Review

Analytical solutions for fast and straightforward study of the effect of the electrode geometry in transient and steady state voltammetries: Single- and multi-electron transfers, coupled chemical reactions and electrode kinetics

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ABSTRACT

We survey recently-reported, analytical solutions for the study of simple and complicated charge transfer reactions by means of any voltammetric technique with electrodes of very different geometries under conditions where the mass transfer takes place only by diffusion, that is, in fully-supported media where migration can be neglected. Under transient conditions, expressions are reported for one-electron and multi-electron reversible transfers, electrode reactions coupled to homogeneous chemical equilibria and the first-order catalytic mechanisms with electrodes of any geometry. The steady-state voltammetric response of the above systems will also be considered at submicro- and nanoelectrodes of very different shapes and arrays. Also, a universal approach to the steady-state voltammetry of sluggish electron transfer processes is presented. Finally, solutions for ion transfer processes across (sub)micrometric liquid|liquid interfaces is discussed.

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1. Introduction

Having at our disposal mathematically analytical equations and solutions for physico-chemical and electrochemical problems is essential for multiple reasons. First, once no approximations are employed for their deduction, analytical solutions provide us with rigorous description of the system in the full range of values of experimental variables. Also, the behavior of the system can be analyzed and predicted directly from closed-form expressions. This enables the identification of the key variables and their influence on the electrochemical response as well as of particular and limit cases and the conditions under which these can be attained (such as steady state conditions). Finally, generally speaking, analytical expressions are easier to compute than numerical methods and the calculations are less time-consuming and computer-demanding. Indeed, analytical solutions are employed to test the accuracy of numerical simulations [1–7].

In recent years we have reported analytical expressions for the response of fundamental electron transfer processes in multipulse voltammetric techniques under transient and steady state regimes [8–17]. Particular attention has been paid to the most widely employed methods (namely, cyclic voltammetry [18,19] and square wave voltammetry [20]) and to the use of disk and hemispherical microelectrodes. The former are ubiquitous in experimental studies given their easy fabrication and cleaning and the reduction of distorting effects with respect to macroelectrodes [18,19,21–26]. However, the modeling of the electrochemical response at microdisks is not straightforward and it has been almost exclusively performed by means of sophisticated numerical methods.

Within the above context, the aim of this work is to review simple, analytical solutions such that any electrochemist can get insight into methods. Most exclusively performed by means of sophisticated numerical simulations [8–17].

2. Voltammetric response under transient conditions

2.1. Nernstian one-electron transfers

2.1.1. Equal diffusion coefficients

Let us consider the case of a fast one-electron transfer where both electroactive species are stable within the timescale of the measurements and they do not take part in chemical reactions in solution (the so-called E mechanism):

$$O + e^- \rightarrow R$$

(Scheme I)

where $E^0$ is the formal potential of the redox couple O/R. Taking into account that in most electrochemical experiments, semi-infinite diffusion is the only active mass transport mechanism and that in conventional solvents the diffusion coefficients of O and R are usually very similar ($D_O = D_R = D$), the variation of the species concentrations when applying a potential-controlled perturbation ($E(t)$) is described by Fick’s second law:

$$\frac{\partial C_O}{\partial t} = 0 \quad \frac{\partial C_R}{\partial t} = 0$$

(1)

with the following boundary value problem corresponding to a reversible electrode reaction:

$$t < 0, \quad q > q_{\text{surface}}$$

$$t > 0, \quad q < \infty$$

(2)

$$c_O(q, t) = c_O^0, \quad c_R(q, t) = c_R^k$$

$$C_O(q_{\text{surface}}) = c_O^k(q_{\text{surface}}) \exp \left( \frac{F}{RT} (E - E^0) \right)$$

(4)

where $\delta$ is the diffusion operator given in Table 1, $q_{\text{surface}}$ refers to the values of the spatial coordinates ($q$) at the surface of the electrode and $q_k$ is the spatial coordinate normal to the electrode surface.

From Eqs. (1)–(3), it is concluded that when the diffusion coefficients of the participating species are equal, the total concentration of electroactive species does not vary with time and it is the same at any point in solution:

$$c_O(q, t) + c_R(q, t) = c_O^0 + c_R^k \quad \forall q, \ t.$$  

(5)

Note that Eq. (5) holds independently of the reversibility of the electron transfer process and the geometry of the electrode (i.e., the form of the diffusion operator $\delta$). Furthermore, when the electrode reaction is reversible, it can be deduced from Eqs. (4) and (5) that the surface concentrations are time-independent and their values are defined by the value of the applied potential, $E_b$, for as follows:

$$c_O(q_{\text{surface}}) = c_O^{k, s} = \frac{F}{RT} \left( c_O^0 + c_R^k \right)$$

$$c_R(q_{\text{surface}}) = c_R^{k, s} = \frac{F}{RT} \left( c_O^0 + c_R^k \right)$$

(6)

where:

$$\eta_k = \frac{F(E - E^0)}{RT}$$

(7)

This is valid for typical time-scales of the perturbation ($< 10^2$) and volume of electrochemical cells (much larger than the depletion layer). Otherwise, mass transport by convection in very long experiments and thin layer effects must be considered, respectively.
Expressions for the function \( f_c(t_{an}, q_c) \) for the most common electrode geometries, \( q \) and \( t \) are the spatial and time coordinates, respectively, and \( q_c \) the characteristic dimension of the electrode. The expressions for \( f_c(t_{an}, q_c) \) are rigorous in the case of macro- and (hemi)spherical electrodes [18,21,25] while empirical for disk (0.6% accuracy [37]), bands (1.3% accuracy [38]) and cylinders (1.3% accuracy [38]).

Table 1

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Diffusion operator ( \hat{b} )</th>
<th>Function ( f_c(t_{an}, q_c) )</th>
</tr>
</thead>
</table>
| Macroelectrodes    | \[
\dot{c} = \frac{\partial}{\partial \tau} - \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \partial \tau} \right) \] | \[
\frac{1}{\sqrt{\pi D_{tot}}} \exp \left( -\frac{t}{\sqrt{D_{tot}}} \right)
\] |
| (Hemi)spherical (radius \( r \)) | \[
\dot{c} = \frac{\partial}{\partial \tau} - \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \partial \tau} \right) \] | \[
\frac{1}{\sqrt{\pi D_{tot}}} \exp \left( -\frac{t}{\sqrt{D_{tot}}} \right)
\] |
| Cylindrical (radius \( r \), length \( l \)) | \[
\dot{c} = - \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \partial \tau} \right) \] | \[
\frac{1}{\sqrt{\pi D_{tot}}} \exp \left( -\frac{t}{\sqrt{D_{tot}}} \right)
\] |
| Band (height \( w \), length \( l \)) | \[
\dot{b} = - \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \partial \tau} \right) \] | \[
\frac{1}{\sqrt{\pi D_{tot}}} \exp \left( -\frac{t}{\sqrt{D_{tot}}} \right)
\] |
| Disk (radius \( r \)) | \[
\dot{b} = - \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \partial \tau} \right) \] | \[
\frac{1}{\sqrt{\pi D_{tot}}} \exp \left( -\frac{t}{\sqrt{D_{tot}}} \right)
\] |

Relationships [5] and (6) offer two simple and rigorous criteria for a first validation of in-house electrochemical simulations whatever the voltammetric technique and the electrode geometry (Eqs. (5) and (6)) and even regardless of the electron transfer kinetics (Eq. (5)).

Given that Fick’s second law is subject to constant initial (Eq. (2)) and limiting (Eqs. (2) and (6)) conditions, the influence of time and the electrode geometry on the concentration is given by the function \( f_c(t_1, q_c) \) for the electrode geometry ‘G’ (see Table 1) and it can be separated from the influence of the applied potential \( g(E) \) whatever the shape and size of the electrode. As will be discussed below, the function \( f_c(t_1, q_c) \) is associated with the diffusion phenomenon and it can be directly related to the corresponding mass transport coefficient (Eq. (16)) and the thickness of the depletion layer (Eq. (18)).

Upon the application of a single-potential step \( E \), over the period \( 0 \leq t_1 \leq \tau_1 \), the current can be written as follows independently of the electrode geometry:

\[
\frac{f^{(1)}}{FAcD} = \left( \frac{\partial c_0}{\partial q} \right)_{q=q_{an}} \quad \text{g}(E_1) \quad f_c(t_1, q_c) \tag{8}
\]

with \( A_c \) being the area of the electrode of a given geometry ‘G’. Note that, in the case of non-uniformly accessible electrodes (i.e., \( G = \) disks, bands), the surface flux of the electroactive species is not uniform over the electrode surface and so \( \left( \frac{\partial c_0}{\partial q} \right)_{q=q_{an}} \) in Eq. (8) and hereafter has an average character for such geometries.

The function of potential is independent of the electrode geometry and it is given by:

\[
g(E_1) = c_0 - c_0^{(1),s}
\]

where \( c_0^{(1),s} \) is given by Eq. (6) with \( p = 1 \). For a given electrode, the form of \( f_c(t_1, q_c) \) is independent of the applied potential and therefore it is identical to that in the expression for the corresponding limiting current (Table 1 includes \( f_c(t_1, q_c) \) for the most common electrode geometries):

\[
\frac{f^{(1)}}{FAcD} = g(E_1) f_c(t_1, q_c) = g(E_1) \frac{f^{(1)}_{\text{diff.cat}}}{FAcD} \tag{10}
\]

where \( f^{(1)}_{\text{diff.cat}} \) is the cathodic limiting current (see below). Finally, the current can be written as:

\[
\frac{f^{(1)}}{FAcD} = \left( c_0 - c_0^{(1),s} \right) f_c(t_1, q_c) \tag{11}
\]

From Eqs. (10) and (11) one can also demonstrate that the surface concentrations of the electroactive species can be expressed in the simple way:

\[
\begin{align*}
c_0^{(p),s} &= c_0 \left( 1 - \frac{f^{(1)}}{f^{(1)}_{\text{diff.cat}}} \right) \\
c_0^{(p),a} &= c_0 \left( 1 - \frac{f^{(1)}}{f^{(1)}_{\text{diff.an}}} \right)
\end{align*}
\]

where \( f^{(1)}_{\text{diff.cat}} \) and \( f^{(1)}_{\text{diff.an}} \) are the cathodic and anodic limiting currents, respectively:

\[
\begin{align*}
f^{(1)}_{\text{diff.cat}} = c_0 f_c(t_1, q_c) \\
f^{(1)}_{\text{diff.an}} = c_0 f_c(t_1, q_c)
\end{align*}
\]

such that it is also obtained that, independently of the electrode geometry, the following is fulfilled:

\[
E = E^0 + RT \ln \left( \frac{f^{(1)}_{\text{diff.cat}} - f^{(1)}}{f^{(1)}_{\text{diff.an}}} \right) \tag{14}
\]

Eqs. (10) and (11) can also be written in terms of the mass transport coefficient \( (m_c/cm \ s^{-1}) \) and the thickness of the linear diffusion layer \( (\delta_c/cm) [18,19,28] \). Both magnitudes are of great interest in order to have a quantitative estimation about the efficiency of the mass transfer by diffusion in electrochemical experiments [29,30]. This information is essential for correct analysis of the electrochemical response, appropriate design of simulations and evaluation of the incidence of convection, thin-layer and convergent-diffusion effects as well as of electron transfer and coupled chemical kinetics. With respect to \( m_c \), the limiting currents can be expressed as:

\[
\begin{align*}
f^{(1)}_{\text{diff.cat}} &= m_c \left( c_0 - c_0^{(1),s} \right) \\
f^{(1)}_{\text{diff.an}} &= m_c c_0
\end{align*}
\]

\[
\begin{align*}
f^{(1)}_{\text{diff.cat}} &= m_c c_0 \\
f^{(1)}_{\text{diff.an}} &= m_c c_0
\end{align*}
\]

such that, from Eqs. (13) and (15) the mass transfer coefficient can be related to the time-function \( f_c \) given in Table 1:

\[
m_c = D f_c.
\]
Regarding the Nernst diffusion layer, by taking into account the definition of the concentration surface gradient:

$$\frac{f^{(1)}}{FA_c} = D \left( \frac{\partial c^{(1)}}{\partial x} \right)_{q=q_{\text{surface}}} = D C \frac{c^{(1)}x}{\partial c}$$

(17)

from Eqs. (11) and (16) it is obtained that:

$$\delta_c = \frac{1}{f_c} \frac{D}{m_c}$$

(18)

