Conditions of applicability of the superposition principle in potential multipulse techniques: implications in the study of microelectrodes

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Abstract

In this article we establish the necessary mathematical conditions for the superposition principle to be applicable to obtaining the faradaic response to a multipulse sequence on plane and spherical electrodes (whether increasing with time or not) and on cylindrical electrodes. These conditions have been partially established by some authors, but to date have not been derived in a rigorous and general form.

The general expressions derived in this paper for the current $I_j$ corresponding to any pulse $j$ are much simpler than those obtained previously in the literature for some specific cases and can easily be used in practice. To illustrate this, we apply these solutions to staircase and square-wave voltammetry. The effect of the size of the electrode on the final solution is also analysed.

Keywords: Superposition principle; Potential multipulse techniques; Microelectrodes

1. Introduction

The difficulty in finding a rigorous and manageable analytical expression for the theoretical analysis of techniques involving several potential pulses, both for irreversible charge transfer processes and for reversible processes during which mass transport occurs with non-planar symmetry, is well known [1–4]. This difficulty arises because, although the system of differential equations which describes the mass transport to the electrode is linear in these cases, this linearity is lost when the boundary value problem is established.

Nevertheless, there are some situations where it is easy to obtain an expression for the current $I_j$ ($j \geq 2$) corresponding to the $j$th pulse of a determined sequence of potential pulses $(E_1, E_2, \ldots, E_j)$. In these cases it can be shown that the boundary value problem is also linear. This allows a problem with $j$ potential pulses to be treated as $j$ independent single-pulse problems. In other words, the superposition principle [4–9] holds and therefore the concentration profiles corresponding to the $j$th pulse, and hence the associated current, are given as a sum of $j$ responses corresponding to $j$ single potential steps. Indeed, the ease with which some of these expressions can be obtained has led to some authors applying this principle in situations where the underlying assumptions are not valid [6].

In this paper we give the necessary mathematical conditions which must be satisfied before this principle can be applied. These conditions have not been established in a rigorous and general form to date, although some of them have been indicated by other authors [4–9]. From them we deduce that rigorous use of the superposition principle is restricted to reversible charge processes and does not depend on the values of the diffusion coefficient of the electroactive couple for any plane electrode whose area increases with an arbitrary power of time. In the case of spherical (static mercury drop electrode (SMDE) and dropping mercury electrode (DME)) or cylindrical electrodes and microelectrodes, this principle can only be applied rigorously if the diffusion coefficients of both species are equal and if the reduced species is soluble in the electrolyte solution.

Starting from the above considerations, we have obtained general expressions for the current $I_j$ for a reversible process. These expressions are valid for all the geometries mentioned above and are applicable to any electrochemical multipulse techniques which might be designed.

The expression obtained for $I_j$ at static spherical ele-
trodos is of particular interest. Indeed, we have found that
the electrode sphericity, which is defined in this case as
being proportional to $1/r_0$ where $r_0$ is the radius of
the electrode, affects only the $j$th potential pulse, whatever
the duration of the previous $j-1$ pulses. In other words, the
solution obtained in non-convective spherical diffusion is
identical with that obtained in planar diffusion except for
the term which corresponds to the last potential pulse. This
surprising result is due to the cancellation of those terms
that are functions of sphericity in the previous $j-1$
pulses. This situation can never exist for a DME or a
 cylindrical electrode.

The general solutions obtained in this paper have been
applied to staircase voltammetry (SCV) and square-wave
voltammetry (SWV) cyclic sweep techniques, giving simpler
and more manageable analytical solutions than those
already existing in the literature [1,2].

2. Theory

Mass transport to the electrode for the charge transfer
reaction

$$A + ne^- \rightarrow B$$

is given by the following system of differential equations:

$$\delta_i c_A = \delta_i c_B = 0$$

where the operator $\delta_i$ ($i = A$ or $B$) is given by

$$\delta_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{z}{2} \frac{\partial}{\partial t} \frac{r_0^2}{r} \frac{\partial}{\partial r} \right)$$

if we consider a spherical electrode whose area increases
with $t^2$, $z \geq 0$, and

$$\delta_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right)$$

for a stationary cylinder. The operators given by Eqs. (2)
and (3) are linear.

