \( \Omega \) for given values of \( \zeta_i \) (Fig. 1(c)). Thus, the curves in Fig. 1(b) have been obtained by “cutting” the 3D plot seen in Fig. 1 according to different planes with \( \Omega \) constant, whereas those in Fig. 1(c) have been obtained by “cutting” the 3D plot according to different planes with \( \zeta_i \) constant. The analysis of Fig. 1(b) and (c) allows us to obtain the limit values of \( \Omega \) and \( \zeta_i \) for which it is possible to approximate the \( Y \) function to its expression under steady state conditions. The stationary form of the \( Y \) function is, in agreement with Eq. (22), \( Y(\zeta, \Omega) \right)_{\text{steady state}} = \sin(\Omega) \), a limit that is reached when the electrode radius becomes very small (ideally, when \( r_0 \to 0 \)).
Thus, in Fig. 1 (b) it can be seen that the function $Y(n_i, X)$ (solid lines) tends to $\sin X$ (dashed lines), as $n_i$ increases. This evolution towards steady state is determined by the values of $X$. In order to see this effect clearly, in the inserted figure we have plotted the evolution of $(Y(\xi, \Omega)/\sin \Omega)$ with $\xi$ for fixed values of $\Omega$ (which are indicated in these curves) and from this figure it can be clearly concluded that this function tends to the unity as $\xi$ increases more quickly the smaller $X$ is. We have estimated the limit values of $n_i$ for which we can consider that the relative difference between $Y(\xi, \Omega)$ and $[Y(\xi, \Omega)]_{\text{steady state}} = \sin(\Omega)$ is smaller than 5%, and we have obtained that, for example, for a value of $\Omega = 2$ the limit value of $\xi$ is 10.4, whereas for $\Omega = 5$, this limit is reached for $\xi = 24.2$

Concerning the evolution of the $Y(\xi, \Omega)$ function with $\Omega$ for given values of $n_i$, which is shown in Fig. 1(c), we can observe that these curves present an oscillating behaviour, which is less damped the lower $r_0$ is, i.e., the evolution of $Y(\xi, \Omega)$ is closer to its steady state form $(Y(\xi, \Omega)_{\text{steady state}} = \sin(\Omega))$, see dashed line), the higher $\xi$ is.

4.2. Transition times

Due to the periodical behaviour of the $\sin(\omega t)$ function, it is possible in the appropriate conditions, to obtain the transition time for the reduction process ($\tau_\alpha$), for the reoxidation one ($\tau_R$) or not to obtain either $\tau_\alpha$ nor $\tau_R$. This behaviour has been previously discussed in [16] for electrodes of conventional size ($r_0 \geq 10^{-2}$ cm). In this paper, due to the fact that the expressions for the surface concentrations have been obtained in a compact form which is valid for any value of the electrode radius (see Eqs. (5), (6), and (14)), we will focus our discussion on the evolution of the transition times values from transient to steady state. We will also determine the limit values of $\omega$ and of the electrode radius, $r_0$, for which the steady state can be reached.

If, for simplicity, we first consider that only oxidised species O is initially in the solution, i.e., $c_O = 0$, the two following possible situations can be distinguished:

(a) The transition time of species O is reached. By making $c_O(r_0, \tau_O) = 0$ in Eq. (5) we obtain:

$$Y(\xi_O, \Omega_\alpha) = \frac{I_d(\infty)}{I_0}$$  \hspace{1cm} (30)

with

$$\Omega_\alpha = \omega \tau_O,$$  \hspace{1cm} (31)

$$\xi_O = \frac{2\sqrt{D_O \tau_O}}{r_0}$$  \hspace{1cm} (32)

Therefore, $\tau_O$ exists if the ratio $I_0/I_d(\infty) > I_d/I_d(\infty)_{\text{min}}$, being:

$$\frac{I_0}{I_d(\infty)}_{\text{min}} = \frac{1}{Y(\xi_O, \Omega)_{\text{max}}},$$  \hspace{1cm} (33)
where $Y(\xi_O, \Omega_{\text{max}})$ is the absolute maximum, i.e., the first maximum, of the $Y(\xi_O, \Omega)$ function for a given $\xi_O$ value (see Fig. 1(c)).