Noting the linearity of the operators in Fick's second law (see Table 1) and by applying the induction principle, it can be proved that the superposition principle applies at any electrode geometry under the conditions considered in this section, that is, when the surface concentrations of the electroactive species are time-independent. Hence, the current corresponding to the kth potential pulse in an arbitrary sequence of pulses $E_1$, $E_2$, ..., $E_k$ (each of them applied over the interval 0 $\leq t_k$ $\leq \tau_k$) can be calculated from:

$$f^{(k)} = \frac{1}{FA_c D} \sum_{m=1}^{k} \left[ \left( c^{(m-1)}_0 - c^{(m)}_0 \right) f_c(t_{m,k} - q_c) \right]$$

(19)

$$c^{(m)}_0 = C_0 + \sum_{m=1}^{k} \left[ \left( c^{(m)}_0 - c^{(m-1)}_0 \right) f_c(t_{m,k} - q_c) \right]$$

(20)

where:

$$t_{m,k} = \sum_{j=m}^{k} \tau_j + t_k$$

From Eq. (19) the current in any multipulse voltammetric technique can be obtained by specifying the form of the potential-time perturbation (i.e., the values of $E_1$, $E_2$, ..., $E_k$ and $\tau_1$, $\tau_2$, ..., $\tau_k$). The expressions are rigorous in the case of macroelectrodes and (hemi)spherical electrodes and very accurate (less than 1% error [10]) for two-dimensional systems and cylindrical electrodes. Fig. 1 shows a comparison of the theoretical response of a reversible, one-electron transfer process in cyclic voltammetry (CV) and square wave voltammetry (SWV) for microelectrodes of different size (Fig. 1A) and shape (Fig. 1B) under transient conditions. The current density–potential curves at large electrodes (Fig. 1A) coincide since diffusion is predominantly linear and the electrode geometry is irrelevant. As the size of the electrode shrinks, the current density becomes dependent on the electrode size increasing with the efficiency of the mass transport by diffusion: disk > spherical > band > cylindrical. It is also worth noting that under these conditions (i.e., reversible electrode process and equal diffusion coefficients), the geometry of the electrode only affects the magnitude of the voltammetric response though not its position, the wave being centered at the formal potential of the redox couple in all cases. Eventually, when the electrode size is very small and/or the time-scale of the experiment very long, a steady-state response can be attained, as will be considered in Section 3.

In the case of macroelectrodes, (hemi)spherical and cylindrical electrodes it is also possible to obtain rigorous solutions for the concentration profiles of the electroactive species $i=0, R$:

$$c^{(k)}_{i, \text{macro}}(x, t) = c_i^0 - \sum_{m=1}^{k} \left( c^{(m-1)}_i - c^{(m)}_i \right) \text{erfc} \left( \frac{x}{2 \sqrt{D t_{m,k}}} \right)$$

(21)

$$c^{(k)}_{i, \text{sph}}(r, t) = c_i^0 - \frac{1}{r} \sum_{m=1}^{k} \left( c^{(m-1)}_i - c^{(m)}_i \right) \text{erfc} \left( \frac{r - r_0}{2 \sqrt{D t_{m,k}}} \right)$$

(22)

$$c^{(k)}_{i, \text{cyl}}(r, t) = c_i^0 - \frac{1}{r} \sum_{m=1}^{k} \left( c^{(m-1)}_i - c^{(m)}_i \right) \left[ 1 - \frac{2}{r_0} \sum_{n=1}^{m} \exp \left( - \frac{r_0^2}{4 \sqrt{D t_{m,k}}} \right) \right]$$

(23)

where $f_0(x)$ and $J_0(x)$ are the Bessel function of the first kind of order one and zero, respectively, and $\alpha_n$ are the positive roots of $J_0(\alpha_n) = 0$ (see [25,31]).

2.1.2. Unequal diffusion coefficients

There are electrochemical systems where the assumption of equal diffusion coefficients for species O and R is not appropriate. These include electron transfers in room temperature ionic liquids (RTILs) [32–34] and ion transfers between conventional solvents and RTILs or

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$Z_m$</th>
<th>$\Delta Z_p = \sum_{i=1}^{p} Z_n$</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-electron transfer (Scheme I)</td>
<td>$\frac{1}{m} - \frac{1}{m+1}$</td>
<td>$\frac{1}{m} - \frac{1}{m+1}$</td>
<td>$\eta_0 = \frac{1}{m} - \frac{1}{m+1}$</td>
</tr>
<tr>
<td>Multi-electron transfer (Scheme IIa)</td>
<td>$\frac{1}{n} - \frac{1}{n+1}$</td>
<td>$\frac{1}{n} - \frac{1}{n+1}$</td>
<td>$\eta_0 = \frac{1}{n} - \frac{1}{n+1}$</td>
</tr>
<tr>
<td>Two-electron transfer (EE mechanism) (Scheme IIIa)</td>
<td>$\frac{1}{2} - \frac{1}{m}$</td>
<td>$\frac{1}{2} - \frac{1}{m}$</td>
<td>$\eta_0 = \frac{1}{2} - \frac{1}{m}$</td>
</tr>
<tr>
<td>Ladder mechanism (Scheme IV)</td>
<td>$\frac{1}{m} - \frac{1}{m+1}$</td>
<td>$\frac{1}{m} - \frac{1}{m+1}$</td>
<td>$\eta_0 = \frac{1}{m} - \frac{1}{m+1}$</td>
</tr>
<tr>
<td>Catalytic mechanism (Scheme V)</td>
<td>$\frac{1}{m} - \frac{1}{m+1}$</td>
<td>$\frac{1}{m} - \frac{1}{m+1}$</td>
<td>$\eta_0 = \frac{1}{m} - \frac{1}{m+1}$</td>
</tr>
</tbody>
</table>

Table 2 Expressions for the potential-function $Z_m$ corresponding to different reaction mechanisms. Expressions for $\Delta Z_p$ are also given, which appears in the expressions for the steady state response (see Eq. (101) in Section 3) [8–17].
liquid membranes [35]. When dealing with such situations, the problem corresponding to reversible charge-transfer processes becomes:

\[ \dot{c}_i = 0 \quad (i \neq O, R) \]  

and the following is then fulfilled:

\[ D_0 \frac{\partial \hat{c}_0}{\partial q_{\text{surface}}} + D_R \frac{\partial \hat{c}_R}{\partial q_{\text{surface}}} = 0 \]  

where \( \hat{c}_0 \) is the diffusion operator given in Table 1 with \( D = D_i \).

In general, the complexity of the resolution of the diffusion differential equation system increases significantly when \( D_0 \neq D_R \). As a result, the surface concentrations of the electroactive species are time-dependent and the superposition principle does not hold such that analytical solutions for the application of more than two consecutive pulses [36] have not been deduced. However, there is the exception of macroelectrodes (and also at micro- and submicromembranes under steady state conditions as discussed in Section 3) where surface concentrations are independent of time when \( D_0 = D_R \):

\[ \gamma (k) \]  

(28)

and the following is then fulfilled:

\[ \gamma \hat{c}_0 + \hat{c}_R = \hat{c}_0 + \hat{c}_R \quad \forall \xi, t \]  

where:

\[ \gamma = \sqrt{\frac{D_0}{D_R}} \]  

Therefore, the response for any multipulse voltammetric technique at macroelectrodes for \( D_0 = D_R \) can be calculated from Eq. (19) with \( D = D_0 \) and \( c_0^{(m)} \) being given by Eq. (28) and \( Z_m \) by:

\[ Z_m^m = \frac{1}{1 + \gamma e^{n_{m+1}}} - \frac{1}{1 + \gamma e^{n_{m-1}}} \]  

Fig. 1. Voltammograms calculated from Eq. (19) for (A) cyclic voltammetry (\( v = 1 \, V \, s^{-1}, \Delta E = 0.01 \, mV \)) and (B) square wave voltammetry (\( f = 50 \, Hz, E_{app} = 25 \, mV, E_{sweep} = 5 \, mV \)) of a reversible, one-electron transfer at electrodes of different radius (A) and shapes (B) as indicated on the graphs. \( D = 10^{-5} \, cm^2 \, s^{-1} \) and \( T = 298 \, K \).

2.2. Nernstian multi-electron transfers

Multi-electron processes will be considered in this section according to the following general scheme of \( n \) successive electrochemical steps:

\[ E_f \]  

(Scheme IIa)

where \( E_f \) is the formal potential of the \( j \)th electron transfer step.

The above situation introduces some complications with respect to the system considered in Section 2.1. First, the present problem includes \( n + 1 \) electroactive species (instead of only 2). Second, disproportionation/comproportionation reactions can take place in solution in the diffusion layer region:

\[ 2O_2 \quad \xrightarrow{k_2} \quad O_1 + O_3 \]  

(Scheme IIb)

and only species \( O_1 \) is initially present in a solution.

Note that for the sake of simplicity only chemically independent homogeneous electron transfer reactions are considered in Scheme IIb.

According to Schemes IIa and IIb, the chemical-diffusional differential equation system that describes the problem when the diffusion coefficients of all the electroactive species are equal \( (D_0 = D_0 = \ldots = D_{n+1} = D) \) and only species \( O_1 \) is initially present in solution is given by:

\[ \dot{c}_0 = \gamma (q, t) \quad (i = 1, 2, \ldots, n + 1) \]  

In the same way, the concentration profiles can be obtained from Eq. (21).
\[ t = 0, \ q \geq q_{\text{surface}} \]
\[ t > 0, \ q \to \infty \]
\[ c_{D_1}(q, t) = c_{D_1} = c^*, \quad c_{D_2}(q, t) = \ldots = c_{D_{n-1}}(q, t) = 0 \]
\[ (33) \]
\[ t > 0, \ q = q_{\text{surface}} \]
\[ D \left( \frac{\partial c_{D_1}}{\partial q_{\text{surface}}} \right) q_{\text{surface}} + D \left( \frac{\partial c_{D_2}}{\partial q_{\text{surface}}} \right) q_{\text{surface}} + \ldots + D \left( \frac{\partial c_{D_{n-1}}}{\partial q_{\text{surface}}} \right) q_{\text{surface}} = 0 \]
\[ (34) \]

\[ c_{D_1}(q_{\text{surface}}) = c_{D_2}(q_{\text{surface}}) \exp \left( \frac{F}{RT} (E - E_0^1) \right) \]
\[ c_{D_2}(q_{\text{surface}}) = c_{D_3}(q_{\text{surface}}) \exp \left( \frac{F}{RT} (E - E_0^2) \right) \]
\[ \vdots \]
\[ c_{D_{n-1}}(q_{\text{surface}}) = c_{D_n}(q_{\text{surface}}) \exp \left( \frac{F}{RT} (E - E_0^n) \right) \]
\[ (35) \]

where \( R(q, t) \) is a kinetic term that comprises all the possible homogeneous electron transfer reactions that involve species \( i \) [15,39,40].

The deduction of the electrochemical response of the above problem when the diffusion coefficients of the participating species are unequal has not been possible by means of analytical mathematical methods. Nevertheless, provided that electron transfers are reversible, diffusion is the only mass transport mechanism and \( D_{D_1} = D_{D_2} = \ldots = D_{D_{n-1}} = D \), the problem can be greatly simplified. Under such conditions it is found that the electrochemical response is not affected by reactions in Scheme IIb [15,39,40] and analytical solutions for the current and the surface concentrations can be obtained (see below). Nevertheless, analytical expressions for the concentration profiles are not available since they are dependent on the homogeneous kinetics (Scheme IIb).

From condition (34) one can suggest the inclusion of the linear combination \( Y(q, t) \) corresponding to the total concentration of electroactive species:

\[ Y(q, t) = \sum_{i=1}^{n-1} c_{D_i}(q, t). \]
\[ (36) \]

According to Eq. (32), the differential equation that describes the variation of \( Y(q, t) \) with time and position is given by:

\[ \frac{\partial Y(q, t)}{\partial t} \frac{\partial q_{\text{surface}}}{\partial q_{\text{surface}}} = 0 \]
\[ (37) \]

and it is subject to the following boundary value problem:

\[ t = 0, \ q \geq q_{\text{surface}} \]
\[ t > 0, \ q \to \infty \]
\[ Y(q, t) = c^* \]
\[ (38) \]
\[ t > 0, \ q = q_{\text{surface}} \]
\[ \left( \frac{\partial Y}{\partial q_{\text{surface}}} \right) q_{\text{surface}} = 0. \]
\[ (39) \]

From the above three equations it can be concluded that:

\[ Y(q, t) = c^* \quad \forall q, \ t. \]
\[ (40) \]

Therefore, as in the case of reversible one-electron transfers (Eq. (5)), the total concentration of electroactive species is independent of time and position whatever the electron transfer kinetics, electrode geometry and number of electron transfer steps \( n \).

