Analytical expressions for transient diffusion layer thicknesses at non uniformly accessible electrodes

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Abstract

Explicit analytical expressions for the diffusion layer thicknesses of disk and band electrodes of any size, under transient conditions have been deduced. We have applied these expressions to constant potential chronoamperometry and Linear Sweep Voltammetry (LSV). The analysis of the diffusion layer thickness and concentration profiles of electroactive species corresponding to the application of a constant potential have allowed us to characterise the evolution of the mass transport from linear (high sizes) to radial (microelectrodes). The influence of the time pulse, scan rate and the electrode radius has been analyzed, with limiting expressions corresponding to $E \gg E^0$ and $E \ll E^0$ were also deduced. The conditions required to attain a stationary state are discussed.

1. Introduction

Electrodes can be classified as either uniformly accessible or non uniformly accessible with respect to mass transport of species in solution [1–4]. Although non uniformly accessible microelectrodes require a much more complex mathematical treatment, they are most useful in electrochemistry due to their easy manufacture [1,4]. Among them, disks and bands are the most used.

The non uniform accessibility of the disk geometry leads to a more efficient mass transport to the electrode edge and to a shielding effect of this on the centre of the electrode [1–3,5,6]. In spite of that, this electrode remains as the most popular and practical for obtaining steady state voltammetry due both to its easy construction in a wide range of sizes (from macro to micro and ultramicro), and for the ease of controlled cleaning of its surface [1,5,7,8]. Concerning bands, they can be fabricated with one microscopic dimension and one macroscopic dimension, resulting in an electrode which displays a microelectrode behavior also giving rise to higher currents [1,2,9,10].

In both the above cases, the theoretical modelling of the mass transport shows that the current is an average quantity resulting from an average mass flux over the electrode surface [1,2,8,11]. Therefore, depending on the electrode size, the current will be the result of mixed mass transport, with a predominant component which could change from linear (high sizes or short times) to radial (small sizes or long times). In order to obtain a deeper physical comprehension of the mass transport at these non uniformly accessible electrodes and to establish conditions for which a stationary response can be obtained. One of the most interesting quantities to analyze is the Nernst diffusion layer thickness $\delta$. This provides an estimation of the spatial variation of the concentration profile of species participating in electrochemical reactions, and their dependence upon experimental control variables [1,12–14], and therefore it allows to characterize the diffusion field. So, it can be compared to the diameter of the electrode or the maximal diffusion length in an electrochemical cell in order to discuss the validity conditions for the approximation of semi-infinite linear diffusion of electroactive species. Also, the influence of convection on the response of a microelectrode can be detected from deviations of its diffusive currents or form the alteration of its diffusion layer [15,16].

In this paper we present analytical explicit expressions for the Nernst diffusion layer thickness of disk and band electrodes of any size under transient conditions, by considering the application of constant potential chronoamperometry. From these expressions we show that both the transient diffusion layer thickness, that changes across the surface of the electrode, and its average are independent of the applied potential when the charge transfer process...
is reversible. Moreover, from the analysis of the concentration profiles of oxidised species, we have characterised the evolution of the mass transport from linear (high sizes) to radial (microelectrodes).

When a linear sweep potential is applied we analyse the influence of the scan rate on the average diffusion layer thickness for disk and band electrodes of different sizes through the parameter $\frac{I_{G}}{Z}r_{d}$ determined from the expression:

$$\frac{I_{G}}{Z}r_{d} = \frac{r_{o}}{\eta} V (\sigma / D)$$

with $r_{o}$ being equal to the disk radius ($r_{d}$) or the band width ($w$), and the conditions under which it is possible to obtain a stationary response are discussed.

In all the cases considered, we have selected appropriate conditions in order that convection does not disturb the diffusive mass transport (see [13,15,16]).

2. Theory

2.1. Constant potential chronoamperometry

We will consider the following reversible charge transfer reaction

$$O + e^- = R$$

which takes place at an electrode of arbitrary geometry.

As the surface concentrations of species $O$ and $R$ are function only on the applied potential independently of the geometry considered [12], the Nernst diffusion layer thickness can be easily determined from the expression:

$$\delta_{G} = \frac{\Delta c_{O}(E)}{c_{O} / FA_{G} D_{O}}$$

$$\Delta c_{O}(E) = \frac{c_{O} - c_{O, surf}(E)}{c_{O}} = \frac{1 - K(c_{O}^{*} / c_{O}^{*})}{1 + K}$$

$$K = \exp\left(\frac{F}{R T} (E^{0} - E^{\circ})\right)$$

In the above equations, $I_{G}$ is the current obtained for the application of a constant potential $E$ and $q_{surf}$ is its value at the electrode surface, $D$ is the diffusion coefficient of oxidised and reduced species, $c_{O}^{*}$ the bulk concentration of species $O$ and $R$ are initially in the solution, $E$ the applied potential and $A_{G}$ the electrode area. The sub-index $G$ refers to the geometry considered.