In Fig. 2, we have plotted the variation with time of the dimensionless alternating applied current, $I(t)/I_0 = \sin(\omega t)$, with $\omega = 1$ s$^{-1}$ (Fig. 2(a)), the theoretical evolution of the surface concentrations of the species O and R (Fig. 2(b)), and the corresponding potential–time ($E(t)$) curve (Fig. 2(c)), when this current is applied to two electrodes of different radius with a constant value of $I_0/I_d(\infty)$. Solid lines in Fig. 2(b) and (c) correspond to the variation of $c_O(r_0, t)/c^*_O$ and $c_R(r_0, t)/c^*_O$ and to the $E(t)$ curve for an electrode radius $r_0 = 2 \times 10^{-4}$ cm, respectively, under conditions in which $\tau_O$ is reached. In these figures, $\tau_O$ is given by the interception of the $c_O(r_0, t)/c^*_O$ line with the time axis and is reached before the $\sin(\omega t)$ function reaches its maximum value (see Fig. 2(a)). According to Eq. (30) for the transition time of O species, it is clear that the smaller the electrode radius is, the smaller the value of $I_0/I_d(\infty)$ necessary to reach the transition time of species O, $\tau_O$ (see Fig. 1(c)).

![Diagram](image)

When we are close to the steady state, Eq. (30) becomes $\sin(\Omega_{\tau_O}) = I_d(\infty)/I_0$, and the expression for $\tau_O$ takes the explicit form:

$$\tau_O^{\text{ss}} = \frac{1}{\omega} \arcsin \left( \frac{I_d(\infty)}{I_0} \right).$$  \hspace{1cm} (34)

(b) When Eqs. (30), or (34) are not fulfilled, i.e., when $\tau_O$ does not exist, the transition time of the reduced species $\tau_R$ is always reached after the alternating current changes in sign and $c_R(r_0, t) = 0$. So, from Eq. (6) we obtain:

$$Y(\xi_R)_{\tau_R} = 0$$  \hspace{1cm} (35)

with

$$\Omega_{\tau_R} = \omega \tau_R,$$  \hspace{1cm} (36)

$$\xi_R(\tau_R) = \frac{2 \sqrt{D_R \tau_R}}{r_0}.$$  \hspace{1cm} (37)

The dashed lines in Fig. 2(b) and (c) correspond to the variation with time of the surface concentrations of species O and R and of the $E(t)$ responses, respectively, when $\tau_O$ is not reached. In these conditions, $\tau_R$ is given by the interception of the $c_R(r_0, t)/c^*_O$ line with the time axis. Note that under these conditions, the $c_O(r_0, t)/c_O^*$ line never intercepts with the time axis, and that the $c_R(r_0, t)/c^*_R$ line first increases and then decreases until it falls to zero.

It is interesting to point out that whereas at conventional sized electrodes the transition time of the reoxidation process, $\tau_R$, is reached for an anodic value of the applied current (see Fig. 2(a)), when we are close to steady state conditions this occurs when the applied current reverts to be null ($I(t = \tau_R^{\text{ss}}) = 0$) since, under stationary conditions it is fulfilled that (see Eqs. (22) and (35)):

$$\sin(\Omega_{\tau_R}) = 0$$  \hspace{1cm} (38)

with the transition time $\tau_R^{\text{ss}}$ given by:
If the species R is initially present in the solution, \( \zeta_R^* \neq 0 \), three possible situations can be observed, instead of the two previously discussed.

(a) If \( \tau_O \) exists, the situation is identical to that treated above.

If \( \tau_O \) is not reached, then the two following cases are possible:

(b) The transition time for the reoxidation process \( \tau_R \) exists, i.e., by making \( c_R(r_0, \tau_R) = 0 \) in Eq. (6) we obtain:

\[
Y(\zeta_R, \Omega_{\text{rs}}) = -\frac{c_R^e}{c_0^e \Omega_{\text{rs}}} \frac{I_d(\infty)}{I_0},
\]

or

\[
\sin(\omega t_{\text{rs}}) = -\frac{c_R^e}{c_0^e \Omega_{\text{rs}}} \frac{I_d(\infty)}{I_0},
\]

under steady state conditions. And

(c) If \( \tau_O \) does not exist and \( |Y(\zeta_R, \Omega)|_\text{min} < |(c_R^e/c_0^e)I_d(\infty)/I_0| \), with \( Y(\zeta_R, \Omega)|_\text{min} \) being the absolute minimum, i.e., the first minimum of the \( Y(\zeta_R, \Omega) \) function for a given \( \zeta_R \) value (see Fig. 1(c)), \( \tau_R \) is not reached. In this case, a periodic \( E/t \) curve is obtained.