When all the electron transfers are reversible, it is also possible to obtain expressions for the surface concentrations, which are independent of time and the electrode geometry and its value is defined by the applied potential, \( E_0 \):

\[ c_{D_i}^{(k,s)} = c_{D_i} \prod_{n=1}^{n} e^{E_0_i} \]
\[ (41) \]

with

\[ \eta_k = \frac{F}{RT} (E_0_i - E_j^0) \]  
\[ (j = 1, 2, \ldots, n). \]

With regard to the current, \( i \), this can be written as the sum of the partial currents of the \( n \) electrochemical steps:

\[ i = \sum_{j=1}^{n} I_j \]
\[ (43) \]

where the partial currents \( I_j \) fulfill the following relationships:

\[ \frac{I_1}{FAC} = D \left( \frac{\partial c_{D_1}}{\partial q_{\text{surface}}} \right) q_{\text{surface}} \]
\[ \frac{I_2 - I_1}{FAC} = D \left( \frac{\partial c_{D_1}}{\partial q_{\text{surface}}} \right) q_{\text{surface}} \]
\[ \vdots \]
\[ \frac{I_n - I_{n-1}}{FAC} = D \left( \frac{\partial c_{D_1}}{\partial q_{\text{surface}}} \right) q_{\text{surface}} \]
\[ \frac{I_n}{FAC} = -D \left( \frac{\partial c_{D_{n-1}}}{\partial q_{\text{surface}}} \right) q_{\text{surface}}. \]
\[ (44) \]

Taking into account Eq. (43), the expression for the current (Eq. (44)) can be written in terms of the electrode surface fluxes as:

\[ \frac{I}{FAC} = D \sum_{j=1}^{n} (n-j+1) \left( \frac{\partial c_{D_j}}{\partial q_{\text{surface}}} \right) \]
\[ (45) \]

Eq. (45) suggests including a second linear combination defined as:

\[ W(q, t) = \sum_{j=1}^{n} (n-j+1) c_{D_j}(q, t) \]
\[ (46) \]

such that the current can be expressed as:

\[ \frac{I}{FAC} = D \left( \frac{\partial W(q, t)}{\partial q_{\text{surface}}} \right) \]
\[ (47) \]

This new variable fulfills the following:

\[ \frac{\partial W(q, t)}{\partial t} = 0 \]
\[ (48) \]

and the corresponding boundary value problem is:

\[ t = 0, \ q \geq q_{\text{surface}} \]
\[ t > 0, \ q \to \infty \]
\[ W = W^* = kc_{D_1} \]
\[ (49) \]
\[ t > 0, \ q = q_{\text{surface}} : W = W^* = \sum_{j=1}^{n} (n-j+1) c_{D_j}. \]
\[ (50) \]
Given that surface concentrations are time-independent (Eq. (41)), the problem of the pseudo-species \( W(q, t) \) is equivalent to that of a reversible, one-electron transfer as discussed in Section 2.1. Therefore, the current for the application of a single potential pulse can be expressed as:

\[
\frac{j^{(1)}}{FAC_D} = f_c(t_1, q_C) \left( W^* - W^{(1)*} \right)
\]

and for a multipulse technique by:

\[
\frac{j^{(k)}}{FAC_D} = \sum_{m=1}^{k} \left( W^{(m-1)*} - W^{(m)*} \right) f_c(t_m, q_C) = \sum_{m=1}^{k} \sum_{n=1}^{m} \sum_{h=1}^{n} \frac{2^{n} \left( \prod_{h=1}^{n} e^{h \eta} \right)}{1 + \sum_{s=1}^{n} \prod_{h=1}^{n} e^{h \eta}}
\]

where:

\[
W^{(m)*} = c_{Wm} \left( \prod_{h=1}^{m} e^{h \eta} \right)
\]

with \( \eta \) being defined in Eq. (42) and the function of time \( f_c(t_m, q_C) \) in Table 1 and \( Z_{\text{muine}} \) in Table 2, which in this case corresponds to the difference of the normalized surface values of the variable \( W \) between pulses \( m = 1, 2, \ldots, k \).

2.2.1. Two-electron transfers

It is worth considering the particular case of two-electron transfers (that is, the \( E_{\text{rev}}/E_{\text{rev}} \) mechanism):

\[
\begin{align*}
O_1 + e^- & \rightleftharpoons O_2 & E_0^O \\
O_2 + e^- & \rightleftharpoons O_3 & E_2^O
\end{align*}
\]

(Scheme IIIa)

\[
2O_2 \rightleftharpoons k_1 \quad O_1 + O_3 \quad K = \frac{k_1}{k_2} = e^{(E_1^O - E_2^O)}
\]

(Scheme IIIb)

where \( K \) is the equilibrium constant of the disproportionation-comproportionation reaction. By making \( n = 2 \) and taking into account the relationship between \( K \) and the difference between the formal potentials (see Scheme IIIb), the expressions for the surface concentrations can be written as:

\[
\begin{align*}
c_{W1}^{(k)} &= \frac{\sqrt{K} e^{\eta_k}}{\sqrt{K} + e^\eta + \sqrt{K} e^{\eta_k}} c_{W1}^0 \\
c_{W2}^{(k)} &= \frac{\sqrt{K} e^{\eta_k}}{\sqrt{K} + e^\eta + \sqrt{K} e^{\eta_k}} c_{W2}^0 \\
c_{W3}^{(k)} &= \frac{\sqrt{K}}{\sqrt{K} + e^\eta + \sqrt{K} e^{\eta_k}} c_{W3}^0
\end{align*}
\]

with

\[
\eta_k = \frac{F}{RT} (E_k - E^O)
\]

and \( E^O \) being the average formal potential:

\[
E^O = \frac{E_1^O + E_2^O}{2}
\]

From Eq. (54), the expressions of the currents can also be written for the \( E_{\text{rev}}/E_{\text{rev}} \) mechanism in function of the disproportionation-comproportionation equilibrium constant and the average formal potential. Thus, for a single potential pulse the current is given by [8]:

\[
j^{(1)} = c_{W1}^0 \frac{2 \sqrt{K} + e^\eta}{\sqrt{K} + e^\eta + \sqrt{K} e^{\eta_k}} f_c(t_1, q_C)
\]

and for multipulse perturbations Eq. (52) applies with \( W^* = 2c_0^O \) and \( W^p = 2c_0^O + c_2^O \) such that:

\[
W^{(m-1)*} - W^{(m)*} = c_{Wm}^0 \left( \frac{2 \sqrt{K} e^{\eta_k} \gamma + e^\eta \gamma}{\sqrt{K} + e^\eta + \sqrt{K} e^{\eta_k} \gamma} - \frac{2 \sqrt{K} e^{\eta_k} \gamma + e^\eta \gamma}{\sqrt{K} + e^\eta + \sqrt{K} e^{\eta_k} \gamma} \right)
\]

Fig. 2 shows the cyclic voltammograms and square wave voltammograms for a two-electron transfer with “normal” ordering of formal potentials: \( E_1^O = E_2^O \). As can be observed, SWV is powerful in the study of multipulse process. This technique enables higher discrimination and a more accurate analysis of the different signals with respect to CV where peaks are less de ned, especially in the case of microelectrodes where sigmoidal CV curves are obtained. Under such conditions, the first derivative of the CV sigmoids can also lead to well de ned peaks for quantitative analysis.

2.3. Coupled chemical equilibria

It is commonly found in electrochemical measurements that the electroactive species involved in the electrode process also take part in chemical reactions in solution, which alters their concentrations and so the electrochemical response [18,19,41–46]. The following scheme corresponds to a quite general situation where species \( O \) is electroreduced to \( R \) and both electroactive species take part in homogeneous chemical equilibria the products of which (\( OL, RL, \ldots, OL_n, RL_n \)) are electroactive as well:

\[
\begin{align*}
O & \xrightarrow{+ L, k_1} OL & \cdots & \xrightarrow{+ L, k_n} OL_n \\
R & \xrightarrow{+ L, k_1} RL & \cdots & \xrightarrow{+ L, k_n} RL_n
\end{align*}
\]

(Scheme V)

Species \( L \) is supposed to be present in large excess with respect to the electroactive species and \( k_m^L \) and \( k_m^R \) (\( m = 1, 2; j = 1, 2, \ldots, n \)) are the (pseudo) first-order forward and backward rate constants of the chemical reactions. The following differential diffusive-kinetic equation system describes the variation of the concentrations of the different species when a constant potential, \( E \), is applied:

\[
\begin{align*}
\frac{dc_{OL}^i}{dt} &= \left( k_2^i + k_1^i \right) c_{OL}^i - \left( k_1^i + k_1^i \right) c_{OL}^i + k_2^i c_{OL}^i \left( i = 0, 1, \ldots, n \right) \\
\frac{dc_{OL}^i}{dt} &= \left( k_2^j + k_1^j \right) c_{OL}^i - \left( k_1^j + k_1^j \right) c_{OL}^i + k_2^j c_{OL}^i \left( i = 0, 1, \ldots, n \right)
\end{align*}
\]

where \( c_{OL}^i = c_0 \). System (59) is associated to the following boundary value problem where electron transfer are assumed to be reversible.
and only oxidized species are initially present at the total concentration $c^t = c_0^t + \sum_{i=1}^{\alpha} c_{Oi}^t$:

$$
t = 0, \quad q \geq q_{\text{surface}};
\begin{cases} 
    c_0(q,0) - c_0(q,t) = -\frac{c}{1 + \sum_{p=1}^{\alpha} \beta_p}; \\
    c_{Oi}(q,0) - c_{Oi}(q,t) = -\frac{c_i^t}{1 + \sum_{p=1}^{\alpha} \beta_p}
\end{cases}
$$

(60)

$$
 t > 0, \quad q = q_{\text{surface}}:
\begin{align*}
    D_0 \left( \frac{\partial c_0}{\partial q} \right)_{q=q_{\text{surface}}} & = -D_0 \left( \frac{\partial c_0}{\partial q} \right)_{q=q_{\text{surface}}} \\
    D_{Oi} \left( \frac{\partial c_{Oi}}{\partial q} \right)_{q=q_{\text{surface}}} & = -D_{Oi} \left( \frac{\partial c_{Oi}}{\partial q} \right)_{q=q_{\text{surface}}}
\end{align*}
\right)
1 \leq i \leq n
$$

(61)

$$
 c_i^t(q_{\text{surface}}) = c_i(q_{\text{surface}}) e^{q_{\text{surface}}/D_i}
$$

(62)

$$
\begin{align*}
    c_0^t(q_{\text{surface}}) & = c_0(q_{\text{surface}}) e^{q_{\text{surface}}/D_0} \\
    c_{Oi}^t(q_{\text{surface}}) & = c_{Oi}(q_{\text{surface}}) e^{q_{\text{surface}}/D_{Oi}}
\end{align*}
$$

(62)

with

$$
\begin{align*}
    \eta_{0/R} & = \frac{F (E - E^0_R)}{RT} \\
    \eta_{Oi/Ri} & = \frac{F (E - E^0_{Oi/Ri})}{RT}
\end{align*}
$$

(63)

and $\beta_i$ is the overall formation constant for the $i$th complex of species $O$:

$$
\beta_i = (c_i^t)^{i} \prod_{m=1}^{\alpha} K_m
$$

(64)

where $K_m$ is the equilibrium constant of the $m$th complexation reaction (see Eq. (65)).