Eqs. (1) and (2) are applicable to any voltammetric technique such as constant potential chronoamperometry or cyclic voltammetry, and to electrodes of any size and geometry.

If the electrode is not uniformly accessible, as with disk and band electrodes, the diffusion layer thickness given by Eq. (1) has an average character [1] and, in this case, it will be namely $\delta_{G}$, being $G = d$ for disks and $G = b$ for band electrodes.

In the following we will focus on the disk and band electrodes, for which we have presented an analytical expression for the current of process (1) valid for any multipotential step and potential sweep techniques. Thus, by taking into account Eqs. (1) and (2) of this paper and (10) in [19], we obtain the following expression for $\delta_{G}(t)$ and $\delta_{b}(t)$.

- Disk electrode (area $= \pi r_{d}^{2}$)

$$\delta_{G}(t) = r_{d} \frac{\pi}{4} f_{d}(\xi)$$

with [20]

$$f_{d}(\xi) = 0.7854 + \frac{0.44315}{\sqrt{\xi}} + 0.2146 \exp\left(- \frac{0.39115}{\sqrt{\xi}}\right)$$

- Band electrode (area $= w l$, with $w$ and $l$ being the band width and length)

$$\delta_{b}(t) = w \sqrt{\frac{f_{b}(\xi)}{l}}$$
\[ f_b(\xi) = \begin{cases} 
1 + \frac{1}{\sqrt{\pi \xi}} & \text{if } \xi < 0.4 \\
0.25 \sqrt{\frac{\pi}{\xi}} \exp(-0.4 \sqrt{\xi}) + \frac{\pi}{\ln(5.2945 + 5.9944/\sqrt{\xi})} & \text{if } \xi \geq 0.4 
\end{cases} \]  
\[ \xi = \frac{D_t}{r_0} \]  

and \( r_0 \) being equal to \( r_d \) or \( w \) in the case of disks and bands, respectively.

Alternative expressions for functions \( f_d(\xi) \) and \( f_b(\xi) \) have been discussed in Refs. [22–24].

Note that, in agreement with Eqs. (4)–(7), the expressions of the diffusion layer thickness for disk and band electrodes do not depend on the applied potential. This is due to the fact that the surface concentrations are constant [13].

The expressions for \( \bar{\delta}_d(t) \) and \( \bar{\delta}_b(t) \) present the following limiting values:

### 2.1.1. Planar limit

Under these conditions, \( \frac{r_0}{\sqrt{D_t}} \ll 1 \) (with \( r_0 \) being equal to \( r_d \) or \( w \)), and Eqs. (4) and (6) become (see also [22]):

\[ \bar{\delta}_d(0) = \bar{\delta}_d(\infty) \approx \sqrt{\pi D_t} \]  

Eq. (9) shows that the short time behavior of these electrodes is identical to that observed for planar electrodes, i.e., under these conditions the particular electrode geometry is not relevant since planar diffusion dominates the diffusion field (see [11,25,26]).

### 2.1.2. Microelectrode limit

In this case \( \frac{r_0}{\sqrt{D_t}} \ll 1 \) (with \( r_0 \) being equal to \( r_d \) or \( w \)), and Eqs. (4) and (6) simplifies to:

\[ \bar{\delta}_d^{\text{micro}} \approx r_d \frac{\pi}{4} \]  
\[ \bar{\delta}_b^{\text{micro}}(t) \approx \frac{w}{\pi} \ln \left( \frac{5.9944 \sqrt{D_t}}{w} \right) \]  

According to Eq. (1), it can be deduced that under these conditions a stationary current is obtained for microdisks (\( \bar{\delta}_d \) is constant, see Eq. (10) and [22,27]), whereas this is not possible for microbands (\( \bar{\delta}_b \) is time dependent, see Eq. (11)).