In Fig. 3, we have plotted the evolution of \( \omega t_R \) vs. \( \zeta_{0,R} = 2\sqrt{D_r}/r_0 \), calculated using Eq. (35) for a value of \( I_d/I_d(\infty) = 0.5 \), for different values of \( \omega \). From these curves it can be concluded that, in line with our previous discussion, \( \omega t_R \) tends to \( \pi \) (i.e., to the stationary value, see Eq. (39)), as the electrode radius decreases. This evolution is quicker the lower the value of \( \omega \) is. From this figure, we can calculate the limit values of the electrode radius \( r_0 \) for which we can consider that the relative difference between \( \omega t_R \) and \( [\omega t_R]_{\text{steady state}} = \pi \) is smaller than the 5%, in a similar way to the calculus carried out in Fig. 1(b). Thus we have obtained that, for a value of \( \omega = 0.5 \text{ s}^{-1} \) the limit value of \( r_0 \) is \( 1.1 \times 10^{-3} \text{ cm} \), whereas for \( \omega = 5 \), this limit falls to \( r_0 = 3.5 \times 10^{-4} \text{ cm} \).

4.3. Potential–time and current–potential curves

In Fig. 4(a) and (b), we have plotted the chronopotentiograms (\( E/t \) curves) corresponding to reversible and irreversible electrode processes, respectively, for \( c_R^e = 0 \), when an alternating current of the form \( I(t) = I_0 \sin(\omega t) \) is applied to spherical electrodes of different radii, i.e., different values of the parameter \( \zeta_{0,a} = 2\sqrt{D_r}/r_0 \), \( i = O \) or \( R \), and a fixed value of \( I_d/I_d(\infty) \) in such a way that there is no transition time for the reduction process, \( \tau_O \), and, therefore, the transition time for the reoxidation of \( R \), \( \tau_R \), always exists.
Moreover, under steady state conditions, for a fixed value of time, which must be chosen from the central zone of the $Elt$ curve, the difference between two chronopotentiograms corresponding to an irreversible process and obtained for fixed $I_0/|dE|/|dx|$ and $\omega$ values at microelectrodes of different radius, $r_{0,1}$ and $r_{0,2}$, is constant independently of the value of $\omega$ (see curves for values of $\xi_{0,1} = 20$ and $100 \text{ s}^{-1/2}$ in Fig. 4(b)). The reason for this behaviour is that, for a totally irreversible process under these conditions, this difference is given by (see Eqs. (22) and (28)):

$$\Delta E_{1,2} = E_1(t) - E_2(t) = \frac{RT}{2nF} \ln \frac{r_{0,1}}{r_{0,2}}.$$  \hspace{1cm} (42)

Concerning the $I/E$ curves shown in Fig. 5, they clearly show two branches – one ascending for values of $\omega t < (\pi/2)$, and the other descending for values of $\omega t > (\pi/2)$, which takes negative values for $\omega t > \pi$. All these curves present a maximum value which corresponds to the highest current applied $I(t) = I_0$.

From these figures, it can be seen that when the electrode radius decreases (i.e., when we approach to the steady state), the reversible $I/E$ curves (Fig. 5(a)) tend to be superimposable, i.e., independent of the electrode radius. For instance, the potential of the maximum current is shifted only about $3 \text{ mV}$ from the case corresponding to a microelectrode of radius $r_0 = 10^{-4} \text{ cm}$ ($\xi_{0,1} = 20 \text{ s}^{-1/2}$), to that corresponding to a microelectrode of radius $r_0 = 2 \times 10^{-5} \text{ cm}$ ($\xi_{0,1} = 100 \text{ s}^{-1/2}$). This fact can be explained by taking into account that the expression for the potential corresponding to the maximum current applied ($I(t) = I_0$) under steady state conditions does not depend on $r_0$ (see Eqs. (22) and (27) with $c_R^0 = 0)$:

$$E_{\text{Max}}^{\text{rev}} = E_0 + \frac{RT}{nF} \ln \left( \frac{1 - r_0^2}{\ell} \frac{I_0}{R} \right). \hspace{1cm} (43)$$

In the case corresponding to irreversible processes (Fig. 5(b)), the influence of the electrode radius on the $I/E$ curves is much more notorious than in the reversible case, with these curves being shifted to more negative potentials as $r_0$ decreases and never becoming superimposable. In this sense, the shift observed in the $I/E$ curves from the response obtained in a microelectrode of radius $r_0 = 10^{-4} \text{ cm}$ ($\xi_{0,1} = 20 \text{ s}^{-1/2}$), to the case corresponding to a microelectrode of radius $r_0 = 2 \times 10^{-5} \text{ cm}$ ($\xi_{0,1} = 100 \text{ s}^{-1/2}$) is of $85 \text{ mV}$. For $k^0 = 10^{-4} \text{ cm s}^{-1}$, $z = 0.5$ and $D_0 = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The reason for this shift lies in the influence of the electrode radius on these curves through the parameter $\chi = (k^0 r_0/D_0)$ (see Eq. (28)). As in the reversible case, it is very simple to obtain the expression of the potential corresponding to the maximum current applied under steady state conditions, which is given by (see Eq. (28)):
\[ E_{\text{rev}}^\text{diff} = E_\text{M}^\text{ox} + \frac{RT}{znF} \ln \chi + \frac{RT}{znF} \ln \left( \frac{1 - I_0}{I_0} \frac{l_0}{l_0(\infty)} \right). \] (44)