The above problem includes the concentration of more than two electroactive species and also the differential equations are coupled through the kinetic terms. However, when the chemical kinetics are sufficiently fast and chemical equilibrium conditions are maintained at any point of the solution and time of the experiment:

$$
\begin{align*}
    K_m & = \frac{c_{Oi/m-1}(q,t) c_{O/m}(q,t)}{c_{O/m-1}(q,t) c_{I/m}(q,t)} \\
    \beta_i & = (c_i^t)^{i} \prod_{m=1}^{\alpha} K_m = \frac{c_{Oi/m}(q,t)}{c_{O/m}(q,t)} \\
    \beta_i & = (c_i^t)^{i} \prod_{m=1}^{\alpha} K_m = \frac{c_{Oi/m}(q,t)}{c_{O/m}(q,t)}
\end{align*}
$$

(65)

the problem can be reduced to that of the following two pseudo-species $c_{O/R}$ and $c_{O/I}$:

$$
\begin{align*}
    c_{O/R}(q,t) & = c_0(q,t) + \sum_{i=1}^{\alpha} c_{Oi}(q,t) \\
    c_{O/I}(q,t) & = c_0(q,t) + \sum_{i=1}^{\alpha} c_{Oi}(q,t)
\end{align*}
$$

(66)
which represent the total concentration of oxidized and reduced species. Taking into account the above definitions, the differential equation system and boundary value problem become equivalent to the problem of reversible, one-electron transfer discussed in Section 2.1:

\[
\begin{align*}
\frac{\partial c_{\text{OT}}}{\partial t} & = D_{\text{O,eff}} \nabla^2 c_{\text{OT}}, \\
\frac{\partial c_{\text{RT}}}{\partial t} & = D_{\text{R,eff}} \nabla^2 c_{\text{RT}},
\end{align*}
\]  
(67)

\[
\begin{align*}
t = 0, & \quad q \underset{\omega}{\rightarrow} q_{\text{surface}}, \\
\frac{\partial c_{\text{OT}}}{\partial t} & = D_{\text{O,eff}} \left( \frac{\partial^2 c_{\text{OT}}}{\partial q_{\text{surface}}^2} \right), \\
\frac{\partial c_{\text{RT}}}{\partial t} & = D_{\text{R,eff}} \left( \frac{\partial^2 c_{\text{RT}}}{\partial q_{\text{surface}}^2} \right),
\end{align*}
\]  
(68)

\[
\begin{align*}
\omega & = \frac{1 + \sum_{i=1}^{n} \beta_i}{1 + \sum_{i=1}^{n} \beta_i'}, \\
D_{\text{O,eff}} & = \frac{D_O + \sum_{i=1}^{n} D_{\text{O,eff}} \beta_i}{1 + \sum_{i=1}^{n} \beta_i}, \\
D_{\text{R,eff}} & = \frac{D_R + \sum_{i=1}^{n} D_{\text{R,eff}} \beta_i'}{1 + \sum_{i=1}^{n} \beta_i'},
\end{align*}
\]  
(71)

and for any arbitrary sequence of potential steps:

\[
\frac{I^{(k)}}{FA_cD} = \sum_{m=1}^{k} \left[ \left( c^{(m-1),}\omega \right) - c^{(m),}\omega \right] f_c(t_{m,k}, q_c),
\]  
(73)

where \( f_c(t, q_c) \) is given in Table 1, \( z_{\text{adder}} \) in Table 2 and:

\[
\begin{align*}
c^{(k),}\omega & = \omega e^{k\eta} (c_O + c_R), \\
c^{(k),}\omega & = \omega e^{k\eta} (c_O + c_R).
\end{align*}
\]  
(74)

Fig. 3 shows the voltammetric response of Scheme IV under the conditions considered of total chemical equilibrium and excess of species L. As can be concluded by analyzing Eq. (73), voltamograms with the same characteristics as that of a one-electron transfer are obtained, the ‘effective’ concentration being the total concentration of oxidized species (\( c' \)), the ‘effective’ diffusion coefficients being given by Eq. (71) and the ‘apparent’ formal potential by:

\[
E_{\text{app}}^\omega = E_{\text{app}}^O + \frac{RT}{T} \ln (\omega).
\]  
(75)

According to the above expression, the voltamograms shifts towards more negative \( E \)-values as the stabilization of the oxidized species by the coupled chemical equilibria increases, that is, as the \( \omega \)-value is larger. The opposite is observed when \( \omega \) decreases, which relates to the reduced species being more stable and the electrode-reduction being thermodynamically more favorable. Note that, according to Eq. (70), the value of \( \omega \) can be changed in experiments by varying the concentration of species L in order to reveal the occurrence of coupled chemical equilibria.

2.4. Coupled chemical kinetics — the (pseudo)first-order catalytic mechanism

In a catalytic process, the product of the electrode reaction R reduces an electroactive species \( Z \) in solution and it is regenerated in line with the following reaction scheme:

\[
\begin{align*}
O & \xrightarrow{e^-} R^* \\
R + Z & \xrightarrow{k_i} O + P
\end{align*}
\]  
(Scheme V)

Fig. 3. Influence of coupled chemical equilibria (through the parameter \( \omega \)) on the response in (A) cyclic voltammetry (\( v = 0.1 \; V \; s^{-1}, \Delta E = 0.01 \; mV \)) and (B) square wave voltammetry (\( f = 50 \; Hz, E_{sw} = 30 \; mV, E_{amp} = 3 \; mV \)) at a spherical microelectrode of radius 50 \( \mu \)m. \( D = 10^{-5} \; cm^2 \; s^{-1} \) and \( T = 298 \; K, \eta_{\text{Cu}} = 1/FA_c\sqrt{BD}/RT \) and \( \eta_{\text{Cu}} = 1/FA_c\sqrt{2FD} \) [9].
where species $Z$ and $P$ are present in a large excess so the homogeneous reaction is of pseudo-first-order: $k_1 = k_1'c^e_Z$ and $k_2 = k_2'c^e_P$. Note that in systems that follow Scheme V the direct electroreduction of species $Z$ at the electrode surface is kinetically impeded and the redox couple $O/R$ acts as a catalyst of such reaction.

Taking into account that the chemical reaction in reaction Scheme V is of (pseudo)first-order kinetics, the corresponding differential equation system and boundary value problem are:

$$\begin{align*}
\frac{\partial c_O}{\partial t} - k_1 c_R - k_2 c_O & = 0, \\
\frac{\partial c_R}{\partial t} + k_1 c_O + k_2 c_R & = 0.
\end{align*}$$

(76)

$t > 0$, $q \geq q_{\text{surface}}$

(77)

$$\begin{align*}
t > 0, \quad q & \geq q_{\text{surface}}, \quad D_O \left( \frac{\partial c_O}{\partial q} \right) \quad \tau = -D_R \left( \frac{\partial c_R}{\partial q} \right) \quad \tau_{\text{surface}}
\end{align*}$$

(78)

$$
\begin{align*}
c_O(q_{\text{surface}}) & = e^0 c_R(q_{\text{surface}})
\end{align*}

(79)

with $\eta = F(E-E^0)/RT$ and $E^0$ being the formal potential of the redox couple O/R.

To simplify the resolution of the problem given by Eqs. (76)–(79), it is convenient to assume that all the diffusion coefficients are equal and to introduce the following variable changes:

$$\begin{align*}
\zeta & = c_O + c_R, \\
\phi & = (c_R - K c_O)e^\chi, \\
\chi & = (k_1 + k_2)t.
\end{align*}$$

(80)

(81)

(82)

By inserting Eqs. (80)–(81) into Eq. (76) the following is fulfilled:

$$\begin{align*}
\frac{\partial \zeta}{\partial t} & = 0, \\
\frac{\partial \phi}{\partial t} & = 0,
\end{align*}$$

(83)

(84)

and:

$$\begin{align*}
\zeta & = \zeta - \phi e^{-\chi}, \\
c_O & = K c_R e^{-\chi}, \\
c_R & = K \frac{e^{-\chi}}{1 + K}.
\end{align*}$$

(85)

Moreover, by assuming that $D_O = D_R = D$ it is obtained that

$$\begin{align*}
\begin{cases}
t > 0, \quad q \geq q_{\text{surface}}, \\
t > 0, \quad q \to \infty,
\end{cases}
\end{align*}$$

(86)

$$
\begin{align*}
\phi & = 0, \\
\frac{\partial \phi}{\partial q} & = 0, \\
\frac{\partial \phi}{\partial q_{\text{surface}}} & = 0.
\end{align*}$$

(87)

Eq. (80) together with conditions (86) and (87) lead to:

$$
\zeta(q, t) = c_O(q, t) + c_R(q, t) = \zeta^* \quad \forall q, t
$$

(88)

Moreover, from Eqs. (79) and (88) it is easily deduced that:

$$\begin{align*}
c_O & = \frac{\zeta^* e^0}{1 + \zeta^*}, \\
c_R & = \frac{\zeta^* e^0}{1 + \zeta^*}.
\end{align*}$$

(89)

According to the above, the resolution of this problem is reduced to the differential Eq. (84) with the following boundary conditions:

$$\begin{align*}
t > 0, \quad q \geq q_{\text{surface}}, \\
t > 0, \quad q \to \infty
\end{align*}$$

(90)

(91)

with $\phi^*$ being the value of variable $\phi$ given by Eq. (81) at the electrode surface.

The current corresponding to the catalytic mechanism is given by:

$$\begin{align*}
\frac{I^{(1)}}{F A_c D} & = -\phi^* - K \frac{F c^e_G}{1 + K} (t_1, q_c),
\end{align*}$$

(92)

For a single potential pulse, the analytical solution is:

$$\begin{align*}
\frac{I^{(1)}_{\text{diff.cat}}}{F A_c D} & = \frac{\phi^*}{1 + K} Z_{\text{cat}}^* f^e_G(t_1, q_c),
\end{align*}$$

(93)

with $Z_{\text{cat}}^*$ being given in Table 2 and $f^e_G(t, q_c)$ in Table 3 for macroelectrodes, spherical and disk electrodes. From Eq. (93) the expressions for the cathodic ($E < E^0$, $e^0 \to 0$) and anodic ($E > E^0$, $e^0 \to \infty$) limiting currents can be easily deduced:

$$\begin{align*}
\frac{I^{(1)}_{\text{diff.cat}}}{F A_c D} & = \phi^* - \frac{1}{1 + K} f^e_G(t_1, q_c), \\
\frac{I^{(1)}_{\text{diff.an}}}{F A_c D} & = -\phi^* - \frac{K}{1 + K} f^e_G(t_1, q_c)
\end{align*}$$

(94)

(95)

Table 3

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$f^e_G(x_{nm}, q_c)$</th>
<th>$f^e_{an}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>$\sqrt{\frac{h_{nm}}{m}} e^{\varepsilon_{an}}$</td>
<td>$\sqrt{\frac{h_{nm}}{m}}$</td>
</tr>
<tr>
<td>Sphere</td>
<td>$\frac{1}{n} + \sqrt{\frac{h_{nm}}{m}} e^{\varepsilon_{an}}$</td>
<td>$\frac{1}{n} + \sqrt{\frac{h_{nm}}{m}}$</td>
</tr>
<tr>
<td>Disk</td>
<td>$\frac{1}{n} + \sqrt{\frac{h_{nm}}{m}} e^{\varepsilon_{an}}$</td>
<td>$\frac{1}{n} + \sqrt{\frac{h_{nm}}{m}}$</td>
</tr>
</tbody>
</table>

$G = \text{‘d’ for disks and ‘s’ for spheres or hemispheres}$ The dimension of $f^e_G(x_{nm}, q_c)$ is 1/m length [11,13]
 Moreover, from Eqs. (93)–(94) it is deduced that for the first-order catalytic mechanism it is also fulfilled that:
\[
E = E^0 + RT \ln \left( \frac{f^{(1)}_{0,m}}{f^{(1)}_{0,m,an}} \right)
\]  
(96)

In the case of multipulse techniques, the current is given by [11,13]:
\[
I_{(k)} = \frac{\zeta^*}{(1 + K)} \sum_{m=1}^{\infty} \left[ Z_{m,k} \frac{f^{cat}_{m}}{f^{cat}_{m,an}} \right]
\]  
(97)
where \( f^{cat}_{m}(X_{m,k},q_G) \) is given in Table 3, \( Z_{m} \) in Table 2 and:
\[
X_{m,k} = (k_1 + k_2) t_{m,k}
\]  
(98)

The cyclic and square wave voltammograms of the first-order catalytic mechanism (Scheme V) are shown in Fig. 4 where the homogeneous chemical process is supposed to be irreversible \((K = 0)\). As the kinetics of the catalysis is faster, the magnitude of the CV and SWV curves increases while their position is not affected. Hence, the voltammograms in Fig. 4 are all centered at the formal potential of the redox couple O/R such that: \( \psi_{SW} = \psi_{CV} \). A peculiarity of the catalytic mechanism is that, as can be observed in the cyclic voltammograms of Fig. 4, the response tends to a stationary behavior as the catalysis is faster and/or the time scale longer independently of the electrode size, including macroelectrodes. The above contrasts with the response of the mechanisms considered in previous sections for which a stationary response can only be attained at microelectrodes (see Section 3).