Eq. (10) is identical to that obtained at a spherical electrode of radius \( r_s \) for the case where \( r_s = r_d(\pi/4) \) for any value of the applied potential [1–3,25,26].
In Fig. 1 we have plotted the concentration profiles of oxidized species corresponding to the application of a potential step to a disk electrode for three values of \( r_d \) (500, 50 and 5 \( \mu \)m), and two values of the applied potential \( (E = E^0 \) and an \( E \) value corresponding to limiting current). These profiles have been numerically obtained by following the procedure described in Refs. [28–30] for a time \( t = 0.5 \) s.

From these profiles we have calculated the linear diffusion layer thickness \( \delta_d \) at any point of the disk surface \( (z = 0, 0 \leq r \leq r_d) \), shown in Fig. 2 (solid lines). We have also included in this figure the average diffusion layer thickness \( \delta_{d, \text{av}} \) calculated from Eq. (4) for comparison (dashed lines).

From Fig. 1 it can be deduced that, although the concentration profiles are necessarily affected by the applied potential, the diffusion layer thicknesses are independent of it. It can also be observed from this figure that the solution region adjacent to the electrode surface disturbed by the mass transport (which is directly related with the linear diffusion layer thickness \( \delta_d \)), is much lower than the disk radius for higher values of \( r_d \) (see also Fig. 2). Moreover, in this case (see curves with \( r_d = 500 \mu m \) in Fig. 1a and b), the dominant mass transport is that corresponding to planar diffusion, i.e., practically all the flux at the surface takes place at the normal coordinate \( z \), with the exception of \( r \) values close to the edge of the disk (in Fig. 2 we can compare the calculated gradient \( (\partial C_0/\partial Z)_{Z=0} \) along the \( R \) axis from Fig. 1a–f). This fact gives rise to a planar front for \( \delta_d \) as can be seen in Figs. 1a and b, and 2, which is practically coincident with the average value. As the disk radius decreases (see Fig. 1c–f), the linear diffusion layer thickness becomes comparable or even higher than \( r_d \), showing a continuous variation between the center and the edge of the disk. For a radius \( r_d = 5 \mu m \) (see Figs. 1e and f), the radial mass transport becomes dominant in the whole response.

Note that the average diffusion layer thickness \( \delta_{d, \text{av}} \) is directly related to the average mass flux at the disk surface. This relationship can be immediately obtained if we take into account that the current for disk and band electrodes can be calculated as [1,2],

\[
\frac{i_d}{F A_D C_{0}} = \frac{2}{R_d} \int_{0}^{R_d} \left( \frac{\partial C_0}{\partial Z} \right)_{Z=0} R dR
\]

\[
\frac{i_b}{F A_B C_{0}} = \frac{2}{W} \int_{0}^{X} \left( \frac{\partial C_0}{\partial Z} \right)_{Z=0} dX
\]

with \( C_0 = C_0/C_{0}^* \), \( R/r_d \), \( X=x/w \) and \( Z=z/w \) (disk) or \( Z=z/w \) (band), \( A_D \) and \( A_B \) denote the area of the disk and band electrodes. As the surface concentrations are independent of time, by comparing Eqs. (12) and (1), the following equivalences can be established:

\[
\frac{\delta_d}{R_d} = \frac{\Delta C_0(E)}{2} \int_{0}^{R_d} \left( \frac{\partial C_0}{\partial Z} \right)_{Z=0} R dR
\]

\[
\frac{\delta_b}{W} = \frac{\Delta C_0(E)}{2} \int_{0}^{X} \left( \frac{\partial C_0}{\partial Z} \right)_{Z=0} dX
\]

with \( \Delta C_0(E) \), \( \delta_d \) and \( \delta_b \) given by Eqs. (2), (4) and (6).

In Fig. 3 we have plotted the temporal evolution of \( \delta_d(t) \) and \( \delta_b(t) \), calculated from Eqs. (4) and (6) for disk (solid lines) and band (solid–dotted lines) electrodes of three sizes \( (r_d = 500, 50 \) and \( 5 \mu m \), with \( r_d \) being equal to \( r_d \) or \( W/2 \)). We have compared these curves with those obtained for spherical (dashed lines) and cylindrical (dotted lines) electrodes considering \( r_d = r_c \) (with \( \delta_c(t) \) and \( \delta_b(t) \) being calculated from Eq. (10) of Ref. [19]).