From Eq. (44) it can be seen that for an irreversible process under steady state conditions the difference between the potential of the maximum current corresponding to two spherical electrodes of radius \( r_{0.1} \) and \( r_{0.2} \) for a fixed value of \( I_0/I_0(\infty) \) is given by \( \Delta E = (RT/znF) \ln \left( r_{0.1}/r_{0.2} \right) \), whereas for a reversible charge transfer this difference must be zero (see Eq. (43)).

It can be also observed on the reversible and totally irreversible \( I/E \) curves of Fig. 5 that both ascending and descending branches become superimposable and that the anodic zone of the descending branch tends to disappear as the electrode radius decreases. This last fact can be explained by taking into account that the final part of the anodic zone of the \( I/E \) curves corresponds to current values close to the transition time \( \tau_R \) of the reduced species, \( I_0 \sin(\omega t) \), which, according to Eq. (35), is reached when \( Y(s) = 0 \). This condition corresponds to a negative value of the applied current (\( \sin(\omega t) < 0 \)) when conventional sized electrodes are considered, whereas under steady state conditions \( \tau_R \) is reached when \( \sin(\omega t) = 0 \), i.e., at null applied current (see Eqs. (24), (36), and (38)). This fact constitutes an additional criteria for distinguishing, through a mere visual inspection of the \( I/E \) curve whether a stationary response has been reached.

### 4.4. Experimental results and discussion

We have studied the reversible oxidation of the 10 mM ferrocene + 0.25 M PF₆TBA/CH₃CN system and the totally irreversible reduction of 10 mM FeCl₃·6H₂O + 0.5M K₂C₂O₄·H₂O system at gold microdisc electrodes of different radii in order to show qualitatively the conditions under which the steady state can be reached. We will not do a quantitative verification of our results because the equivalence between the chronopotentiometric behaviour of microdiscs and spherical microelectrodes has not yet been clearly established [3,23]. We have also studied the reversible reduction of the 10 mM FeCl₃·6H₂O + 0.25 M K₂C₂O₄ (pH 4.40) system and the totally irreversible reduction of the 10 mM CrCl₃·6H₂O + 0.5 M NaClO₄ system at a SMDE (spherical electrode) in order to show how the electrode sphericity affects the response of the different electrode processes, and to determine kinetic and thermodynamic parameters of these experimental systems from the analysis of their transient responses.

Figs. 6 and 7 show the experimental \( E/I \) and \( I/E \) curves, respectively, obtained for the reversible oxidation of the 10 mM ferrocene + 0.25 M PF₆TBA/CH₃CN system (Figs. 6(a) and 7(a)), and for the totally irreversible reduction of the 10 mM FeCl₃·6H₂O + 0.5 M K₂C₂O₄·H₂O system (Figs. 6(b) and 7(b)), when we apply an alternating current of the form \( R(t) = -I_0 \sin(\omega t) \), \( \omega = 1 \text{ s}^{-1} \) (a) and \( \omega = 2 \text{ s}^{-1} \) (b), to the 10 mM ferrocene + 0.25 M PF₆TBA/CH₃CN system and to the 10 mM FeCl₃·6H₂O + 0.5 M K₂C₂O₄ system, respectively, at gold disc microelectrodes of radii (in cm) \( r_0 = 1.25 \times 10^{-3} \) (solid lines), \( 5 \times 10^{-4} \) (dashed lines) and \( 2.5 \times 10^{-4} \) cm (dotted lines). \( I_0/I_0(\infty) = 0.75, T = 293 \text{ K} \).

Fig. 6. Experimental \( E/I \) curves corresponding to the application of an alternating current of the form \( R(t) = -I_0 \sin(\omega t) \), \( \omega = 1 \text{ s}^{-1} \) (a) and \( \omega = 2 \text{ s}^{-1} \) (b), to the 10 mM ferrocene + 0.25 M PF₆TBA/CH₃CN system and to the 10 mM FeCl₃·6H₂O + 0.5 M K₂C₂O₄ system, respectively, at gold disc microelectrodes of radii (in cm) \( r_0 = 1.25 \times 10^{-3} \) (solid lines), \( 5 \times 10^{-4} \) (dashed lines) and \( 2.5 \times 10^{-4} \) cm (dotted lines). \( I_0/I_0(\infty) = 0.75, T = 293 \text{ K} \).
conditions as in Fig. 6.

respectively, at gold disc microelectrodes of different radii. Other irreversible reduction of 10 mM FeCl₃ alternating current of the form $I(t) = I_0 \sin(\omega t)$ (a) and

These facts lead us to conclude that we are close to decreasing, in agreement with the theoretical curves of Fig. 4(b). It can be also seen that they do not present a shoulder around the zone of null current applied. These facts lead us to conclude that we are close to the steady state conditions.

In Fig. 7, we have plotted the experimental $I/E$ curves for the reversible ferrocene + PF₆TBA/CH₃CN system (Fig. 7(a)) and for the irreversible FeCl₃ + K₂C₂O₄ system (Fig. 7(b)) obtained from the $E/t$ curves shown in Fig. 6. These curves present ascending and descending branches, with latter taking negative values for values of $\omega t > \pi$, in line with the theoretical $I/E$ curves of Fig. 5. In all the experimental responses of Fig. 7(a) distortion can be observed in the initial and final part of the same, which is probably due to capacitative effects. This distortion has its origin in the low current at the beginning and at the end of the experiment, since an alternat-

ing current of the form $I(t) = I_0 \sin(\omega t)$ has a null value at $t = 0$ and at $t = \tau_R$ under steady state conditions (see Eq. (38)). However, the central part of the $I/E$ curves, from which we obtain thermodynamic and kinetic information of the charge transfer processes, is barely affected by these effects.

In the case of the $I/E$ curves corresponding to the the reversible ferrocene + PF₆TBA/CH₃CN system (Fig. 7(a)), it can be seen that the potentials of the maximum current applied is shifted 4 mV from the highest ($r_0 = 1.25 \times 10^{-3}$ cm) to the smallest microelectrode ($r_0 = 2.5 \times 10^{-4}$ cm). In fact, the $I/E$ curves corresponding to the two smallest microelectrodes are practically superimposable, which indicates that under these conditions the response is practically stationary (compare Figs. 7(a) and 5(a)). It is interesting to point out that for this species, $\xi_{0, \text{ferrocene}} = 2\sqrt{D_{\text{ferrocene}}}/r_0 \simeq 38.0$ s⁻¹/² for the smallest electrode.

In Fig. 7(b), we have plotted the experimental $I/E$ curves for the irreversible FeCl₃ + K₂C₂O₄ system, and it can be seen that these responses are strongly affected by the electrode radius, and are shifted towards more negative potentials when $r_0$ decreases. Thus, the potential of the maximum current applied suffers a displacement of 124 mV from the highest ($r_0 = 1.25 \times 10^{-3}$ cm) to the smallest ($r_0 = 2.5 \times 10^{-4}$ cm) microelectrode. Moreover, the negative part of the descending branch of the $I/E$ curves tends to disappear and both ascending and descending branches tend to be superimposable as $r_0$ decreases, in such a way that we can consider that the response evolves towards a stationary behaviour. In this case, for the smallest electrode, $\xi_{0, \text{Fe}^{3+}} = 2\sqrt{D_{\text{Fe}^{3+}}}/r_0 \simeq 21.5$ s⁻¹/². Note that the different $\xi_{0, \text{ferrocene}}$ and $\xi_{0, \text{Fe}^{3+}}$ values could be the reason why in the totally irreversible case (reduction of Fe³⁺) steady state has not been reached yet.

In Fig. 8(a) and (b), we have plotted the measured potential vs. time, $E/t$ curves, and the measured potential vs. the applied current, $E/I$ curves, respectively, obtained when an alternating current of the form $I(t) = -I_0 \sin(\omega t)$, $\omega = 1$ s⁻¹, is applied to a microdisc gold electrode of radius $r_0 = 2.5 \times 10^{-4}$ cm, with two different values of $I_0/I_0(\infty) = 0.75$ (solid lines) and 2 (dashed lines), for the reversible oxidation of the ferrocene + PF₆TBA/CH₃CN system. Fig. 8(a) clearly shows that, whereas with the highest value of $I_0/I_0(\infty)$ the transition time for the oxidised species, $\tau_O$, is reached, with the smallest one, $I_0/I_0(\infty) = 0.75$, $\tau_R$ is reached instead of $\tau_O$. In the abscissa of Fig. 8(b), we have plotted the corresponding value of the applied current for each value of time of curves in Fig. 8(a), in such a way that, while in the abscissa in Fig. 8(a), $0 \leq t \leq \pi$, in the abscissa in Fig. 8(b), $0 \leq I(t) = I_0 \sin(\omega t) \leq I(t)$.

