



Analytical solution for Reverse Pulse Voltammetry at spherical electrodes: A remarkably sensitive method for the characterization of electrochemical reversibility and electrode kinetics

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ABSTRACT

Reverse Pulse Voltammetry (RPV) is a powerful double pulse technique for kinetic studies. The theory of this technique for slow charge transfer processes at spherical electrodes is developed. An explicit analytical solution is deduced applicable to electrodes of any size, whatever the reversibility of the system and the length of the two potential pulses. From this solution we examine the influence on the RPV response of the electrode sphericity and the kinetics of the electrode process. It is shown that visual inspection of the curves provides immediate valuable information on electrochemical kinetics. Moreover, simple diagnosis criteria are established and general working curves derived for the quantitative extraction of the kinetic parameters and the formal potential. Some particularities in the morphology of the anodic branch of RPV curves for slow charge transfer processes when the second potential pulse is sufficiently large are also described. The merits of RPV as an exquisitely sensitive measure of electrochemical reversibility and electrode kinetics are advocated.

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1. Introduction

This paper seeks to advocate Reverse Pulse Voltammetry (RPV) as a very powerful double pulse technique for the characterization of electrode reactions [1,2] and of electrochemical reversibility and electrode kinetics in particular. In the method, during the first step the potential is set at diffusion limiting conditions and subsequently the electrogenerated species is electrochemically examined by scanning the second applied potential in the potential region of interest. The current is sampled at the end of the second pulse and RPV curve is a plot of the sampled current vs. the value of the second potential.

RPV technique offers several advantages against other common electrochemical techniques such as cyclic voltammetry, permitting a higher control of the reaction conditions, minimization of charging current effects and it is more convenient for quantitative analysis [3]. In addition, the mathematical treatment needed to tackle this technique is considerably less complex.

Among other applications, this technique has been employed for evaluation of the electrochemical reversibility of electrode

processes [3,4], in the study of electrogenerated products [3] and reaction mechanisms [5–8] and for determination of diffusion coefficients [9], being particularly valuable when unstable products are involved.

According to the potential program of RPV technique, before the application of each double pulse, equilibrium conditions are recovered [5,8,10]. So, from a theoretical point of view, the RPV problem is equivalent to that of the application of a double potential pulse for which the first step is controlled by diffusion. The theory of RPV technique for charge transfer processes with finite kinetics has been only developed for planar diffusion [11–15], but no analytical solution is available for electrodes of spherical geometry. The aim of this paper is to fill this gap by presenting an easily manageable rigorous and explicit analytical solution for the current–potential–time response under RPV conditions, valid for spherical electrodes of any size, for any length of the two potential pulses and whatever the reversibility of the charge transfer process. We solve the problem by means of a mathematical procedure based on an extension of Koutecky's dimensionless parameter method detailed in Appendix A.

Having at our disposal an explicit analytical solution is a great advance with respect to numerical calculations since from the analytical equation the variables determining the system response can be entirely examined and simplified expressions for particular cases of interest can be derived. Thus, from the solution obtained we analyze the effect of the electrode sphericity as well as the

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value of the RPV for the determination of the electrode kinetics. In this paper it is shown that the electron transfer coefficient and the electrochemical reversibility can be easily estimate by analysis of RPV curves. Indeed, at spherical electrodes the width of RPV curves strongly depends on the heterogeneous rate constant and the symmetry on the transfer coefficient, in such a way that simple visual inspection of RPV curves provides an assessment of the kinetic character of the charge transfer reaction. An additional insight of this paper is that single point measurements in RPV curves (the half wave potentials of the anodic and cathodic branches) are good enough to achieve the complete characterization of the system from RPV experiments performed with different double pulse durations, making unnecessary the use of complex fitting procedures. For this purpose, working curves for the extraction of the kinetic parameters and the formal potential are given.

The case at which both electroactive species are initially present in solution is also covered by the theory here developed. This aspect is of great interest since there exist several situations at which the presence of both members of the redox couple is expected, such as for the study of metal species [16] or of some ions which disproportionate into two electroactive species [17].

It is worth highlighting that these theoretical results are valid for any value of the duration of either potential pulses, which is especially valuable when studying charge transfer processes with finite kinetics. The appearance of a maximum in the anodic branch of the RPV curve is described for charge transfer processes with finite kinetics when the duration of the second pulse is similar to that of the first one. This behaviour is analyzed and the conditions under which it is most obvious are pointed out.

The clear merits of RPV for quantitative voltammetric measurements of electrode processes are evident.