2.5. Non-Nernstian electron transfers

When the electron transfer kinetics is finite, it is found that the surface concentrations of the electroactive species are time-dependent unless micro- or submicroelectrodes are employed (see Section 3). Therefore, the superposition principle does not hold and so, in general, no analytical solutions are available for the transient voltammetric response of quasireversible and irreversible processes in multipulse techniques, with the exceptions of the non-pseudo, analytical, integral-form solution derived by Nicholson and Shain for cyclic voltammetry at macroelectrodes [47] as well as the explicit solutions reported for single- and double-potential pulse techniques at (hemi)spherical electrodes of any size [48].

3. Micro and sub-microelectrodes and stationary response

3.1. Nernstian behavior

The general expression for the current corresponding to the processes following Schemes I-V when an arbitrary sequence of potential pulses \( E_1, E_2, \ldots, E_n \) is applied to an electrode of a given geometry “\( G^*\)”, and the diffusion coefficients of species of species O and R are assumed as equal, is [8–17]:
\[
f^{(k)}_{m} = (\zeta_G + q_G) \sum_{m=1}^{\infty} \left[ Z_m f_c(t_{m,k}, q_G) \right]
\]  
(99)
where \( Z_m \) is given in Table 2 for the different reaction mechanisms considered, and \( f_c(t_{m,k}, q_G) \) in Table 1 for the most common electrode geometries.

A microelectrode is usually defined as an electrode with at least one characteristic dimension \( q_G \) in the micrometer scale (a few tens of micrometers or less) [21–24]. As is well known, as the electrode size is reduced the mass transport between the electrode surface and the bulk solution is enhanced. This leads to important advantages in electrochemistry like the fast attainment of stationary responses.

The expression for the current at a (sub)microelectrode of a given geometry is deduced from Eq. (99) by making \( q_G \ll \sqrt{D_t} \) in the time-function:
\[
f_{c,micro} = [f_c(t,q_G)]_{q_G \ll \sqrt{D_t}}
\]  
(100)
Thus, a stationary current–potential response will be attained only if \( f_{c,micro} \) reaches a constant value. Accordingly, it is crucial to obtain the form of \( f_{c,micro} \) for the analytical characterization of the stationary or

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Expressions for function ( f_{c,micro} ) for different electrode geometries. ( q_G = \bar{t}_s ) for disks; ( q_G = r ) for spheres or hemispheres; ( q_G = \bar{t}<em>s ) for cylinders; ( q_G = w ) for bands. Note that functions ( f</em>{c,micro} ) have dimensions of ( 1/length ) [10,21].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>( f_{c,micro} )</td>
</tr>
<tr>
<td>Sphere (radius ( r_s ), Area = ( 4\pi r_s^2 ))</td>
<td>( \frac{1}{r_s} )</td>
</tr>
<tr>
<td>Disk (radius ( r_d ), Area = ( \pi r_d^2 ))</td>
<td>( \frac{4}{r_d^3} )</td>
</tr>
<tr>
<td>Spherical nanoparticle (radius ( r_s ), Area = ( 4\pi r_s^2 ))</td>
<td>( \frac{1}{r_s} )</td>
</tr>
<tr>
<td>Cylinder (radius ( r_c ), length ( l ), Area = ( 2\pi rl ))</td>
<td>( \frac{1}{r_c l} )</td>
</tr>
<tr>
<td>Band (width ( w ), length ( l ), Area = ( w ))</td>
<td>( \frac{1}{w l} )</td>
</tr>
</tbody>
</table>
pseudo-stationary response of a given reaction scheme at micro or sub-
microelectrodes. The expressions for \( f_{\text{G, micro}} \) corresponding to different
electrode geometries are given in Table 4, including the most usual ones:
microhemispheres, microdisks, single conductive microspheres,
microcylinders and microbands. Among them, the condition \( f_{G, \text{micro}} = \text{constant} \) can be attained at disk, hemispherical and single spherical
electrodes such that the expression of the current (Eq. (99)) simplifies to:

\[
\frac{i_{\text{p, dis}}^{(k)}}{FAD} = (c_0^k + c_k^k) f_{G, \text{micro}} \sum_{m=1}^{k} Z_m = (c_0^k + c_k^k) f_{G, \text{micro}} \Delta Z_k
\]  

(101)

with \( \Delta Z_k \) being given in Table 2. On view of Eq. (101), it is obvious that
the true stationary current \( i_{\text{p, dis}}^{(k)} \) only depends on the applied potential
through \( \Delta Z_k \) and not on the previous history of the perturbation (i.e.,
the previous potential pulses applied). Under these conditions, the
current has the same dependence with the applied potential as
that deduced for the application of a single potential pulse in
Section 2, since the expression for \( \Delta Z_k \) is formally identical to \( Z_1 \)
by changing \( E_1 \) by \( E_k \). It also worth highlighting that when the time-
dependence of \( f_{G, \text{micro}} \) does not disappear, as in the case of
microcylinders and microbands, it is not possible to extract \( f_{G, \text{micro}} \)
from the sum in the right-hand side of Eq. (99).

### 3.1.1. Reversible one-electron transfers

In agreement with Eq. (101), under true stationary conditions the
current for the \( p \)th potential pulse depends only on the geometrical features
of the electrode (through the function \( f_{G, \text{micro}} \)) and on the \( E_k \)-value.
For reversible, one-electron transfers with \( D_0 = D_e \), Eq. (101) becomes:

\[
\frac{i_{\text{p, sph}}^{(k)}}{FAD} = (c_0^k + c_k^k) \Delta Z_k f_{G, \text{micro}} = \frac{c_0^k - \varepsilon \eta \varepsilon c_k^k}{1 + \varepsilon \eta c_k^k} f_{G, \text{micro}}
\]  

(102)

with \( \eta_k = \frac{\overline{E}_k - E} {\overline{E}_k} \).

It is also possible to obtain the expression for the stationary current at
(hemi)spherical microelectrodes when the diffusion coefficients of
species O and R are different. The corresponding problem is given by:

\[
d_i^2 c_i + \frac{2}{r} \frac{dc_i}{dr} = 0 \quad i = O, \quad R \quad \quad \quad r \rightarrow \infty \quad c_0 = c_0^k, \quad c_R = c_R^k \quad \quad \quad (104)
\]

\[
r \geq r_0 : D_0 \left( \frac{\partial c_0}{\partial r} \right)_{r=r_0} = -D_R \left( \frac{\partial c_R}{\partial r} \right)_{r=r_0}
\]  

(105)

\[
c_0(r_0) = \varepsilon \eta c_k(r_0)
\]  

(106)

with \( \eta = (F/RT)(E - E) \). By introducing the change \( y_i = d c_i / d r \) in
Eq. (103), this is transformed into:

\[
\frac{dy_i}{dr} + 2 \frac{dy_i}{r} = 0 \quad i = O, \quad R
\]  

(107)

which can be directly integrated to yield:

\[
\frac{dc_i}{dr} \bigg|_{r=r_0} = \left( \frac{dc_i}{dr} \right)_{r=r_0} (r_0/r)^2
\]  

(108)

By integrating Eq. (108), one obtains:

\[
c_i(r) - c_i(r_0) = \left( \frac{dc_i}{dr} \right)_{r=r_0} (r_0/r) (1 - r/r_0)
\]  

(109)

and, by introducing condition into Eq.:

\[
\left( \frac{dc_i}{dr} \right)_{r=r_0} = c_i^0 + (c_i(r_0) - c_i^0) \frac{r_0}{r}
\]  

(110)

such that the concentration profiles of the electroactive species have the form:

\[
c_i(r) = c_i^0 + (c_i(r_0) - c_i^0) \frac{r_0}{r}
\]  

(111)

From Eqs. (105), (106) and (111), the surface concentrations expressions are deduced:

\[
c_0(r) = \frac{\gamma^2 c_0^k + c_R^k}{1 + \gamma^2 \varepsilon \eta}
\]

(112)

\[
c_R(r_0) = \varepsilon \eta \left( \frac{\gamma^2 c_0^k + c_R^k}{1 + \gamma^2 \varepsilon \eta} \right)
\]

(113)

with \( \gamma \) being given by Eq. (30).

Finally, the following expression is obtained for the steady-state current–potential response at (hemi)spherical microelectrode when
\( D_0 \neq D_r \): [23,49]:

\[
\frac{i_{\text{lim, c}}}{FAD} = \frac{c_0^k - \varepsilon \eta \varepsilon c_k^k}{1 + \varepsilon \eta c_k^k} \frac{1}{r_0}.
\]

(114)

Note that the above expression can also be obtained by making \( r_0 \ll \sqrt{n D_0 t} \) (with \( i = O, R \) in equation (41) of reference [49]).

The analytical solutions for the cathodic and anodic steady state
limiting currents can be immediately deduced from Eq. (113) by making
\( E_k \rightarrow -\infty \) and \( E_k \rightarrow +\infty \), respectively [23,49,50]:

\[
\frac{i_{\text{lim, c}}}{FAD} = \frac{c_0^k - \varepsilon \eta \varepsilon c_k^k}{1 + \varepsilon \eta c_k^k} \frac{1}{r_0}.
\]

(114)

In the case of (sub)microdisks, the diffusion equations depend on
two spatial coordinates, \( z \) and \( r \), in the way:

\[
\frac{d^2 c_i}{dz^2} + \frac{1}{r} \frac{dc_i}{dr} + \frac{d^2 c_i}{dr^2} = 0 \quad i = O, \quad R
\]  

(115)

that are subject to the following boundary conditions,

\[
\begin{align*}
\forall r, & \quad z = -\infty \quad \quad \quad c_0 = c_0^k, \quad c_R = c_R^k \\
\forall z, & \quad r = -\infty \quad \quad c_0 = c_0^k, \quad c_R = c_R^k \\
z = 0, & \quad r \leq r_d : c_0(z = 0) = e^{r_d} c_k(z = 0)
\end{align*}
\]

(116)

\[
D_0 \left( \frac{\partial c_0}{\partial z} \right)_{z=0} = -D_R \left( \frac{\partial c_R}{\partial z} \right)_{z=0}.
\]

(117)

Under the assumption that the surface concentrations of O and R are constant
over the disk surface (that is, their value is independent of \( r \)
for \( z \leq r_d \), the following is a solution for Eq. (115) [25]:

\[
c_i(r) = c_i^0 + (c_i(z = 0) - c_i^0) \int_0^z \frac{\sin(mr)}{m} J_0(mr) e^{-mr} dm
\]

(119)
with $J_0(x)$ being the 0th order Bessel function. Therefore:

$$\frac{\partial C}{\partial z} \bigg|_{z=0} = -\frac{2}{\pi} \left( C_0^+ - C_0^- \right) \int_0^\infty \frac{\sin(mr) J_0(mr) dm}{r}. \quad (120)$$

By introducing Eq. (120) into Eq. (118) it can be easily deduced that:

$$D_0 (C_0^+ - C_0^-) = -D_k (C_k^+ - C_k^-) \quad (121)$$

and by combining Eqs. (117) and (121) the expressions for the surface concentrations are obtained:

$$C_0(z = 0) = \frac{\gamma^2 C_0^+ + C_k^+}{1 + \gamma^2 e^{\eta_k}}, \quad (122)$$

$$C_k(z = 0) = e^{\eta_k} \left( \frac{\gamma^2 C_0^+ + C_k^+}{1 + \gamma^2 e^{\eta_k}} \right).$$

The quantity of species electrolyzed at the total electrode surface per unit of time, $C$, is given by:

$$C = 4D_0 (C_0^+ - C_0^-) \int_0^\infty \frac{r}{\sqrt{r^2 - s^2}} dr = 4r_0 D_0 (C_0^+ - C_0^-) \quad (123)$$

and the current is obtained by multiplying it by the Faraday constant 
[25,51]:

$$I = 4r_0 F D_0 (C_0^+ - C_0^-) \quad (124)$$

that can be re-written as:

$$\frac{I_{\text{micro,ss}}}{F A} = \frac{\gamma}{2} \left( e^{\eta_k} \frac{C_0^+ - C_k^+}{1 + \gamma^2 e^{\eta_k}} \right) \frac{C_k^+ - e^{\eta_k} C_k^+}{1 + \gamma^2 e^{\eta_k}} R_0 \frac{r_0}{\eta_k} \quad (125)$$

from which the cathodic and anodic steady-state limiting currents are immediately derived:

$$I_{\text{micro,ss}}^{\text{cat}} = 4Fr_0D_0C_0^+, \quad (126)$$

$$I_{\text{micro,ss}}^{\text{an}} = -4Fr_0D_0C_k^+. \quad (126)$$

Noting Eqs. (113) and (125), it is clear that the current density ($i = I/A$) at disk and microspheres of the same radius for reversible electrode processes at any value of the applied potential follow the equivalence relationship (see Fig. 5A) [52]:

$$\frac{I_{\text{micro,ss}}}{I_{\text{micro,ss}}^{\text{hemisphere}}} = \frac{4}{\eta_k}. \quad (127)$$

Also, it can be concluded that for the above geometries 'G' that it is fulfilled that:

$$E = \frac{E_{\text{micro}}^{\text{hemisphere}}}{2} + \frac{RT}{F} \ln \left( \frac{1}{\sqrt{\frac{\eta_k}{C_{k}^+} - \frac{\eta_k}{C_{k}^+}}} \right). \quad (128)$$

where the reversible half wave potential is given by:

$$E_{1/2}^{\text{micro}} = E^G + \frac{RT}{F} \ln \left( \frac{1}{\sqrt{\frac{\eta_k}{C_{k}^+} - \frac{\eta_k}{C_{k}^+}}} \right), \quad (129)$$

with $\gamma$ being given by Eq. (30).