These figures show several indications that we are approximately under steady state conditions:
– From the E/t curves in Fig. 8(a) it can be observed that the transition times of the oxidised, \( \tau_O \), and reduced, \( \tau_R \), species approximately obey Eq. (34) \( \tau_O = 0.57 \, s \approx (1/\omega) \arcsin(\tau_d(\infty)/I_0) \), for \( \omega = 1 \, s^{-1} \) and \( I_d/I_d(\infty) = 2 \), and Eq. (39) \( \tau_R = 3.20 \approx \pi/\omega \), for \( \omega = 1 \, s^{-1} \), respectively, which corresponds to steady state conditions.

– Concerning the E/I curves in Fig. 8(b), they are superimposable in the central zone, which is scarcely affected by capacitative effects, although they have been obtained in very different experimental conditions (reaching \( \tau_O \) or \( \tau_R \) depending on \( I_0/I_d(\infty) \) value). This independence of the E/I curve with the current amplitude, \( I_0 \), of the current time function applied is characteristic of a stationary response [1].

– From the E/I curves in Fig. 8(b), we can observe that the steady state limit values of the current axis correspond to \( I(\tau_O)/I_d(\infty) \rightarrow 1 \) when \( \tau_O \) exists (dashed line, see Eq. (34)), and to \( I(\tau_R)/I_d(\infty) \rightarrow 0 \) when \( \tau_R \) exists (solid line, see Eq. (38)).

Fig. 9. Experimental E/t curves corresponding to the application of an alternating current of the form \( I(t) = I_0 \sin(\omega t) \) to the 10 mM FeCl₃·6H₂O + 0.25 M K₂C₂O₄ (pH 4.40) system (a), and to the 10 mM CrCl₃·6H₂O + 0.5 M NaClO₄ system (b), at a SMDE. The values of the electrode radii \( r_0 \) (in cm) are: 1.912 \( \cdot 10^{-2} \) (solid lines), 1.644 \( \cdot 10^{-2} \) (dashed lines) 1.480 \( \cdot 10^{-2} \) (dashed-dotted lines) and 1.258 \( \cdot 10^{-2} \) cm (dotted lines) cm. \( I_d/I_d(\infty) = 2 \), \( \omega = 2 \, s^{-1} \). \( T = 293 \, K \).

Figs. 9 and 10 show the transient E/t and I/E responses, respectively, obtained for the application of an alternating current of the form \( I(t) = I_0 \sin(\omega t) \) to the reversible 10 mM FeCl₃·6H₂O + 0.25 M K₂C₂O₄ (pH 4.40) system (Figs. 9(a) and 10(a)), and to the totally irreversible 10 mM CrCl₃·6H₂O + 0.5 M NaClO₄ system (Figs. 9(b) and 10(b)) at a SMDE. These curves have been obtained for the following radius values (in cm): 1.910 \( \times 10^{-2} \), 1.644 \( \times 10^{-2} \), 1.480 \( \times 10^{-2} \) and 1.258 \( \times 10^{-2} \), with \( I_d/I_d(\infty) = 2 \) and \( \omega = 2 \, s^{-1} \). From the reversible and irreversible chronopotentiograms shown in Fig. 9, it can be observed that the values obtained for \( \tau_B \) are in all cases higher than that corresponding to the steady state, \( \pi/\omega \), a fact that indicates that the response is not stationary. There are several features in the E/t and I/E curves which also lead us to this conclusion. Thus, the reversible E/t curves in Fig. 9(a) are not superimposable and they are affected by the electrode radius decrease, being shifted about 16 mV from the smallest to the largest electrode, contrary to what
occurs under steady state conditions (compare with Fig. 6(a)). Moreover, the irreversible Elt curves in Fig. 9(b) are also shifted with the decrease of \( r_0 \) and they clearly show a shoulder which appears around the times at which the applied current is null. This characteristic shoulder disappears when the steady state is reached (see Fig. 4(b)).

In the case of the I/E curves of Fig. 10(a) (reversible) and Fig. 10(b) (totally irreversible), we can see that an anodic response can be seen in both cases although it reaches its greatest absolute value at similar potential values to the cathodic response if the process is reversible (Fig. 10(a)), and at much more positive potentials if the process behaves as totally irreversible (Fig. 10(b)). Moreover, the effect of the electrode radius on totally irreversible I/E curves (Fig. 10(b)) is less notorious than in conditions close to the steady state.

