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The pathways towards the steady state *E*/*t* and *I*/*E* responses when using an alternating current

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Abstract

Equations corresponding to the application of an alternating current to spherical electrodes, including as limit cases planar electrodes and spherical microelectrodes have been deduced. We have also analyzed the evolution from transient to stationary potential–time and current–potential responses. This technique is particularly interesting when the reduction transition time does not exist since, when only the oxidized species is initially present, the reoxidation transition time for a transfer charge reaction under steady state conditions is only dependent on the frequency of the alternating current applied and, therefore, it is possible to detect any kinetic complication relating to the behaviour of the reduced species. We also propose methods for the accurate determination of thermodynamic and kinetic parameters of the charge transfer process from the analysis of the broad central zone of transient and stationary *E*/*t* and *I*/*E* curves, a region which is barely affected by capacitative distortion. The validity of the theoretical predictions has been experimentally tested with different reversible and irreversible systems.

Keywords: Steady state; Chronopotentiometry; Alternating currents; Ultramicroelectrodes

1. Introduction

In recent papers [1,2], we have analysed the application of Chronopotentiometry and Reciprocal Derivative Chronopotentiometry with programmed current at microelectrodes, since these present great advantages for carrying out electrochemical measurements and allow the rapid establishment of steady state signals, due to the enhancement of mass transport [3–10].

As has been previously pointed out, the use of programmed (time variable) currents at microelectrodes is needed in order to obtain a time dependent potential since, when a constant current is applied to an electrode of very small size, a constant, and therefore useless, potential is obtained [11–14]. Moreover, the application of programmed currents allows us to obtain $I(t)/E$ responses (with $I(t)$ being the applied current and E the measured potential), which are independent of the particular form of the current applied and also identical to that obtained when any time variable potential $E(t)$ is applied (voltammetric steady state I/E curve) [1]. This curves behaviour is observed independently of the degree of reversibility of the electrode process.

In this paper, we present the theory corresponding to the application of an alternating current of the form $I(t) = I_0 \sin(\omega t)$ to spherical electrodes of any size, including as limiting cases those corresponding to planar electrodes and to spherical microelectrodes. The theoretical treatment of spherical and sphere-cap microelectrodes under conditions of voltammetric steady state diffusion limited current has been previously reported by Oldham et al. [13–15] but in these references the application of programmed currents has not been considered. The analytical solutions obtained by us in this paper present great interest since they allow us to deduce

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compact and easily programmable expressions for the potential–time and current–potential curves corresponding to the following cases: (a) there is depletion of the oxidised species at the electrode surface and its reduction transition time is observed; (b) the surface concentration of the oxidised species does not become null and the depletion of the reduced species takes place, so that the reoxidation transition time is reached; (c) neither oxidised nor reduced species are depleted in the electrode surface and as a consequence, an oscillating potential–time curve is obtained.

The use of an alternating current at spherical microelectrodes is particularly interesting when the reduction transition time does not exist because: (a) it is possible to determine the behaviour of the reduced species by applying a single current, whereas when other programmed currents are used, this information cannot be obtained under steady state conditions unless both electroactive species are initially present [1]; (b) when only the oxidized species is initially present, the reoxidation transition time under steady state conditions is only dependent on the frequency of the alternating current applied and, therefore, its measurement leads to the detection of any kinetic complication relating to the behaviour of the reduced species; (c) the potential–time (*E*/*t*) curves obtained in this case present a broad central zone, barely affected by capacitative distortion, which leads to an accurate determination of thermodynamic and kinetic parameters of the electrode process.

Given that the expressions for the surface concentrations have been obtained in a compact form which is valid for any value of the electrode radius, we have also analysed the evolution from "transient" to "steady state" of the *E*/*t* and *I*/*E* responses for any degree of reversibility of the electrode process, deducing the limit electrode radius (r_0) and frequency (ω) values for which these curves can be considered as practically identical to those corresponding to stationary conditions. Moreover, easy criteria to determine kinetic and thermodynamic parameters of the process from the analysis of the stationary and transient *E*/*t* and *I*/*E* curves are presented.

Equations deduced in this paper have been tested with different well known experimental systems at different gold disc microelectrodes in order to show qualitatively the conditions under which the steady state can be reached. We have also studied the electrochemical behaviour of two experimental systems at a static mercury drop electrode (SMDE), in order to show how the electrode sphericity affects the response of the different electrode processes, and also to determine kinetic and thermodynamic parameters of the same systems from the analysis of their transient responses. The values obtained are in good agreement with those in the literature.

2. Experimental

The computer driven potentiostat-galvanostat was designed and constructed by QUICELTRON (Spain).

Pulse and waveform generation and data acquisition were performed using i-SBXDD4 and DAS16-330i (ComputerBoards, USA) boards, respectively. All computer programmes were written in our laboratory. Experimental *E*/*t* curves were sampled at a frequency 2000 times higher than that of the alternating current and then digitally filtered in order to reduce the noise. The *I*/*E* curves were obtained by plotting the alternating applied current, $I_0 \sin(\omega t)$, vs. the measured potential, *E*, in the interval $0 \leqslant t \leqslant \tau$, with τ being the transition time of the process.

A three electrode cell was employed in the experiments. Static mercury-drop electrode (SMDE) and gold disc microelectrodes of different radii served as working electrodes. The SMDE was constructed using a DME, EA 1019-1 (Metrohm) to which a homemade valve was sealed. The electrode radii of the SMDE were determined by weighing a large number of drops (in this case, the errors observed were negligible). The counter electrode was a Pt foil and the reference electrode was a Ag|AgCl| 1.0 M KCl electrode.

All the kinetic and thermodynamic values obtained correspond to series of five replicates. The results obtained are the mean of the five experimental values. The errors correspond to the standard deviation.

Ferrocene, tetrabutylammonium hexafluorophosphate (PF_6TBA), CH_3CN, $FeCl_3$, $K_2C_2O_4$, $H_2C_2O_4$, $CrCl_3$ and $NaClO_4$ were of Aldrich, reagent grade. All chemical reagents were used without further purification.

Nitrogen gas was passed through solutions for deaeration for 15 min prior to measurements.

The diffusion coefficients of Cr^{3+}, ferrocene and Fe^{3+} were determined by chronoamperometric measurements of Cr^{3+} in $NaClO_4$ 0.5 M solutions at a SMDE ($r_0 = 1.644 \times 10^{-2}$ cm), and ferrocene 10 mM in CH_3CN + 0.25 M PF_6TBA and $FeCl_3$ 10 mM + 0.5 M $K_2C_2O_4$ at a gold electrode ($r_0 = 5 \times 10^{-2}$ cm), obtaining $D_{Cr^{3+}} = (6.48 \pm 0.06) \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$, $D_{\mathrm{ferrocene}} = 2.26 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ and $D_{Fe^{3+}} = 7.23 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$. All the values obtained are in agreement with previous results in the literature (see [1,14,16–19]).

3. Theory

We will consider the charge transfer reaction,

$$\mathrm{O} + n\mathrm{e}^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{R}, \tag{I}$$

which takes place at a stationary spherical electrode of area $A = 4\pi r_0^2$, with r_0 being the electrode radius, when