Another case of interest corresponds to a microsphere at a non-electroactive flat substrate because it is used as a model for spherical nanoparticles (of radius $r_{np}$) impacting on a surface [53,54]. The theoretical treatment of this problem is notably more complex than those above-presented. Nevertheless, an analytical solution was deduced for the average stationary current when the diffusion coefficients of the electroactive species are equal [55–57] as detailed in reference [55]:

$$\frac{I_{\text{micro,ss}}}{F A r_{np}} = \frac{C_0^+ - e^{\eta_k} C_k^+}{1 + e^{\eta_k}} \frac{\ln 2}{r_{np}} \quad (130)$$

Note that according to the above expression, Eq. (128) also applies in the present case.

In the case of microcyclinders and microbands, $f_{r,\text{micro}}$ is time-dependent (see Table 4) and only a pseudo-stationary response can be achieved since not all the electrode dimensions (in this case the length...
of the cylinder or the band) fall in the scale of microns. Consequently, the expressions for the pseudo-stationary current–potential responses when the diffusion coefficients of species O and R fulfills $D_O = D_R$ must be calculated with Eq. (99). However, it is common to find expressions for the pseudo-stationary current at cylinders and bands that consider that the response is given by [21,52]:

$$\frac{i_{\text{cylinder, pss}}}{FA_D} \approx \frac{C_0 - e^{n_f \eta_f}}{1 + e^{n_f \eta_f}} \frac{1}{F} \frac{2}{R_c} \ln \left( \frac{4D \tau}{w^2} \right)$$ (131)

$$\frac{i_{\text{microcylinder, pss}}}{FA_D} \approx \frac{C_0 - e^{n_f \eta_f}}{1 + e^{n_f \eta_f}} \frac{1}{F} \frac{2\pi}{w^2} \ln \left( \frac{64D \tau}{w^2} \right)$$ (132)

From Eqs. (131) and (132), it is possible to obtain a constant relationship between the expressions for the current at both microelectrodes for certain geometrical conditions. Thus, for microbands and microhemicylinders fulfilling $R_c = w/4$, a constant ratio is obtained if the same experimental time-scale is employed [21,58]:

$$\frac{i_{\text{microcylinder, pss}}}{i_{\text{microhemicylinder, pss}}} = 1.$$ (133)

One must be cautious with the equations for microcylinders and microbands (131) and (132) since their use can lead to significant errors in the evaluation of the response of micro or submicroelectrodes. As an example, Fig. 5 shows the current–potential response corresponding to microcylinders of 1 (a) and 0.1 µm (b) radius in cyclic voltammetry (CV) obtained by numerical methods [27,49] (dashed red line), and that obtained from Eq. (131) (solid line), which can be re-written as follows for CV and $c^* = 0$:

$$i_{\text{CV, pss}}^{\text{microcylinder}} = \frac{1}{1 + e^n} \frac{2}{R_c} \frac{1}{F} \frac{4}{n_f} \ln \left( \frac{4D \tau}{w^2} \right)$$ (134)

with

$$R_c = \frac{r_c}{r_c} \sqrt{\frac{v}{RTD}}$$ (135)

where $v$ and $r_c$ are the voltammetric scan rate and the radius of the cylinder, respectively. The response calculated from Eq. (99) by using a potential amplitude $\Delta E = 0.001$ mV and the $f_{\text{cylinder, micro}}$ given in Table 4 has also been included for comparison (dashed blue line). As can be seen in the figures, the agreement between the voltammograms calculated numerically (red line) and that obtained from Eq. (99) is very good (with a maximum error of 1.1% associated to the potential amplitude employed). On the other hand, Eq. (134) only shows a good agreement with the numerical results at the foot of the wave of the cathodic scan of the CV curves. Beyond this potential-region, the response obtained from Eq. (134) has a stationary nature (i.e., a sigmoidal current–potential curve is obtained with a constant current plateau corresponding to the value predicted by Eq. (134) by making $I_k \rightarrow -\infty$) that is not predicted either from numerical simulations or from Eq. (99) that yield curves with a clean quasistationary characteristics (for example, a small degree of hysteresis in the current of the cathodic and anodic scans). The relative difference between the plateau current observed in the CV current calculated from Eq. (134) and that obtained at the inversion potential for the numerical CV curve increases with the electrode radius: 22% for 0.1 µm and 38% for 1 µm. Comparisons in Fig. 5 have been carried out by considering that diffusion is the only mode of mass transport. When natural convection is included, as has been done in reference [59] for the case of band and microband electrodes, it is found that a stationary current can be attained even with band widths in the range of 30–50 µm.

In recent years, the design of new micro and submicroelectrodes has led to the appearance of other electrode geometries. Only in few cases there have been theoretical attempts to determine the specific form of function $f_{\text{cylinder}}$. In Tables 4 and 5 some of the expressions found for these geometries are given. The reason for the lack of analytical expressions for the diffusion-controlled stationary current at these geometries, and therefore for the particular expression of $f_{\text{cylinder}}$ is very likely the complexity of the mass transport problems involved (even although they correspond to stationary conditions). An example of this corresponds to the cases of micro and nanowires. There have been different works reporting the fabrication of single wires of different materials with the radius and length in the micro- to nano-metric ranges [53,60, 61]. Nevertheless, no analytical expression for function $f_{\text{micro}}$ (or the mass transfer coefficient or the diffusion layer thickness) has been deduced yet since it is necessary to deal with a three-dimensional diffusion problem with strong edge effects. While it seems that the use of numerical simulation methods is imperative for the rigorous description of such systems, analytical solutions for geometries similar to wires, such as bands or cylinders, have been used to characterize the stationary limiting currents obtained [60,62]. Initially, these solutions should be considered, at best, as approximate and the values obtained for the different parameters as ballpark estimations.

### 3.1.2. Multi-electron and two-electron transfers

The current for a reversible multi-electron mechanism (i.e., a multi-E mechanism) can reach a time-independent value when microelectrodes are used since under these conditions the function $f_{\text{cylinder}}$ in Eq. (99) is identical to that corresponding to one-electron transfers. Hence, it takes the form of $f_{\text{cylinder}}$ given in Table 4. For those microelectrode geometries for which $f_{\text{micro}}$ is constant, the current–potential response can be written as [14,15,17]:

$$i_{\text{CV, pss}}^{\text{microcylinder}} = \frac{FA_D D_{\text{O1}}}{1 + e^n} f_{\text{micro}}^{\text{multi-electron}} = \frac{FA_D D_{\text{O1}}}{1 + e^n} \sum_{k=1}^{n-1} \sum_{m=1}^{n-1} e^{n_f \eta_f} f_{\text{micro}}$$ (136)

where “n” is the number of electron transfer steps. For the particular case of a two-electron transfer (i.e., $n = 2$, EE mechanism), Eq. (136) becomes (see Table 2)

$$i_{\text{CV, pss}}^{\text{microcylinder}} = \frac{FA_D D_{\text{O1}}}{1 + e^n} f_{\text{micro}}^{EE} \sum_{k=1}^{n} \sum_{m=1}^{n} e^{n_f \eta_f} f_{\text{micro}}$$ (137)

In Fig. 6 the steady-state response of the EE mechanism at microdisks and microspheres has been calculated from Eq. (137) for different values of $mA$. Obviously, the equivalence relationship for microspheres and microdisks established for a single charge transfer process (see Eq. (127)) also holds in this case. As mentioned above, at microbands or microcylinders $f_{\text{micro}}$ is not constant and only a pseudo-stationary response can be achieved.

### 3.1.3. Coupled chemical equilibria

When species O is electro-reduced to R and both take part in a number of chemical equilibria in solution as indicated in Scheme IV, the stationary current–potential curve for the pseudo-stationary current at cylinders and bands that correspond to the appearance of other electrode geometries. Only in few cases there have been theoretical attempts to determine the specific form of function $f_{\text{cylinder}}$. In Tables 4 and 5 some of the expressions found for these geometries are given. The reason for the lack of analytical expressions for the diffusion-controlled stationary current at these geometries, and therefore for the particular expression of $f_{\text{cylinder}}$ is very likely the complexity of the mass transport problems involved (even although they correspond to stationary conditions). An example of this corresponds to the cases of micro and nanowires. There have been different works reporting the fabrication of single wires of different materials with the radius and length in the micro- to nano-metric ranges [53,60, 61]. Nevertheless, no analytical expression for function $f_{\text{micro}}$ (or the mass transfer coefficient or the diffusion layer thickness) has been deduced yet since it is necessary to deal with a three-dimensional diffusion problem with strong edge effects. While it seems that the use of numerical simulation methods is imperative for the rigorous description of such systems, analytical solutions for geometries similar to wires, such as bands or cylinders, have been used to characterize the stationary limiting currents obtained [60,62]. Initially, these solutions should be considered, at best, as approximate and the values obtained for the different parameters as ballpark estimations.

In Fig. 6 the steady-state response of the EE mechanism at microdisks and microspheres has been calculated from Eq. (137) for different values of $mA$. Obviously, the equivalence relationship for microspheres and microdisks established for a single charge transfer process (see Eq. (127)) also holds in this case. As mentioned above, at microbands or microcylinders $f_{\text{micro}}$ is not constant and only a pseudo-stationary response can be achieved.
Table 5
Expression for the function \( f_{G,micro} \) corresponding to different electrode geometries. The current is given by \( \frac{i^{cat}}{F} = F \alpha D Z_{p} f_{G,micro} \).

