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Singularities of the catalytic mechanism in its route to the steady state

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Abstract

Transient and stationary electrochemical behaviours for a first-order catalytic process have been analysed in order to show that a true stationary response only depends on the homogeneous rate constant values is obtained, in contrast to the cases of CE and EC processes. The general chronopotentiometric and voltammetric responses of a first-order catalytic process are compared.
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1. Introduction

In this paper, we will analyse the general behaviour of a first-order catalytic process by studying both its transient and stationary electrochemical responses. To do this, we compare this mechanism with the well-known first-order CE and EC processes pointing out that the necessary conditions for reaching an independent of time response are different for CE and EC processes and for a catalytic one. Indeed, the steady-state response sensitive to the kinetic of the homogeneous reaction of CE and EC processes is conditioned to the electrode radius of the microelectrode being comprised between the reaction and the diffusion layers thicknesses, whereas for a catalytic process this steady state can be reached even with large electrodes, and for its application to determine homogeneous rate constants the size of the electrode is conditioned only by the reaction layer thickness. As far as we know, this important difference has not been highlighted before.

This different behaviour between the CE (and also EC) and catalytic processes for high values of the rate constants is due to the fact that, for the CE mechanism

(see Scheme (I) of this paper), C species is required by the chemical reaction, whose equilibrium is distorted in the reaction layer, and by the electrochemical one, which is limited by the diffusion layer. For a catalytic mechanism (see Scheme (III) of this paper), C species is also required for both the chemical and the electrochemical reactions, but this last stage gives the same species, B, which is demanded by the chemical reaction in such a way that only in the reaction layer do the concentrations of B and C species take values different from those of the bulk of the solution.

Moreover, we examine the differences between chronopotentiometric and voltammetric transient responses for a catalytic mechanism and demonstrate that for steady state being reached and voltammetric and chronopotentiometric I/E responses being coincident, independently of the electrode size (from ultramicroelectrodes ($r_0 \rightarrow 0$) to planar electrodes ($r_0 \rightarrow \infty$)), it is only necessary that the chemical rate constants reach a sufficiently high value. This coincidence is due to the particular route for reaching the steady state presented by a catalytic mechanism, and it can never be expected for CE and EC processes, unless the electrode radius is small enough.

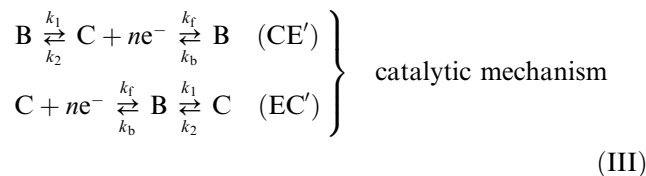Despite the fact that steady state can be achieved even with planar electrodes for a catalytic mechanism
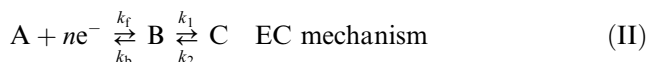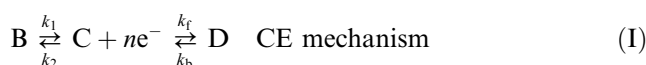
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whereas this fact is impossible for an E process, normalized transient voltammetric responses of both processes show identical behaviour if the equilibrium constant of the catalytic mechanism coincides with the quotient between the initial concentrations of the two electroactive species of the E mechanism.

2. Theory

2.1. General considerations about first- and pseudo-first-order CE, EC and catalytic mechanisms

We will simultaneously analyse the following reaction schemes:

$$B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + ne^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} D \quad \text{CE mechanism} \tag{I}$$

$$A + ne^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C \quad \text{EC mechanism} \tag{II}$$

$$\left.\begin{array}{l} B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + ne^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} B \quad (CE') \\[2mm] C + ne^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C \quad (EC') \end{array}\right\} \quad \text{catalytic mechanism}$$

$$\tag{III}$$

being k_f and k_b the rate constants of the heterogeneous reduction and oxidation processes, respectively. We define

$$K = \frac{k_2}{k_1} = \frac{c_B^*}{c_C^*}, \tag{1}$$

$$\kappa = k_1 + k_2, \tag{2}$$

where K is the equilibrium constant, c_B^* and c_C^* the equilibrium concentrations of two forms of the reactant, and k_1 and k_2 are the homogeneous rate constants.