From these curves it can be seen that \( \delta_c \) increases with time in all cases. Moreover, in Fig. 3a it can be seen that these curves are all coincident at short times and only small differences appear between the couples bands and cylinders and spheres and disks at times higher than 0.2 s. This behavior indicates that for this electrode size and times below 0.2 s the prevalent diffusion field is planar, in such a way that the electrode geometry becomes irrelevant (see Eq. (9)). As the electrode size decreases (Fig. 3b and c), so does the temporal dependence of \( \delta_c \) and the different curves begin to separate until they reach a steady state in the case of disks and spheres or a quasi-steady state in the case of bands and cylinders (Fig. 3c). Note that the ratio between \( \delta_{d, \text{micro}} \) and \( \delta_{b, \text{micro}} \) tends to the value \( \pi/4 \) in agreement with Eq. (10) (see also [26,27]).

### 2.2. Staircase Voltammetry and Linear Sweep Voltammetry

Now we consider the application of a staircase of potential steps \( E_1, E_2, \ldots, E_p \), of pulse amplitude \( \Delta E \) and duration \( \tau \) in which the current is measured at time \( \tau \) (i.e., at the end of each potential step, Staircase Voltammetry, SCV), and also a linear ramp of potentials (which corresponds to the limit of pulse amplitude tending to zero for a given sweep rate, \( E = \Delta E/\tau \) as corresponds to Linear Sweep Voltammetry, LSV), in the way discussed in [13,31,32].

For the electrode process given in (I), the surface concentration of both species for any potential pulse are constant and do not depend on the previous history of the process. Moreover, in

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**Fig. 4.** Variation of the dimensionless linear diffusion layers \( (\delta_{d, \text{micro}}/r_d) \) and \( (\delta_{b, \text{micro}}/w) \) with the potential, calculated using Eqs. (18) and (19) for disks and bands, respectively, in Linear Sweep Voltammetry for different values of the \( \sigma \) parameter (shown in the curves): \( \eta_{\text{scv}} \) = 0.0, \( -E = 0.3 \) V, \( T = 298.15 \) K.
Ref. [19], we have presented a general expression for the current (or the surface concentration gradient) of electrodes of any geometry (Eq. (22)), in such a way the diffusion layer thickness for any potential pulse $p$ of the above sequence is given by:

$$\delta^p_G(E_p, t) = \frac{\Delta \rho^p}{I_p/(FA_G D c_0)}$$

From these curves it can be also observed that, for any electrode radius and for anodic potential values $E > E^0$, the average diffusion layer thickness takes a constant value in both disk and band electrodes given by:

$$\left(\frac{\delta_G^p}{r_d}\right)_{E=E^0} = \frac{1}{1.18 + 1.38\sqrt{\sigma}}$$

for disk electrodes and

$$\left(\frac{\delta_G^p}{w}\right)_{E=E^0} = \frac{1}{0.88 + 1.41\sqrt{\sigma}}$$

for bands.

This anodic limit behavior of Eqs. (23) and (24) is observed for $E - E^0 > 50$ mV with errors below 5%.

Moreover, for cathodic potential values $E < E^0$, the linear diffusion layer thickness takes the following limiting expressions:

$$\left(\frac{\delta_G^p}{r_d}\right)_{E=E^0} = \frac{\pi/4}{I_p/\vartheta_d} (\varrho)$$

for disk electrodes and

$$\left(\frac{\delta_G^p}{w}\right)_{E=E^0} = \frac{1}{I_p/\vartheta_d (\varrho)}$$

for bands, $\varrho_d$ and $\varrho_b$ are given in Eqs. (5) and (7), respectively.

The agreement between Eqs. (18) and (19) and their cathodic limiting behavior (Eqs. (25) and (26)) is observed for $E - E^0 \leq -180$ mV with errors below 5%.

3. Conclusions

Analytical explicit expressions for the Nernst diffusion layer thickness, $\delta$, of disk and band electrodes of any size under transient conditions have been deduced.

These equations have been applied to constant potential chronoamperometry, and it has been shown in a very simple way that the transient Nernst diffusion layer thickness, that changes along the surface of the electrode, and its average value are independent of the applied potential when the charge transfer process is reversible.

The study of the Nernst diffusion layer thickness together with the study of the concentration profiles of the electroactive species also allows the characterisation the evolution of the mass transport from linear (high sizes) to radial (microelectrodes).
We have also studied of the average diffusion layer thickness at disk and band electrodes when a linear sweep potential is applied. Limiting values for $i$ have corresponding to $E \gg E_0$ and $E \ll E_0$ have been obtained. We have also analyzed the variation of $i$ as a function of the parameter $\sigma = (Fv/RT)(r_0^2/D)$, with $r_0$ being equal to $r_d$ and $w$, which contains both the scan rate and the electrode radius.

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