2. Theory

We will study the case of a charge transfer reaction taking place at a stationary spherical electrode:



After applying an electrochemical perturbation, the diffusion mass transport of the electroactive species is described by the following differential equation system:

$$\hat{\delta}c_O^{(j)}(r, t) = \hat{\delta}c_R^{(j)}(r, t) = 0; \quad j \equiv 1, 2 \quad (2)$$

where the superscript refers to the j th pulse and $\hat{\delta}$ is the diffusion operator for spherical geometry:

$$\hat{\delta} = \frac{\partial}{\partial t} - D \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \quad (3)$$

We assume that both electroactive species have the same value of the diffusion coefficient ($D_O = D_R = D$).

The RPV waveform consists of successive double potential pulses, the first potential value being set at diffusion limiting conditions ($E_1 \rightarrow -\infty, 0 \leq t \leq t_1$) and the value of the second one varying towards anodic potentials ($E_2, t_1 \leq t \leq t_2$) [1,2,11]. The current is sampled at the end of the second pulse ($I_2(t_2)$) and plotted vs. E_2 value (see Fig. 1).

Given that the initial equilibrium conditions are re-established before each double potential pulse, the theory for RPV technique matches that for the application of two potential steps with $E_1 \rightarrow -\infty$. By dividing the double pulse time into two periods ($0 \leq t \leq t_1$ and $t_1 \leq t \leq t_2$), the solution for the first step corresponds to the well-known solution for a charge transfer process at a spherical electrode under limiting conditions, the current-time expression being [1,2]:

$$I_{1d}(t) = I_d(\infty) \left(1 + \frac{r_0}{\sqrt{\pi D t}} \right) \quad (4)$$

For $t \geq t_1$ the applied potential is stepped to E_2 and the boundary value problem is given by:

$$\left. \begin{array}{l} \tau_2 \geq 0, \quad r \rightarrow \infty \\ \tau_2 = 0, \quad r \geq r_0 \end{array} \right\} c_O^{(2)} = c_O^{(1)}, \quad c_R^{(2)} = c_R^{(1)} \quad (5)$$

$$\tau_2 > 0, \quad r = r_0 : \quad \left(\frac{\partial c_O^{(2)}(r, t)}{\partial r} \right)_{r=r_0} = - \left(\frac{\partial c_R^{(2)}(r, t)}{\partial r} \right)_{r=r_0} \quad (6)$$

$$D \left(\frac{\partial c_O^{(2)}}{\partial r} \right)_{r=r_0} = k^0 K_2^{-\alpha} c_O^{(2)}(r_0, t) - k^0 K_2^{1-\alpha} c_R^{(2)}(r_0, t) \quad (7)$$

In Eq. (7) we assume that the transition state does not change with potential and so the same value of α applies to the forward and reverse processes.

We introduce the following variable change:

$$u_i^{(j)}(r, t) = \frac{c_i^{(j)}(r, t) \cdot r}{c_i^* \cdot r_0}; \quad \begin{array}{l} i \equiv O, R \\ j \equiv 1, 2 \end{array} \quad (8)$$

so that the differential equation system becomes equivalent to that of linear diffusion:

$$\frac{\partial u_i^{(j)}(r, t)}{\partial t} - D \frac{\partial^2 u_i^{(j)}(r, t)}{\partial r^2} = 0; \quad \begin{array}{l} i \equiv O, R \\ j \equiv 1, 2 \end{array} \quad (9)$$

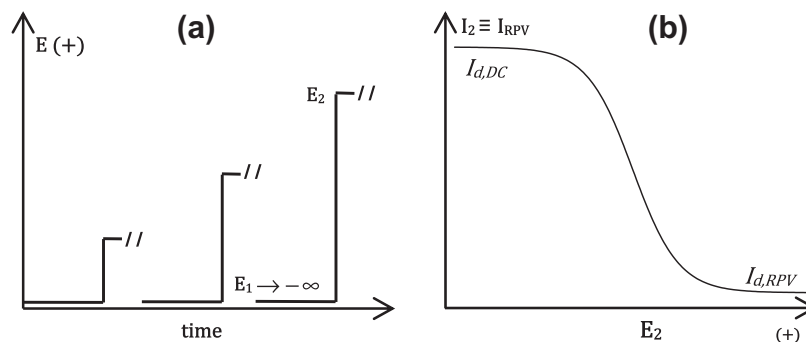


Fig. 1. Reverse Pulse Voltammetry technique: (a) potential–time program; (b) RPV curve.

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