<table>
<thead>
<tr>
<th>Electrode geometry</th>
<th>( A_G )</th>
<th>( f_{G,micro} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylindrical nanopore electrode (recessed disk)</td>
<td>( \pi a^2 )</td>
<td>( \frac{1}{1 + \frac{a}{H} \arctan \left( \frac{a}{H} \right) \arcsin \left( \sqrt{1 - \frac{h^2}{H^2}} \right) \arcsinh(\sqrt{1 - \frac{h^2}{H^2}}) } )</td>
<td>[63]</td>
</tr>
<tr>
<td>Conical nanopore electrode 1</td>
<td>( \pi a^2 )</td>
<td>( \frac{1}{1 + \frac{a}{H} \arctan \left( \frac{a}{H} \right) \arcsin \left( \sqrt{1 - \frac{h^2}{H^2}} \right) \arcsinh(\sqrt{1 - \frac{h^2}{H^2}}) } )</td>
<td>[64]</td>
</tr>
<tr>
<td>Conical nanopore electrode 2</td>
<td>( \pi a^2 )</td>
<td>( \frac{1}{1 + \frac{a}{H} \arctan \left( \frac{a}{H} \right) \arcsin \left( \sqrt{1 - \frac{h^2}{H^2}} \right) \arcsinh(\sqrt{1 - \frac{h^2}{H^2}}) } )</td>
<td>[65]</td>
</tr>
<tr>
<td>Nanotrench electrode (recessed nanoband)</td>
<td>( \pi a^2 )</td>
<td>( \frac{1}{1 + \frac{a}{H} \arctan \left( \frac{a}{H} \right) \arcsin \left( \sqrt{1 - \frac{h^2}{H^2}} \right) \arcsinh(\sqrt{1 - \frac{h^2}{H^2}}) } )</td>
<td>[66]</td>
</tr>
<tr>
<td>Conical microelectrode</td>
<td>( \frac{2}{\pi} \ln \left( \frac{1 - \frac{d}{h}}{1 + \frac{d}{h}} \right) \arcsin \left( \sqrt{1 - \frac{h^2}{H^2}} \right) \arcsinh(\sqrt{1 - \frac{h^2}{H^2}}) )</td>
<td>( H &gt; 1 )</td>
<td>[67]</td>
</tr>
<tr>
<td>Spheroid electrode</td>
<td>( \frac{2}{\pi} \ln \left( \frac{1 - \frac{d}{h}}{1 + \frac{d}{h}} \right) \arcsin \left( \sqrt{1 - \frac{h^2}{H^2}} \right) \arcsinh(\sqrt{1 - \frac{h^2}{H^2}}) )</td>
<td>( H &lt; 1 )</td>
<td>[68,69]</td>
</tr>
</tbody>
</table>

In the case of micro(hemi)spheres and microdisks, it is also possible to write an expression for the stationary current when \( D_{O,eff} \neq D_{R,eff} \).

\[
\frac{i_{G,stat}}{FA_G D_{eff}} = \frac{C_{O,stat}}{1 + \gamma F \omega e^{\omega/\gamma}} f_{G,micro}
\]  

(139)

where ‘G’ refers to microspheres or microdisks, \( \omega \) is given in Eq. (70) and \( \gamma = \sqrt{D_{O,eff}/D_{R,eff}} \). Thus, under these conditions the reversible half-wave potential is given by:

\[
E_{1/2}^{G} = E^G + \frac{RT}{F} \ln \left( \frac{1}{\gamma} \right) + \frac{RT}{F} \ln \left( \frac{1}{\omega} \right).
\]  

(140)

3.1.4. Pseudo-first order catalytic mechanism

The general expression for the current corresponding to a (pseudo)first-order catalytic mechanism upon the application of an arbitrary sequence of potential pulses is:

\[
\frac{i_{cat,G}}{FA_G D} = \frac{\xi^*}{(1 + K)} \sum_{m=1}^{n} \left( \frac{\omega_{cat}}{F} \right) \chi_{m,k} (\chi_{m,k} \theta_{G})
\]  

(141)
where $f_G^{\ssss}$ is given in Table 3, $Z_m$ in Table 2, $t_m$ by Eq. (20) and

$$X_{m,k} = (k_1 + k_2) t_{m,k}. \quad (142)$$

For a catalytic mechanism, it is possible to reach a stationary response whenever the condition $X_{m,k} > 1.5$ is fulfilled [13,70]. Under these conditions it is fulfilled that

$$J_G^{\text{cat}} (X_{m,k} > 1.5, \eta_c) = f_G^{\ssss} \quad (143)$$

and, provided that $f_G^{\ssss} = \text{constant}$, Eq. (141) can be simplified to:

$$\frac{f_{\text{cat},G,ss}}{FA_G D} = \frac{k}{(1 + R)} \frac{G_{\text{cat},ss}}{K_{\text{cat}}} \sum_{i=1}^{m} x_i = \frac{k}{(1 + R)} \frac{G_{\text{cat}}}{K_{\text{cat}}} \Delta G_{\text{cat}} \quad (144)$$

where $\Delta G_{\text{cat}}$ is given in Table 2.

In agreement with Eq. (144) and Table 3, a stationary current–potential response can be achieved even at macroelectrodes in the case of the first-order catalytic mechanism. Note that this does not occur with single electron transfers, for which the attainment of steady state conditions is restricted to the use of microelectrodes.

The stationary current–potential curve given by Eq. (144) has a sigmoidal shape with the plateau currents at very positive (an) or negative (cat) potentials being given by

$$f_{\text{cat},G,ss}^{\text{diff.cat.}} = \frac{G_{\text{cat}}}{K_{\text{cat}}} \quad (145)$$

such that the ratio between the cathodic and anodic plateau currents fulfill that:

$$\frac{f_{\text{cat},G,ss}^{\text{diff.cat.}}}{f_{\text{cat},G,ss}^{\text{diff.an.}}} = K \quad (146)$$

independently of the electrode geometry.

Moreover, Eq. (144) leads to two limiting cases, depending on the relationship between $\sqrt{D/(k_1 + k_2)}$ and $\eta_c$:

- For $\sqrt{D/(k_1 + k_2)} \geq 10 \eta_c$, the kinetics of the homogeneous chemical reaction is masked (the catalytic process behaves as a simple charge transfer process), and the following relationship between the current densities ($i$) obtained at disk and spherical electrodes can be established (in an analogous way to what happens in single charge transfer processes),

$$f_{\text{cat},G,ss}^{\text{diff.cat.}} = \frac{4 \sqrt{D}}{\pi D^2} \frac{G_{\text{cat}}}{K_{\text{cat}}} \quad (147)$$

- For $\sqrt{D/(k_1 + k_2)} \leq 10 \eta_c$, a kinetic steady state is attained and the resulting CV curve is independent of the electrode radius and geometry:

$$f_{\text{cat},G,ss}^{\text{diff.cat.}} = \frac{k}{(1 + R)} \frac{G_{\text{cat}}}{K_{\text{cat}}} \sqrt{\frac{k_1 + k_2}{D}} \quad (148)$$

3.2. Non-Nernstian behavior. One-electron transfers

Let us consider the one-electron reduction reaction:

$$O + e^{-} \kappa_{\text{red}} \rightarrow \kappa_{\text{ox}} \quad (I)$$

where $\kappa_{\text{red}}$ and $\kappa_{\text{ox}}$ are the heterogeneous rate constants for the electro-reduction and electro-oxidation processes. The particular form of $\kappa_{\text{red}}$ and $\kappa_{\text{ox}}$ depends on the electrode kinetic model chosen.

The above process will be analyzed by assuming that the diffusion coefficients of species O and R are equal and that a large excess of supporting electrolyte is present in the solution in such a way that migration can be neglected. Thus, when the boundary values of the concentrations of electroactive species at the electrode surface and in the bulk are constant, the solution for the diffusion equation at any electrode geometry can be written as [57]:

$$c_i(q,t) = c_i^0 + \left( \frac{c_i^{\text{surf}} - c_i^0}{f(q,t)} \right) f(q,t) \quad i = O, R \quad (149)$$

where $q$ denotes the appropriate coordinates for the electrode geometry considered and $c_i^{\text{surf}}$ and $c_i^0$ are the constant values of the concentration of species $i$ at the electrode surface and at the bulk solution, respectively. $f(q,t)$ is a continuous function dependent on the particular electrode geometry and on time, $t$.

It is clear that Eq. (149) can be rigorously applied in the study of a charge transfer process under transient conditions if the charge transfer is reversible and the diffusion coefficients of species O and R are equal (see [10,12]). When one of the above assumptions is not fulfilled (i.e., non-reversible electrode processes or unequal diffusion coefficients), Eq. (149) is not strictly valid since $c_i^{\text{surf}}$ depends on time (except for the case of planar diffusion, for which, under reversible conditions, the surface concentrations remain independent of time even if the diffusion coefficients are different, see Section 2.1.2).

As the electrode size decreases, the electrochemical response of the system tends to become stationary or quasi-stationary such that both the average surface concentrations of electroactive species and the average normal surface concentration gradient become independent of time even for non-reversible electrode processes. Under these conditions, Eq. (149) may be again applicable. This is of great interest since, based on this reasoning, it is possible to obtain general, albeit approximate, simple analytical solutions for microelectrodes of different geometries when the steady state is reached.

It can be easily deduced that under the above conditions the sum of concentrations of both electroactive species remains constant, regardless of the extent of reversibility of the electrode reaction, i.e.,

$$c_0(q,t) + c_\text{a}(q,t) = c_0^0 + c_\text{a}^0 \forall q, t. \quad (150)$$

Under steady conditions, i.e., $\partial c_0/\partial t = \partial c_\text{a}/\partial t = 0$, the following general expression for the current for any electrode geometry can be written:

$$I_{\text{G.micro}} = D \left( c_0^0 - c_\text{a}^0 \right) f_{\text{G.micro}} = \left( \kappa_{\text{red}} + \kappa_{\text{ox}} \right) c_\text{a}^0 - k_\text{ox} c_\text{a} \quad (151)$$

with $c^* = c_0^0 + c_\text{a}^0$, with $c_\text{a}^{\text{surf}}$ being the average surface concentration.

By manipulating Eq. (151), it is possible to obtain a general expression for the average surface concentration of the oxidized species for any of the geometries considered (see below):

$$c_\text{a}^{\text{surf}} = c_0^0 + \frac{\kappa_{\text{ox}} c_\text{a}^0}{\kappa_{\text{red}} + \kappa_{\text{ox}}} \quad (152)$$

where:

$$\kappa_{\text{red}} = \frac{1}{f_{\text{G.micro}}} \frac{1}{\kappa_{\text{ox}}} \quad (153)$$

$$\kappa_{\text{ox}} = \frac{1}{f_{\text{G.micro}}} \frac{1}{\kappa_{\text{red}}} \quad (154)$$
The general expression for the current is given by Eq. (151). By making \( c_0^{\text{diff}} = 0 \) in this equation the limiting current is obtained:

\[
I_{\text{diff}} = F A_0 D c_0^0 \frac{f_{\text{micro}}}{c_0^0} \quad (155)
\]

such that:

\[
\frac{1}{I_{\text{diff}}} = 1 - \frac{c_0^{\text{diff}}}{c_0^0} - \frac{C_{\text{red}}}{C_{\text{ox}}} \frac{\kappa_{\text{red}}}{\kappa_{\text{ox}}} \frac{1}{1 + \kappa_{t}} \quad (156)
\]

with:

\[
\mu = \frac{c_k}{c_0^0} \quad (157)
\]

In the following, the Butler–Volmer kinetic formalism will be employed. Thus, the current can be written in the general way:

\[
\frac{1}{I_{\text{diff}}} = \frac{k_0^0 e^{-\alpha \eta}(1 - \mu e^K)}{1 + k_0^0 e^{-\alpha \eta}(1 + e^K)} = \frac{1 - \mu e^K}{1 + e^K + \frac{1}{k_0^0} e^{-\alpha \eta}} \quad (158)
\]

with \( \eta = \left( \frac{RT}{F} \right) \left( E - E^0 \right) \).

There is an alternative expression for the dimensionless rate constant given by Eq. (154) in which the mass transport coefficient \( m \) (Eq. (16)) is used instead of \( f_{\text{micro}} \). By taking into account the expression of the mass transfer coefficient given by Eqs. (16), Eq. (154) can be re-written as:

\[
\begin{align*}
R_{\text{ox}} &= \frac{k_{\text{ox}}}{m} \\
R_{\text{red}} &= \frac{k_{\text{red}}}{m}
\end{align*} \quad (159)
\]

Note that, in agreement with Eqs. (15) and (16), the mass transfer coefficient can be measured from the steady state limiting current (once the electrode area is known) or deduced theoretically from the expression of \( f_{\text{micro}} \) for a given electrode geometry.

Rigorously speaking, Eq. (158) can only be applied to the characterization of non-reversible stationary current–potential responses of uniformly accessible micro and nano-electrodes as microhemispheres or nano-hemispheres \([57,71,73]\). For non-uniformly accessible electrodes, such as microdisks or single conductive microspheres, this equation can be considered only as approximate and a particular approach for a given electrode geometry is needed. For example, for microdisks, an alternative semi-analytical expression to Eq. (158) has been deduced in reference \([74]\).

In reference \([57]\) the validity of Eq. (158) has been tested for the case of microdisks and single microspheres by comparison of stationary current–potential curves obtained by means of numerical simulation and calculated from this equation. As an example, Fig. 7 shows the simulated steady-state voltammograms at a sphere on an insulating surface for a variety of \( k_0^0 = k_0^0 r_s / \ln 2 \) values from fully irreversible to fully reversible electrode processes. Also shown are analytical results from Eq. (158). It is observed that this equation corresponds closely to the simulated results over the whole range of \( k_0^0 = k_0^0 r_s / \ln 2 \). A maximum error of 2.6% is obtained between the simulated steady state voltammograms and those calculated from expression (158).