If we assume that the charge transfer process (1) is
reversible, from the solution previously found for a first
pulse [5,10,11,14] and for a second pulse [15], if $D_A = D_B =
D$ and both species are soluble in the electrolytic solution,
we have deduced by induction that, for any pulse $j$ in the
electrode surface, the following is satisfied:

$$\frac{c_j^A(r_0, t)}{c_j^A} = \frac{K_j}{1 + K_j}$$

$$c_j^A(r_0, t) + c_j^B(r_0, t) = c_j^A$$

with

$$K_j = \exp \left[ nF(E_j - E^0)/RT \right] j \geq 1$$

The superscript $j$ in $c_j^i$ ($i = A$ or $B$) in Eqs. (4)
and henceforth refers to the number of potential pulses consid-
ered. Eqs. (4) are independent both of the geometry of the
electrode and of whether its area is constant or variable
with time. However, if $D_A \neq D_B$ and/or $B$ is amalga-
mated into the electrode, $c_j^i(r_0, t)$ and $c_j^B(r_0, t)$ depend
on the time for non-planar electrodes [10–13].

For any pulse $j \geq 2$, the linearity of Eqs. (1) implies
that

$$c_j^A(r, t) = c_j^{-1}(r, t) + \sum_{m=2}^{j-1} \tilde{c}_m^A(r, t)$$

$$c_j^A(r, t) = c_j^{-1}(r, t) + \sum_{m=2}^{j-1} \tilde{c}_m^B(r, t)$$

where

Using Eqs. (4) and (6) we can now express the boundary
value problem for any pulse $j$ in terms of the unknown
$\tilde{c}_j^A(r, t)$, where $t = t_1 + t_2 + \ldots + t_j$ ($0 \leq t_j \leq t_j$), in the
form

$$\gamma_j = 0, \quad r \geq 0$$

$$\gamma_j > 0, \quad r \to \infty$$

$$\tilde{c}_j^A(r, t) = \tilde{c}_j^B(r, t) = 0$$

$$\gamma_j > 0, \quad r = r_0$$

$$\left[ \frac{\partial \tilde{c}_j^A(r, t)}{\partial r} \right]_{r=r_0} = - \left[ \frac{\partial \tilde{c}_j^B(r, t)}{\partial r} \right]_{r=r_0}$$

$$\tilde{c}_j^A(r_0, t) = K_j \tilde{c}_j^B(r_0, t) + \frac{K_{j-1} - K_j}{1 + K_{j-1}} c_j^*$$

This generalization of the boundary value problem for
any pulse (Eqs. (7)–(9)), combined with the linearity
conditions given by Eqs. (6), allows the current $I_j$
corresponding to the $j$th pulse to be expressed as the sum of $j$
terms corresponding to $j$ single potential steps [16]. In
other words, the principle of superposition for spherical
and cylindrical electrodes is satisfied when process (1) is
reversible, the diffusion coefficients of the two species are
equal and species B is soluble in the electrolytic solution.
If these three conditions are not satisfied, the surface
concentrations depend on time and Eq. (9) does not hold.
Then the linearity of the problem is lost and the solution is
much more complex [15–17].

Similarly, for any plane electrode with a surface area
increasing with an arbitrary power of time, it can be shown
that the superposition principle is satisfied for reversible
processes for all values of $D_A$ and $D_B$ and if species B is soluble in either the electrolytic solution or the electrode.

From the above, by applying the superposition principle
and using the dimensionless parameters method [13], we
obtain

$$I_j = nFA(t_j)| \sqrt{\frac{D}{\pi}} c_j^* \sum_{m=1}^j \frac{Z}{\sqrt{m}} \left[ h^{(0)}_m(\beta_m) + \frac{\sqrt{\pi}}{2} \xi_m h^{(1)}_m(\beta_m) + \xi_m^2 h^{(2)}_m(\beta_m) \right]$$

$$j \geq 1$$
Eq. (10) is a general expression for the current corresponding to the application of any sequence of potential pulses without any restrictions on the duration of each pulse. Moreover, Eq. (10) is valid for any plane \((\xi_x = 0)\) or spherical electrode whose area increases with an arbitrary power of time.

In Eq. (10)
\[
Z_m = \frac{1}{1 + K_m} \quad m > 1
\]
(11)
\[
Z_1 = \frac{1}{1 + K_1}
\]
(12)
\[
t_{m_j} = \sum_{k=m}^j t_k \quad \text{if} \quad m = j \rightarrow t_{jj} = t_j
\]
(13)
where \(t_k\) is the duration of pulse \(k\),
\[
\xi_1 = \sqrt{\frac{4D_{ij}}{2z+1}} \frac{1}{r_0}
\]
(14)
\[
\xi_m = \sqrt{\frac{2D_{m-j}}{r_0}}
\]
(15)
and
\[
h_0^0(\beta_m) = \sqrt{\frac{(2z+1) \beta_m}{1 - (1 - \beta_m)^{2z+1}}}
\]
(16)
\[
h_1^0(\beta_m) = 1 - \frac{3z(7z-2)}{128} \beta_m^2 + \frac{z(z-4)(7z+2)}{256} \beta_m^3 + \ldots
\]
(17)
\[
h_2^0(\beta_m) = \frac{z(29z+4)}{160} \beta_m^2 + \ldots
\]
(18)
For a static spherical electrode \((z = 0)\), Eq. (10) simplifies to
\[
I_j \quad \frac{\sqrt{\pi}}{nFAc_{\chi}^j} \sqrt{D} \quad \frac{1}{1 + K_j} + \frac{\sqrt{\pi D} / r_0}{1 + K_j}
\]
(19)
\[
+ \sum_{m=1}^{j-1} \frac{t_{m-j}^{1/2} - t_{m-j}^{1/2+1}}{1 + K_m}
\]
(20)
\[
\tau = t_1 = t_2 = \ldots = t_j
\]
(21)
\[
t_{m-j} = \sum_{k=m}^j t_k = (j + 1 - m) \tau
\]
(22)
Under these conditions Eq. (17) and (18) transform to
\[
I_j \quad \frac{\sqrt{\pi}}{nFAc_{\chi}^j} \sqrt{D} \quad \frac{1}{1 + K_j} + \frac{\sqrt{\pi D} / r_0}{1 + K_j}
\]
(23a)
where the function \(f_x(t_{m-j})\) can be expressed as
\[
\begin{align*}
&\left(\frac{1}{\sqrt{\pi y}} e^{-0.422 y + 0.0675 \log(y)} + 0.0058 \gamma_E [\log(y) - 1.47]^2 \right) \\
&\times \left(\frac{2}{\ln(4y) - 2 \gamma_E} \left[\ln(4y) - 2 \gamma_E\right] \right)^2
\end{align*}
\]
(24)
with
\[
y = D_{m-j}/r_0^2
\]
(25)
\[
\gamma_E = 0.577216
\]
(26)
\[
\gamma_E \text{ is Euler’s constant.}
\]

### 3. Applications to multipulse electrochemical techniques in spherical and cylindrical microelectrodes

This section deals with the study of the two multipulse techniques most often used experimentally: SCV, SWV and square-wave polarography (SWP). Nevertheless, the solutions deduced above for a DME (Eq. (10)) and for spherical and cylindrical microelectrodes (Eqs. (17) and (18) respectively) are valid for any pulse sequence that may be designed regardless of the applied potential, the pulse duration and the electrode size.

In SCV, SWV and SWP techniques all pulses have the same duration \(\tau\), and therefore
\[
\tau = t_1 = t_2 = \ldots = t_j
\]
(21)
\[
t_{m-j} = \sum_{k=m}^j t_k = (j + 1 - m) \tau
\]
(22)
Under these conditions Eq. (17) and (18) transform to
\[
I_j \quad \frac{\sqrt{\pi}}{nFAc_{\chi}^j} \sqrt{D} \quad \frac{1}{1 + K_j} + \frac{\sqrt{\pi D} / r_0}{1 + K_j}
\]
(23a)
for spherical electrodes or microelectrodes and to
\[
\frac{I_j}{nFAcA} \sqrt{\frac{\pi}{D}} = \frac{\sqrt{\pi D}}{r_0} \left( f_1(\tau) \right) \left( 1 + K_j \right) + \sum_{m=1}^{j-1} \frac{f_1((j + 1 - m)\tau) - f_1((j - m)\tau)}{1 + K_m}
\]
(23b)

for cylindrical electrodes or microelectrodes. It can be seen from these equations that the expected behaviour for spherical and cylindrical electrodes is different when \( r_0 \to 0 \). Thus while a stationary response
\[
\left( \frac{I_j}{nFAcA} \sqrt{\frac{\pi}{D}} \right) \rightarrow \frac{\sqrt{\pi D}}{r_0} \frac{1}{1 + K_j}
\]
(24)
is expected for spherical electrodes under these conditions, such a situation cannot be expected from Eq. (23b) for cylindrical electrodes [18,19]. This is discussed below in greater detail.

3.1. Cyclic staircase voltammetry (CSCV)

In this technique all the pulses have the same height \( \Delta E \). The sign of \( \Delta E \) may be positive or negative according to the potential sweep.

If we use the same nomenclature as in linear sweep voltammetry (LSV) [20], we can define
\[
u = |\Delta E| / \tau
\]
(25)
\[a = (nF/RT) \nu
\]
(26)
where \( \nu \) is the potential sweep rate.

The dimensionless function of the current for spherical electrodes or microelectrodes is defined as
\[
\psi_j = \frac{I_j}{nFAcA} \sqrt{\pi D} a
\]
\[= \frac{1}{\sqrt{\pi \tau a}} \left[ \frac{1 + \sqrt{\pi D} \tau / r_0}{1 + K_j} \right]
\]
\[+ \sum_{m=1}^{j-1} \frac{(j + 1 - m)^{-1/2} - (j - m)^{-1/2}}{1 + K_m}
\]
(27)

Fig. 1 shows three examples of application of the above equation in which calculations corresponding to two consecutive sweeps for \( \tau = 25 \) ms and \( |\Delta E| = 10 \) mV (\( \nu \) = 400 mV s\(^{-1}\)) have been performed. Fig. 1(a) shows the case of a plane electrode where \( \sqrt{\pi D} \tau / r_0 = 0 \). It can be seen that the current decreases on the negative sweep of the second cycle because the initial conditions have not been fully re-established. Fig. 1(b) corresponds to the case where \( \sqrt{\pi D} \tau / r_0 = 0.5 \) (\( r_0 = 1.77 \times 10^{-3} \) cm). It can be seen that the difference between the first and second cycles is less than in the previous case. Similarly, the voltammetric peak is less pronounced than when \( r_0 \to \infty \). Finally, Fig. 1(c) shows the situation when \( \sqrt{\pi D} \tau / r_0 = 50 \) (\( r_0 = 1.77 \times 10^{-3} \) cm). In this case it can be seen that the different cycles produce the same current signal with the response of each pulse being independent of the previous pulse sequence, unlike the case of plane electrodes and larger spherical electrodes where a memory of the previous pulses exists. Under the conditions of Fig. 1(c) (\( r_0 \to 0 \)), Eq. (27) transforms to
\[
\psi_j = \frac{1}{\sqrt{a}} \left( \frac{1}{1 + K_j} \right) r_0
\]
(28)

Similar extreme behaviour has been predicted for LSV with microelectrodes [21]. Eq. (28) corresponds to a stationary state of the system. Obviously, this stationary state is the same as that observed in chronoamperometry with spherical electrodes when \( \tau \to \infty \) [5]. Similarly, Eq. (28) predicts the existence of a plateau \( \psi_{max} = \sqrt{D}/a \) (1/r_0), at high overpotentials (K_j \to 0).

From Eq. (23b), following the operations of equation (27), we obtain
\[
\psi_j = \frac{1}{\sqrt{aD}} \left( f_1(\tau) \right) \left( 1 + K_j \right) + \sum_{m=1}^{j-1} \frac{f_1((j + 1 - m)\tau) - f_1((j - m)\tau)}{1 + K_m}
\]
(29)
for a cylindrical electrode. Fig. 2 shows an example of the application of this equation. As can be seen, Figs. 2(a) and 2(b) show similar behaviour to that in Figs. 1(a) and 1(b) for spherical electrodes. However, it can be seen in Fig. 1(c) (\( r_0 = 1.77 \times 10^{-3} \) cm) that neither the negative and