Schemes (I) and (II) correspond to a CE (chemical–electrochemical) and an EC (electrochemical–chemical) first-order mechanisms, respectively, in which one of the species participating in the electrode process (the oxidised C, in the CE mechanism, and the reduced, B, in the EC mechanism) are chemically coupled to another species. Moreover, a catalytic electrode process is represented by Scheme (III). Note that the catalytic mechanism can be considered as a particular case of the CE mechanism (CE′) or of the EC mechanism (EC′), as is shown in Scheme (III). However, as far as we know to date, it has been only considered as a particular case of an EC process. This fact is probably because in most cases Scheme (III) has been treated when $K = 0$ [1–15].

If we assume $D_B = D_C$, we must consider the equations shown in Table 1 in order to deduce rigorously the expression for the transient response obtained for the three above reaction schemes when any electrical perturbation (i.e., a potential or a current) is applied

to an electrode. Note that Eqs. (I.1)–(I.11) in Table 1 are independent of the diffusion field (planar, spherical, cylindrical, etc.), the size of the electrode and the degree of reversibility of the charge transfer process. Thus, $\hat{A}$ is the diffusion operator corresponding to Fick's second law, which depends on the electrode geometry and on the time, and has the general linear form

$$\hat{A} = \frac{\partial}{\partial t} - D \cdot \nabla^2 + v \cdot \nabla, \tag{3}$$

where v is the velocity field and ∇ and ∇^2 the gradient and the Laplacian operators, respectively.

In the particular case of spherical diffusion, $\hat{A}$ takes the following form:

$$\hat{A} = \hat{A}_{\text{spher}} = \frac{\partial}{\partial t} - D\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]. \tag{4}$$

According to Table 1 it is clear that, in the case of CE or EC mechanisms, a system of three differential equations (Eqs. (I.5)–(I.7) or Eqs. (I.5), (I.6) and (I.9), respectively) and three unknown functions ($\phi(r,t)$, $\zeta(r,t)$, and $c_D(r,t)$ or $\phi(r,t)$, $\zeta(r,t)$ and $c_A(r,t)$, respectively) have to be solved, whereas in the case of a catalytic mechanism, $\zeta(r,t)$ always remains constant ($= c_B^* + c_C^*$, see Eq. (I.11)) [9,12,13] in such a way that only one differential equation (Eq. (I.5)) with one unknown function ($\phi(r,t)$) has to be solved [9,12,13]. This does not depend on whether the steady state has been reached or not.

2.2. Comparison of the stationary responses corresponding to CE and EC mechanisms with that for a catalytic mechanism

2.2.1. First- and pseudo-first-order CE and EC mechanisms

If we impose the condition

$$\frac{\partial \phi(r,t)}{\partial t} = 0 \tag{5}$$

that is fulfilled in fast kinetic reactions ($k_1 + k_2 \gg 1$, with $K \gg 1$ in CE and $K \ll 1$ in EC) when planar or spherical electrodes are used, a non true stationary response is obtained in voltammetry with constant potential [16–18] and in chronopotentiometry with constant current [19,20]. This is due to the responses in both electrochemical techniques being also related with $\zeta(r,t)$ function (Eq. (I.2)) through the corresponding boundary value problem, and this function depends on time, in agreement with Eq. (I.6).

Therefore, it is evident that an independent of time current in voltammetry with constant potential and/or an independent of time potential in chronopotentiometry with constant current will be obtained only when the following condition is also fulfilled [18]: