Derivation of a general theory for reversible multistep electrode processes in voltammetry with constant potential at spherical electrodes

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Abstract

The rigorous theory for a reversible multistep electrode process in voltammetry with constant potential at spherical electrodes is derived. The expressions for the surface concentrations, the concentration profiles of species participating in the different steps and the current as a function of time have been deduced. These expressions are valid for any number of steps in which the initial species is oxidized/reduced, whatever the relative values of the formal potentials of the different steps and for any electrode radius value, including plane electrodes and ultra-microelectrodes. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The study of electrode processes in which oxidation or reduction takes place in several steps is of great interest and very topical [1–7]. Thus, for example, fullerenes in general and C60 in particular can present up to five reversible one-electron reductions [8–12].

Nevertheless, the theoretical treatment of this type of process in voltammetry is not easy. Indeed, while the case of a two-step electron transfer (EE mechanism) has been widely dealt with in the literature [1,13–15], the theory corresponding to electrode processes with three or more steps is, to date, not very advanced [3,16,17].

The aim of this paper is to find a general analytical expression for the response of multistep electrode processes in voltammetry with constant potential at spherical electrodes. The use of spherical electrodes, such as the SMDE, for the study of multistep reactions, is very advantageous compared with solid plane electrodes (e.g. a glassy carbon or carbon electrode, a platinum or gold electrode). On the one hand, this electrode has the advantages afforded by its smooth and homogeneous surface and, on the other, which is fundamental in our case, the large overpotential for hydrogen evolution makes mercury the material of choice for cathodic processes [10]. As indicated in Ref. [10]: “the reduction of fullerenes, especially C60, should be performed at sufficiently negative potentials if one wants to generate highly charged anions (for example C60 6− and C70 6−). Therefore, the mercury electrode is very suitable for investigating the electrochemical behavior of fullerenes”.

As indicated above, although the solution for this type of problem is difficult in general, certain situations do exist where it is easy to obtain such expressions for these cases. In these situations, a problem of k steps can be treated as k independent problems of only one step. To this end, we must demonstrate that the boundary value problem can be expressed in the same general form for any step: i.e. the superposition principle is fulfilled [18,19]. This is the case when all steps are reversible and the diffusion coefficients of all species are equal when spherical diffusion is considered [20].

Taking into account the above considerations, we have deduced general expressions for the surface concentrations of species participating in the different steps, concentrations in terms of distance and time (concentration profiles) and current as a function of time for the spherical stationary electrode model. These expressions are valid for any number of steps considered in the multistep electrode process and whatever the relative values of the formal potentials of the different steps. The equations obtained are also valid for any electrode radius value, including plane electrodes ($r_0 \to \infty$) and ultra-microelectrodes ($r_0 \to 0$). Thus, the equations previously

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obtained in the literature for an EE mechanism at plane electrodes [13] and spherical microelectrodes [15] and for an EEE mechanism in plane electrodes [16] are easily deduced from our general equations.

2. Theory

The following mechanism represents the reduction of species $O_1$ in $k$ steps

step

1. $O_1 + n_1 e^- \leftrightarrow O_2 \quad E''_1$

2. $O_2 + n_2 e^- \leftrightarrow O_3 \quad E''_2$

... ...

$j$. $O_j + n_j e^- \leftrightarrow O_{j+1} \quad E''_j$

... ...

$k$. $O_k + n_k e^- \leftrightarrow O_{k+1} \quad E''_k$

where $E''_j$ ($j=1$ to $k$) is the formal potential for the corresponding step, all of which are totally independent, and $n_j$ is the number of electrons transferred in step $j$.

If we suppose that (a) only species $O_1$ is initially present in solution, (b) diffusion coefficients of all species are equal ($D$), (c) all steps are reversible and (d) spherical semi-infinite diffusion to and from the surface of the electrode takes place, then we have:

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

(2)

with the superindex $k$ being the number of steps of the electrode process and the subindex $i$ referring to the species considered.

It can be appreciated that the boundary value problem can be expressed by the following general equations for any value of $k$ (see Appendix A):

\[
\begin{align*}
t = 0, \quad r & = r_0; \\
t > 0, \quad r & \to \infty \\
& \quad (i=2, 3, \ldots, k+1)
\end{align*}
\]

(3)

\[
\begin{align*}
t > 0, \quad r & = r_0; \\
\sum_{i=1}^{k+1} \left( \frac{\partial \delta}{\partial r} \right)_{r=r_0} & = 0 \\
\delta_O(r_0, t) & = J_f \delta_{O_{i+1}}(r_0, t) \quad (j=1, 2, \ldots, k)
\end{align*}
\]

(4)

with

\[ J_f = \exp \left( \frac{n_1 F}{RT} (E - E''_{j}) \right) \]

(5)

By solving the differential equations system (1) with the above initial and limiting conditions for $k = 1$ and $k = 2$, it can easily be demonstrated that (see Eqs. (A6), (A13) and (A14) in Appendix A):

\[ \sum_{i=1}^{k+1} c_{O_i}^k (r_0, t) = c_{O_1}^0 \quad \forall k \]

(7)

and taking into account the surface conditions given by Eqs. (5) and (7) we obtain ($\forall k$) the following expressions, which are dependent only on the applied potential $E$, for the surface concentrations of species $O_i$ ($i=1, 2, \ldots, k+1$) (see Scheme (1)).

\[
\begin{align*}
c_{O_i}^k (r_0) & = \frac{1}{1 + \sum_{p=1}^{k} (\prod J_p)} c_{O_1}^0 \quad (i=k+1) \\
c_{O_i}^k (r_0) & = \prod J_p c_{O_1}^0 \quad (i=1, 2, \ldots, k)
\end{align*}
\]

(8)

The independence of time of the surface concentrations shown in these expressions allows us to carry out the generalization of the solution for this problem to any number of electrochemical steps, $k$. Thus, by applying the superposition principle (see Appendix A) we find the following expressions for the concentration profiles:

\[
\begin{align*}
c_{O_i}^k (r,t) & = c_{O_i}^0 + \Phi_t \frac{r_0}{r} \operatorname{erfc} \left( \frac{r - r_0}{2(Dt)^{1/2}} \right) \\
c_{O_i}^k (r,t) & = \Phi_t \frac{r_0}{r} \operatorname{erfc} \left( \frac{r - r_0}{2(Dt)^{1/2}} \right) \quad i=2, 3, \ldots, k+1
\end{align*}
\]

(9)

where

\[
\begin{align*}
\Phi_t & = \frac{1}{1 + \sum_{p=2}^{k} (\prod J_p)} c_{O_1}^0 \\
\Phi_t & = \prod J_p c_{O_1}^0 \\
\Phi_t & = \frac{1}{1 + \sum_{p=1}^{k} (\prod J_p)} c_{O_1}^0 \quad i=2, 3, \ldots, k
\end{align*}
\]

(10)

Once the concentration profiles are available, the expression for the current can be deduced. So, for mechanism (1) it holds that
\[
\frac{I^n}{n_1 FA} = D \left( \frac{\partial c_{2n}^*}{\partial r} \right)_{r=r_0} \\
\frac{I^n}{n_2 FA} - \frac{I^n}{n_1 FA} = D \left( \frac{\partial c_{2n}^*}{\partial r} \right)_{r=r_0} \\
\vdots \\
\frac{I^n}{n_{k-1} FA} - \frac{I^n}{n_{k-2} FA} = D \left( \frac{\partial c_{2n}^*}{\partial r} \right)_{r=r_0} \\
\frac{I^n}{n_k FA} - \frac{I^n}{n_{k-1} FA} = D \left( \frac{\partial c_{2n}^*}{\partial r} \right)_{r=r_0} \\
\]

(13)

Thus, from Eqs. (9) and (13) we obtain:

\[
\frac{I^n}{n_j FA} = - \left( \frac{D}{\pi n} \right)^{1/2} \left( 1 + \frac{\pi D \Delta t}{r_0} \right)^{1/2} \sum_{p=1}^{j} \Phi_n \]

(14)

where the functions \( \Phi_n \) are given by expressions (10)–(12).

The total current is

\[
I^k = I^n + I^{n+1} + \ldots + I^n = \sum_{j=1}^{k} I^n \\
\]

(15)

3. Results and discussion

We have analysed the above current expression in the following particular cases.

3.1. Planar electrode

From Eq. (16) with \( r_0 \rightarrow \infty \) we obtain the following expression for the current:

\[
\frac{I^k}{FA} = \frac{c_{2n}^*}{1 + \sum_{p=1}^{k} \left( \frac{\prod J_p}{\prod J} \right)} \\
\times \left\{ \sum_{j=1}^{k} \prod_{p=1}^{j} \prod_{f=p+1}^{j} J_f \right\} \\
\]

(17)

This expression is valid for any number of electrochemical steps \( k \) at a plane electrode. For multistep electrode processes, two particular cases of Eq. (17) have been treated in the literature:

(a) For \( k = 2 \) (EE mechanism) Eq. (17) simplifies to

\[
\frac{I^2}{FA} = \frac{c_{2n}^*}{1 + J_2 + J_2} \left( \frac{D}{\pi n} \right)^{1/2} (n_1 + n_2 + n_3) \\
\]

(18)

Eq. (18) can be rewritten as

\[
\frac{I^2}{FA} = \frac{1 + n_1 J_2/(n_1 + n_2)}{1 + J_2 + J_2} \\
\]

(19)

where \( I^{lim} \) is the current for \( E \) approaching \(-\infty\) (the limiting current), which is given by Eq. (18) with \( J_1 = J_2 = 0 \):

\[
I^{lim} = AF c_{2n}^* (n_1 + n_2) \left( \frac{D}{\pi n} \right)^{1/2} \\
\]

(20)

(b) From Eq. (17) with \( k = 3 \) (EEE mechanism) we obtain:

\[
\frac{I^3}{FA} = \frac{c_{2n}^*}{1 + J_2 + J_2 + J_2} \left( \frac{D}{\pi n} \right)^{1/2} (n_1 + n_2 + n_3) \\
\times (n_1 + n_2 + n_3) \\
\]

(21)

This equation, for \( n_1 = n_2 = n_3 = 1 \), becomes coincident with that previously derived by Lovric in Ref. [16] by making the diffusion coefficients of all species equal in this reference.

3.2. Ultramicrospherical electrode

The expression of current for a multistep electrode process in ultramicrospheres, when the steady state is reached, can be deduced from Eq. (16) setting \( r_0 \rightarrow 0 \):

\[
\frac{I^k}{FA} = \frac{c_{2n}^*}{1 + \sum_{p=1}^{k} \left( \frac{\prod J_p}{\prod J} \right)} \\
\times \left\{ \sum_{j=1}^{k} \prod_{p=1}^{j} \prod_{f=p+1}^{j} J_f \right\} \\
\]

(22)

The particular case of Eq. (22) for an EE mechanism \( (k=2) \) has been studied in the literature. In this case:

\[
\frac{I^2}{FA} = \frac{c_{2n}^*}{1 + J_2 + J_2} \left( \frac{D}{n_1 + n_2 + n_3} \right) \\
\]

(23)

Eq. (23), with \( n_1 = n_2 = n \) and \( J_1 = J_2 \) (i.e. \( E_{1} = E_{2}^2 \)) becomes coincident with Eq. (8) in Ref. [15].
From the general expression for the current (Eq. (16)) we have analysed the influence of electrode sphericity \((D/r_0)^{1/2}\) on the response obtained for a multistep process. Fig. 1 shows the \(I/E\) curves \(I^*(FAc_0^2(D/\pi)^{1/2} E - E_0^0)\) for a process with six successive electrochemical steps \((k=6)\). The values of formal potentials for the successive reductions and the diffusion coefficient have been taken from the experimental results in Ref. [10] for the reduction of fullerene \(C_{60}\). In this case \(E_{1}'^0 \gg E_{2}'^0 \gg E_{3}'^0 \gg E_{4}'^0 \gg E_{5}'^0 \gg E_{6}'^0\) and well-separated one-electron waves are obtained. From this figure it is clear that the current increases strongly when \(r_0\) decreases and it is also shown how the steady state is approached when \(r_0\) assumes values lower than \(5 \times 10^{-4}\) cm for \(t \geq 0.1\) s. So for \(r_0 = 10^{-4}\) cm, the relative difference between the limit currents corresponding to any step is less than 5% when the time varies between 0.1 and 1 s (see plot c).

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**Appendix A**

The theory presented in this work for a multistep electrode process is a generalization for any number of steps \(k\) of the equations obtained for \(k=1\) (E mechanism) and \(k=2\) (EE mechanism).

**A.1. E mechanism \((k=1)\)**

\[\text{O}_1 + n_1 \text{e}^- \leftrightarrow \text{O}_2 \quad \text{E}_1^0\]

Eq. (1) for \(k=1\) is

\[\frac{\partial c_{\text{O}_1}}{\partial r} = \frac{\partial c_{\text{O}_2}}{\partial r} = 0 \quad (A1)\]

and the boundary value problem is given by (Eqs. (3)–(6) with \(k=1\))

\[t=0, \quad r=r_0\]

\[t>0, \quad r \rightarrow \infty \quad c_{\text{O}_1} = c_{\text{O}_2}^0, \quad c_{\text{O}_2}^0 = 0 \quad (A2)\]

\[t>0, \quad r=r_0: \]

\[\frac{\partial c_{\text{O}_1}}{\partial r} \left|_{r=r_0} \right. + \frac{\partial c_{\text{O}_2}}{\partial r} \left|_{r=r_0} \right. = 0 \quad (A3)\]

\[c_{\text{O}_1}(r_0,t) = J_1 c_{\text{O}_2}(r_0,t) \quad (A4)\]

The resolution of the differential equations system (A1) with the above conditions (A2–A4) [21] gives the following expressions for the concentration profiles of species \(\text{O}_1\) and \(\text{O}_2\):

\[c_{\text{O}_1}(r,t)/c_{\text{O}_1}^0 = 1 - \frac{1}{1 + J_1} \left[ \frac{r_0}{r} \right] \text{erfc} \left( \frac{r-r_0}{2(Dt)^{1/2}} \right) \quad (A5)\]

\[c_{\text{O}_2}(r,t)/c_{\text{O}_2}^0 = \frac{1}{1 + J_1} \left[ \frac{r_0}{r} \right] \text{erfc} \left( \frac{r-r_0}{2(Dt)^{1/2}} \right) \quad (A6)\]

From these equations it is fulfilled that

\[c_{\text{O}_1}(r,t)+c_{\text{O}_2}(r,t)=c_{\text{O}_1}^0 \quad (r \geq r_0) \quad (A6)\]

For the particular case \(r=r_0\) (electrode surface), from Eq. (A5) we obtain the expressions for the surface concentrations (see Eq. (8)). The expression for the current is given by Eq. (16) with \(k=1\) [21].
A.2. EE mechanism \((k=2)\)

\[
\begin{align*}
O_1 + n_1 e^- &\rightarrow O_2 \quad E_1^{0*} \\
O_2 + n_2 e^- &\rightarrow O_3 \quad E_2^{0*}
\end{align*}
\]

In this case, Eq. (1) is

\[
\dot{c}_0^1 = \dot{c}_0^2 = \dot{c}_0^3 = 0
\]

(A7)

and the boundary value problem is now (Eqs. (3)–(6) with \(k=2\))

\[
\begin{align*}
t &= 0, \quad r \geq r_0 \\
r &= 0, \quad r \rightarrow \infty
\end{align*}
\]

(A8)

\[
\begin{align*}
t &= 0, \quad r = r_0 \\
\frac{\partial c_0^1}{\partial r} \bigg|_{r=r_0} + \frac{\partial c_0^2}{\partial r} \bigg|_{r=r_0} &= 0 \\
\frac{\partial c_0^1}{\partial r} &= J_1 c_0^1, \\
\frac{\partial c_0^2}{\partial r} &= J_2 c_0^2.
\end{align*}
\]

(A9)

(A10)

(A11)

We now have a system of differential equations (Eq. (A7)) and a set of boundary conditions (Eqs. (A8), (A9), (A10) and (A11)) with a new unknown, but they are formally identical to those of the E mechanism \((k=1)\) (Eqs. (A1), (A2), (A3) and (A4)). Thus, the resolution of differential equations system (A7) is analogous to that of Eq. (A1) and we have deduced (by applying the dimensionless parameters method [22]) the following expressions for the concentration profiles of species \(O_1, O_2\) and \(O_3\):

\[
\begin{align*}
\frac{c_0^1(r,t)}{c_0^1} &= 1 - \frac{1 + J_2}{1 + J_2 + J_1 J_2} \frac{r_0}{r} \text{erfc} \left( \frac{r-r_0}{2(D_t)^{1/2}} \right) \\
\frac{c_0^2(r,t)}{c_0^1} &= \frac{J_2}{1 + J_2 + J_1 J_2} \frac{r_0}{r} \text{erfc} \left( \frac{r-r_0}{2(D_t)^{1/2}} \right) \\
\frac{c_0^3(r,t)}{c_0^1} &= \frac{1}{1 + J_2 + J_1 J_2} \frac{r_0}{r} \text{erfc} \left( \frac{r-r_0}{2(D_t)^{1/2}} \right)
\end{align*}
\]

(A12)

Once again we see that

\[
\sum_{i=1}^{3} c_i^0(r,t) = c_0^1 \quad (r \geq r_0)
\]

(A13)

is fulfilled. At the electrode surface \((r=r_0)\), Eq. (A13) simplifies to those corresponding to surface concentrations (Eq. (8) with \(k=2\)), and the expression obtained for the current is given by Eq. (16) for \(k=2\).

Thus, from the results of Eqs. (A6) and (A13) and by applying the simple induction method, it is easily demonstrated that for any number of steps \(k\):

\[
\sum_{i=1}^{k+1} c_i^0(r,t) = c_0^0 \quad (r \geq r_0)
\]

(A14)

and, therefore, as a particular case of this equation for \(r=r_0\), Eq. (7) in this paper is fulfilled. The introduction of equation (7) as boundary condition considerably simplifies the resolution of the problem, which can be performed in a general way following the procedure outlined in the theory.

References