From all these features we can conclude that these experimental I/E and Elt curves are transient and, therefore, we must use the potential–time relationships given in Eqs. (27) and (28) to carry out an accurate determination of the thermodynamic and kinetic parameters of reversible and totally irreversible processes.

Thus, for a reversible electrode process we can rewrite Eq. (27) for the Elt curves when \( c_R^i = 0 \) in the following way:

\[
E(t) = O^{rev} + P^{rev} \ln g^{rev},
\]

where

\[
O^{rev} = E_0^{o} + \frac{RT}{nF} \ln \frac{1}{\gamma^2},
\]

\[
P^{rev} = \frac{RT}{nF},
\]

\[
g^{rev} = \frac{1 + \frac{I_0}{I_{0i}(\infty)} Y(\Omega, \xi_O) + \pm \frac{I_0}{I_{0i}(\infty)} Y(\Omega, \xi_R)}{\frac{R}{D}}
\]

with the upper sign in Eq. (48) referring to the positive values of the applied current and the lower sign to the negative ones. Thus, by plotting the experimental values of \( E(t) \) vs. \( \ln g^{rev} \) we obtain two straight lines for \( I(t) > 0 \) and \( I(t) < 0 \), which must be coincident and whose intercept gives us the value of \( E_0^{o} + RT/nF \ln 1/\gamma^2 \) [16]. We have applied this method to the experimental Elt curves of Fig. 9(a) corresponding to the 10 mM FeCl₃·6H₂O + 0.25 M K₂C₂O₄ (pH 4.40) system and, by supposing that the diffusion coefficient of both oxidised and reduced species are practically equal, we have obtained the following value for the formal potential, \( E_0^{o} + RT/nF \ln 1/\gamma^2 = -0.234 \pm 0.001 \text{ V vs. Ag|AgCl|KCl 1 M} \), which is in agreement with the literature [17,24].

In the case of a totally irreversible process, it is possible to distinguish between the two following situations:

(a) \( I(t) > 0 \). In this case Eq. (26) for the Elt curve becomes:

\[
E(t) = O^{cat} + P^{cat} \ln g^{cat},
\]

where

\[
O^{cat} = E_0^{o} + \frac{RT}{2nF} \ln \frac{k_{0i} r_0}{D_A},
\]

\[
P^{cat} = \frac{RT}{2nF},
\]

\[
g^{cat} = \frac{1 - \frac{I_0}{I_{0i}(\infty)} Y(\Omega, \xi_O)}{\frac{R}{D} \sin (\omega t)}
\]

(b) \( I(t) < 0 \). Eq. (26) for the Elt curve can be written as

\[
E(t) = O^{anod} + P^{anod} \ln g^{anod},
\]
where
\[ O^{\text{mod}} = E^{\text{th}} - \frac{RT}{(1 - z)nF} \ln \frac{k^{\text{th}}r_0}{D_0}, \]  
(54)
\[ P^{\text{mod}} = -\frac{RT}{(1 - z)nF}, \]  
(55)
\[ g^{\text{mod}} = \mu + \gamma_2 \frac{k_4}{r(t)} Y(\Omega, \xi_i) \frac{-\mu_0}{1 - \mu_0} \sin (\theta t), \]  
(56)

By plotting \( E \) vs. \( \ln g^{\text{mod}} \) for \( I(t) > 0 \) (Eq. (49)) and \( E \) vs. \( \ln g^{\text{mod}} \) for \( I(t) < 0 \) (Eq. (53)), we have to obtain two straight lines from whose slopes and intercepts accurate determination of the thermodynamic and kinetic parameters of an irreversible process can be carried out [16].

This method has been applied to the Elt curves of CrCl$_2$·6H$_2$O + NaClO$_4$ system shown in Fig. 9(b), obtaining \( x = 0.493 \pm 0.004 \) and \( (1 - x) = 0.549 \pm 0.008 \) from \( P^{\text{cat}} \) and \( P^{\text{pan}} \), respectively (see Eqs. (51) and (55)), and \( \log (k_0/\text{cm s}^{-1}) = -4.81 \pm 0.05 \) and \( E^{\text{th}} = -0.658 \pm 0.004 \) V vs. Ag/AgCl/KCl 1 M, by combining equations for \( O^{\text{cat}} \) and \( O^{\text{pan}} \) (see Eqs. (50) and (54)). The values obtained are in agreement with those previously reported [16].