Therefore, it can be concluded that the latter yields accurate steady state voltammograms for the sphere on a surface geometry over the full range of electrochemical reversibility.

Eq. (158) has been applied to other micro or submicroelectrode geometries, even to nanoelectrodes such as nano-wires \([60,62]\). However, no comparison with numerical results has been presented in this case and so no information about the validity of this equation for such geometries is available.

4. Nanoelectrodes

Recent years has seen a growth in the design of electrodes of different geometries with their characteristic dimension lying in the scale of a few nanometers \([53,75,76]\). The characterization of a nanoelectrode includes the evaluation of its geometrical nature (i.e., its geometry, radius, area, thickness of the insulating sheath, etc.) and this task can be very problematic for non-flat electrodes. The simplest way to do it is with steady state voltammetry.

In the case of nanoelectrodes, it is important to consider that their reduced dimensions could lead to deviations from the “classical” theory for voltammetry. An implicit assumption in electrochemical theoretical treatments is that the electrode dimensions are much larger than the thickness of the diffuse double layer and incomparably larger than the radii of the species involved in the charge transfer. A number of theoretical and experimental studies have focused on possible deviations from the conventional theory at nanometer-sized electrodes in recent years \([76–78]\). The effect of diffuse layer on mass-transfer by migration effects \([79]\) is the most extensively discussed, and it is expected to be significant if the depletion layer thickness caused by the faradaic process is comparable to that of the diffuse double layer (see \([80,81]\)). The extent of this effect and its influence on the values of kinetic parameters extracted depend on several factors including the charge of the electroactive species, their standard potential (with respect to the potential of zero charge), and the ionic strength of the electrolytic solution.

To describe the interplay between the electrical double layer and charge transfer reactions at nanointerfaces a model which combines the Poisson equation, the Nernst–Planck equation, the stationary current–potential relationship (Eq. (158)) and the Faraday law has been reported \([82]\). From the results reported it can be concluded that in most cases, the predicted deviations should be more significant at radii below 100 nm whereas for sizes above this limit Eq. (158) can be used. Furthermore, the theoretical study of systems with comparable diffusion and diffuse layers taking into account the distance-dependent nature of electron transfer of solution-phase redox systems reveal that the traditional Frumkin effect is over-estimated \([83]\).

In the case of kinetic studies, it has been predicted that the empirical Butler–Volmer formalism for the rate constants of the charge transfer would become inapplicable at electrodes of nanometer size \([84]\). Under these conditions, more realistic formalisms like the Marcus–Hush (MH) or Marcus–Hush–Chidsey (MHC, this last one is specially indicated for electrode processes with small reorganization energies) could be used for the description of the electron transfer kinetics \([85,86]\).
Other size-related electrochemical phenomena and their effects on the rates of the charge transfer process have yet to be explored, such as, the stochastic character of charge transfer events at nanointerfaces, the more rapid potential drops within the diffuse double layer at spherical electrodes smaller than 50–100 nm, or the effect of charges residing on the insulating surface on the mass transfer at glass-sealed nanoelectrodes, among others.

5. Arrays

A microelectrode or sub-microelectrode array consists of a series of micro or sub-microelectrodes separated by an insulating material [19, 56, 76]. The microelectrodes can be regularly or randomly distributed (in the latter case the term “ensemble” is also used). Arrays containing hundreds or even thousands of microelectrodes wired in parallel have been extensively used in electrochemical analysis for sensing multiple reactive species and probing signal transformation in a network of biological cells [19, 87]. These devices gather most of the advantages of microelectrodes but add several more: high amplification of the current, adequate output signals and an improved ratio of the faradaic to charging current. Various types of array electrodes have been fabricated, including flat or recessed microdisks, microbands, interdigitated microelectrodes, linear microelectrodes and 3D microelectrodes.

A voltammetric experiment in a microelectrode array is highly dependent on the thickness of the individual diffusion layers, \( \delta \), compared with the size of the microelectrodes themselves, and with the interelectrode distance and the time of the electrochemical experiment. So, for a given array, at short time scales (very high scan rates in cyclic voltammetry), microelectrodes can behave as diffusionally independent, i.e., the diffusion layer thickness is much smaller than the microelectrode size and diffusion is approximately linear. On the other hand, for long time experiments (very low scan rates), the depletion region around each microelectrode grows until complete overlapping with those of the adjacent microelectrodes take place. Under these conditions, the overall concentration profile can be considered as planar [88]. The analytical characterization of the response of an array is very complicated for intermediate situations and numerical studies have mainly been carried out [56].

In the simplest case where it can be assumed that the inter-electrode spacing is large enough to assure that each electrode in the array behaves in an independent way from the others (i.e., there is no overlapping of the individual diffusion fields), the overall current for an array with \( x \) microelectrodes is given by \( x \) times the current of a single microelectrode. For example, in references [89–91] this model has been applied to characterize the behavior of arrays of different electrode geometries (inlaid and recessed micro and nanodisks and nanobands).

When overlapping between adjacent diffusion fields takes place, different theoretical approaches have been developed to characterize the electrochemical response of arrays. The great majority of theoretical treatments of arrays consider a large number of microelectrodes on an infinite electroinactive plane surface. Recently, Amatore et al. have demonstrated that, by using disks and recessed disks, the approximation based on the 2-D geometry of unit cells delimited by cylinders is valid regardless of the mean distance between the centers of symmetry axes of adjacent active elements of the array, i.e., even when the electroactive disks are almost touching. However, this model cannot mathematically reproduce the paveling of a plane [92].

6. Micro and submicro-ITIES

In the last thirty years and in parallel to the develop of microelectrodes, the use and manufacturing of micrometer and nanometer sized ITIES have been widely extended since the reduction of the size of the interface leads to important advantages as the achievement of time-independent current–potential responses (which is therefore independent of the electrochemical technique employed), minimization of the ohmic drop, improvement of the ratio of faradaic to the charge current and enhancement of the mass transport [35, 71, 76, 93]. Moreover, small electrode size permits the use of small sample volumes, which is consistent with their use as sensors in living organisms. The first micro-ITIES was introduced by Taylor and Girault in 1986 by using a glass micropipet pulled down to a fine tip of around 25 \( \mu \)m to support the interface [94–97]. The smaller size of micropipet is advantageous for sensor applications, providing the possibility of studying microenvironments as living cells, and they can also be used as probe in scanning electrochemical microscopy (SECM). Recently, Mirkin et al. [98] have developed a nano-pipet with the inside fluid motion electrochemically controlled by voltage variations. Volumes from attoliter to picoliter can be sampled or dispensed.

In general terms the modelization of microITIES is rather more complex than that of microelectrodes for the following reasons:

1. In the ion transfer (IT) processes it is necessary to take into account in most cases that the diffusivities of the target ion in the aqueous phase and in the non-aqueous phase (e.g., liquid membranes, room temperature ionic liquids, organic solvents) are always different unlike in electron transfer processes. This constraint is not at all trivial and it complicates the theoretical treatment in such a way that it is hard to find accurate, closed-form expressions for the \( I–E \) response, even under stationary conditions.

2. Whereas at microelectrodes the oxidized and reduced species are subject to the same diffusive geometry (except when amalgamation takes place), the study of the IT at microITIES requires, almost always, considering two different diffusive fields. The latter are placed symmetrically with respect to the separating interface at micropores and one on each side of the interface in the case of droplets, capillaries and pipets. Moreover, in these last three cases it is not possible to reach a steady state response mainly due to the predominant semi-infinite linear mass transport inside the cavity.

The above hindrances result in most of expressions obtained for the I/E response of microITIES being fairly approximate. Moreover, they have the disadvantage of not being able to be extended to transient conditions. The latter is of great interest when high sweep rates are used to study very rapid reactions or when there are two very asymmetrical mass transport regions. Although this problem can be tackled with numerical methods, these can be excessively time-consuming when dealing with very small interfaces.

For the case of glass micropipets, different theoretical approach have been described. For example, for the uptake of ions of charge \( z \) into the pipet, it has been assumed that the orifice is a disk and therefore the mass transport obeys the same mathematical expressions as that for a microdisk electrode outside the pipet [94]:

\[
I = 4zFD_2 \omega c^*_0 \left( \frac{r^2}{2} \right)
\]

where \( D_2 \) and \( c^*_0 \) are the diffusion coefficient and concentration of the transferred species in the solution outside the pipet and \( r \) the radius of the orifice. However, for a micropipet the steady state current is 2.6 times higher than that given by Eq. (160). Such difference can be attributed to a small amount of the filling aqueous solution escaping from the pipet and forming a thin layer on its outer wall around the orifice. This results in an important increase of the effective radius of the pipet, and a larger current can be observed. Thus, the following approximate expression obtained empirically has been proposed for non-silanized micro- or nanopipets [99]:

\[
i = 3.35zFD_2 c^*_0 a.
\]

Other factors that affect the response are the thickness of the wall of the pipet, \( t_p \) \( = a \), which can be until ten times greater than the orifice radius, and the pipet inner angle \( \theta \) (see Fig. 8). In the case of nanopipets, its radius and angle can be examined by AFM and SECM.
\[ i = 3.35\pi D_2 a c_2 \]

Fig. 8. Schematic view of the nano-pipet geometry.

The approximate equation corresponding to the diffusion limiting steady state current for the ingress of the ion through the orifice of a silanized pipet is:

\[ I = 4xzFD_2 a c_2^z \tag{162} \]

with \( x \) being a function of the ratio \( r_g/a \) \([100]\).

If the target ion is initially present in the bore, the current is determined by transport inside the pipet and its geometry depends on the radius and the inner angle \( \theta \). In these conditions it is possible to reach a steady state response if \( \theta \geq 4\)° at slow scan rates, and the following expression for the diffusion limiting current can be used

\[ I = 4f(\theta) zFD_2 c_2^a \tag{163} \]

where \( D_1 \) and \( c_2^a \) are the diffusion coefficients and bulk concentration of ion inside the pipet, and \( f(\theta) \) is a function of the tip inner angle given by \([101]\):

\[
f(\theta) = 0.0023113912 + 0.013191803\theta + 0.00031738596\theta^{3/2} + 5.8554625 \times 10^{-5} \theta^2. \tag{164}
\]

For very small values of \( \theta \) and/or very fast scan rates, the steady state is not reached since diffusion inside the pipet is almost linear. Hence, it is more appropriate to use the recently deduced analytical expression for microcapillaries (corrected, if necessary, by the pipet inner angle), which is applicable to any voltammetric technique and allows us to obtain a very accurate expression for the half-wave potential of an ion of charge \( e' \) [102]:

\[
\Delta \phi_{1/2}^\text{CV} = \Delta \phi_{1/2}^\text{diff} \left[ \frac{RT}{2F} \ln \xi_{\text{CV}} - 0.47 \frac{RT}{2F} \right] \tag{165}
\]

with:

\[ \xi_{\text{CV}} = \frac{4}{\pi a} \sqrt{\frac{D_{\text{out}}}{D_{\text{in}}}} \sqrt{\frac{D_{\text{out}} RT}{2F}} \tag{166} \]

and \( \Delta \phi_{1/2}^\text{diff} \) being the formal transfer potential.

7. Conclusions

Rigorous or very accurate analytical solutions are available for prediction, study and fitting of multipulse voltammetries of very common electrochemical systems, as well as for testing numerical simulations. The analytical expressions included in this review enable fast and direct analysis of the main experimental variables under transient and steady-state conditions. Thus, the solutions are valid for electrodes of any size and shape, such that the influence of the character of the mass transport field can be examined as a function of the electrode geometry and the experiment timescale. Common situations where the electroactive species transfer multiple electrons and/or take part in chemical equilibria or a catalytic process in solution have also been considered.

Expressions for the steady-state voltammetry of the above processes have been included, together with a general theoretical treatment for sluggish electrode processes. The analytical solutions obtained are applicable to submicroelectrodes and their arrays, provided that the inter-electrode distance is sufficiently long to avoid overlapping of diffusion fields. Regarding submicroliquidliquid interfaces, approximate expressions for the most widely-used platforms (pores, pipets and capillaries) have been discussed, although rigorous modeling of these systems often requires numerical simulations given the complications derived from the fact that the target species diffuse in two different fields and with very different diffusivities.

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