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Appendix A

The \( Y(\xi_i, \Omega) \) function that appears in the expressions for the surface concentrations (Eqs. (5) and (6)), can be written as:
\[ Y(\xi_i, \Omega) = \sum_{n=0}^{\infty} (-1)^n \Omega^{2n+1} (2n + 1)! X_n(\xi_i), \]  
(A.1)
with
\[ X_n(\xi_i) = \sum_{j=0}^{\infty} (-1)^j \frac{\xi_i^{j+1}}{P_{2n+3+j}}, \]  
(A.2)

Taking into account that
\[ \exp \left( \frac{\xi_i}{2} \right) \text{erfc} \left( \frac{\xi_i}{2} \right) = p_0 \sum_{j=0}^{\infty} \frac{(-1)^{j+1}}{n!} \frac{\xi_i^{j+1}}{P_{2n+3+j}}, \]  
(A.3)
we found, after the appropriated manipulations, the following, more compact, form of the \( X_n(\xi_i) \) series:
\[ X_n(\xi_i) = \frac{2(2n + 1)!}{(\xi_i/2)^{2n+2}} \left[ -\frac{1}{2} \left( \frac{\xi_i}{2} \right) \text{erfc} \left( \frac{\xi_i}{2} \right) - \frac{1}{2} \sum_{j=0}^{\infty} \frac{\xi_i^{j+1}}{j! P_{2n+3+j}} \right], \]  
(A.4)
in such a way that Eq. (A.1) can be rewritten as:
\[ Y(\xi_i, \Omega) = \sum_{n=0}^{\infty} (-1)^n \phi_i^{2n+1} \left[ -\left( \frac{\xi_i}{2} \right) \text{erfc} \left( \frac{\xi_i}{2} \right) - \sum_{j=0}^{\infty} \frac{\xi_i^{j+1}}{j! P_{2n+3+j}} \right], \]  
(A.5)
where
\[ \phi_i = \frac{4\Omega}{\xi_i}. \]  
(A.6)

Moreover, the new infinite series which appears in Eq. (A.5) can be written in the following, more compact, forms:
\[ \sum_{n=0}^{\infty} (-1)^n \phi_i^{2n+1} = \frac{\phi_i}{1 + \phi_i}, \]  
(A.7)
\[ \sum_{n=0}^{\infty} (-1)^n \phi_i^{2n+1} \sum_{j=0}^{\infty} \frac{\xi_i^{j+1}}{j!} = \frac{\sin(\Omega)}{1 + \phi_i} + \phi_i \cos(\Omega), \]  
(A.8)
\[ \sum_{n=0}^{\infty} (-1)^n \phi_i^{2n+1} \sum_{j=0}^{\infty} \frac{\xi_i^{j+1}}{j! P_{2n+3+j}} = \frac{\xi_i/2 \phi_i}{1 + \phi_i} G_c - \frac{\xi_i/2 \phi_i}{1 + \phi_i} G_s, \]  
(A.9)
being
\[ G_c(\Omega) = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n}}{(2n + 1)! P_{2n+1}}, \]  
(A.10)
\[ G_s(\Omega) = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n + 1)! P_{2n+3}}. \]  
(A.11)

So, by taking into account Eqs. (A.7)-(A.9), the \( Y(\xi_i, \Omega) \) function can be rewritten in the following, totally compact, form with respect the \( \xi_i \) parameter:
\[ Y(\xi_i, \Omega) = \frac{1}{1 + \phi_i} \left[ -\phi_i \exp \left( \frac{\xi_i}{4} \right) \text{erfc} \left( \frac{\xi_i}{2} \right) + \frac{\phi_i \cos(\Omega) - \xi_i \phi_i G_c(\Omega) + \xi_i \phi_i^2 G_s(\Omega)}{1 + \phi_i^2} \right]. \]  
(A.12)
In order to carry out accurate numerical computations of \(Y(n, X)\) function for large values of \(n\) (i.e., for ultramicroelectrodes), it is necessary to resort to the asymptotic solution for the first addend in the above equation. This term, \(\exp(\xi_i/2)^2 \text{erfc}(\xi_i/2)\), is directly related to the Koutecký function [25], which is defined by

\[
F(x) = \sqrt{\pi} x \exp\left(\frac{x^2}{2}\right) \text{erfc}\left(\frac{x}{2}\right),
\]

whose asymptotic develop in series of powers of the argument, \(x\), is given by [25]:

\[
F(x) = 1 + \sum_{j=1}^{\infty} (-1)^j \left( \prod_{i=1}^{j} p_i \right) (2x)^{-j}.
\]

For \(x > 5.0\).

References