



Numerical simulation study on cyclic reciprocal derivative chronopotentiometry of reversible electrode reaction coupled with Langmuir adsorption

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ARTICLE INFO

Article history:

Received 2 October 2012

Received in revised form

15 December 2012

Accepted 23 December 2012

Available online 23 January 2013

Keywords:

Cyclic reciprocal derivative

chronopotentiometry

Langmuir adsorption

Diffusion

Adsorption coefficient

Finite difference

ABSTRACT

Theoretical modeling and analyzing of reversible electrode reaction coupled with Langmuir adsorption is presented using cyclic reciprocal derivative chronopotentiometry (CRDCP) with symmetrical programmed current applied, in which the finite difference method was firstly used to solve the boundary value problem corresponding to the electrode processes. The algorithm described in this paper is available to solve analogous difference equations with nonlinear boundary conditions. Distinct features of $dt/dE-E$ curves for typical models of electrode processes are obtained. If the adsorption coefficients of the electroactive species are of different orders of magnitude, the predominant peak splitting of the $dt/dE-E$ curves can be observed, corresponding to the adsorption peaks and diffusion peaks. The sequence of the diffusion and adsorption peaks can indicate the strong adsorption of either reactant or product.

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1. Introduction

The adsorption of electroactive species on the electrode surface is a prevalent phenomenon for electrode processes, and is actually pivotal to the mechanisms of the electron transfer reactions [1–5]. Thermodynamic and kinetic parameters of adsorption process obtainable in electrochemical methods not only provide information related to the adsorption properties, but also allow understanding the microstructure of the electrode surface and the adsorption layers at the solid/liquid interface [6–10]. Therefore, special attentions have been paid to electrochemical studies on adsorption processes involved in electron transfer reactions [11–17].

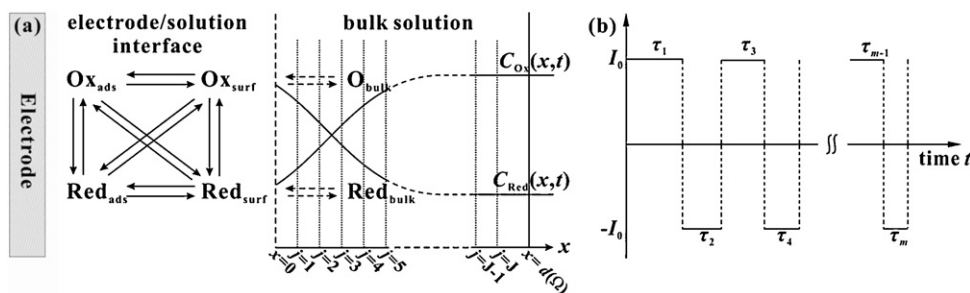
In the early works, Anson, Bard and Murray et al. have resorted to the use of chronopotentiometry to study the adsorption behavior of electroactive species on the electrode surface [18–22]. Then, Wopshall and Shain carried out systematic theoretical study on the stationary electrode polarograms for electrode reaction in the presence of adsorption [23]. Over the past four decades, both potential- and current-controlled electrochemical methods have been developed to study electrode reactions complicated with adsorption

processes (see Table S1 and references therein). Accordingly, different mathematical models were analyzed and so that, various methods for determination of the electrochemical parameters were proposed and adsorption mechanisms were then discriminated [24–32]. As reported in the literature, a variety of mathematical methods have been applied to solve the equations for analysis of the adsorption behavior on the electrode surface. However, treatments of the mathematical models in which diffusion conditions complicated with adsorption isotherms, especially the non-linear ones, were of mathematical complexity. Consequently, theoretical derivations and analysis have been restricted to certain limiting cases or only the approximate solutions were obtained even for the basic reversible charge transfer reaction [24,33–36].

Cyclic reciprocal derivative chronopotentiometry (CRDCP) [37–40], derived from the classic chronopotentiometric methods (see Ref. [41] and references therein), is sensitive to the adsorption species involved in electrode reactions [42–48]. In the current-controlled techniques, the current depletion at the electrode/solution interface is related to the variation of the electrode potential, which is based on the surface concentrations of the electroactive species. On the one hand, the balance area of the potential–time ($E-t$) response indicates that the Faradic behavior dominates the electrode process and thus, yields the extreme values of the $dt/dE-E$ curves deduced from the reciprocal of the time derivative of the $E-t$ expressions. On the other hand, at both the

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Scheme 1. Schematic illustration of (a) the Nernst electrode reaction coupled with Langmuir adsorption and (b) successive symmetrical programmed currents applied, referring to the literature [39,66].

beginning and end of the electrode process, the rapid change in potential with time causes the near zero base line, while the charging effect of the electric double-layer may slow down the rapid change and raise the base line. The S-shaped $E-t$ curves obtained in ordinary chronopotentiometry [18,49] thus can be converted to the peak-shaped curves, which provide well-defined electrochemical signatures and have higher sensitivity [50,51]. Furthermore, the accompanied flux of the electroactive species involved in the electrode processes coupled with adsorption and/or chemical reactions divides the contribution of the applied current and consequently, results in the perturbation of the $E-t$ and $dt/dE-E$ responses. Similar to cyclic voltammetry (CV), CRDCP can also provide insight view into the mechanisms of the charge transfer reactions occurring at the electrode/solution interface, and possess distinct superiority in both theoretical and experimental studies as an improved current-controlled technique [52–54].

In this work, CRDCP with symmetrical programmed current applied is extended to study the reversible electrode reaction coupled with Langmuir adsorption. Finite difference method is outlined and firstly used to solve the boundary value problem corresponding to the theoretical model of the electrode process under current-controlled condition. $dt/dE-E$ curves of six typical models of electrode processes with successive programmed currents applied are simulated. The peak splitting observed in the $dt/dE-E$ curves is interpreted.

2. Theory and computation

Langmuir isotherm is the most common model used to describe the adsorption equilibrium at the electrode/solution interface [55–57]. The Langmuir parameters obtained in electrochemical methods are related to the adsorption capacity, the adsorption site of the adsorbent, the adsorbate size and its orientation on the adsorbent surface, as well as the adsorption Gibbs free energy, entropy and enthalpy [58,59]. Langmuir isotherm is often selected in the theoretical modeling of various electrochemical processes, such as electrosynthesis [60], electrocatalysis [61], electropolymerization [62] and the self-assembly monolayer [63] of the adsorption process. In the experimental studies such as the corrosion inhibition effect [64,65] and the adsorption remove of heavy metal ions [59], Langmuir isotherm is also applied for data fitting.

In a previous study, Molina' group reported the application of cyclic chronopotentiometry and CRDCP for the characterization of the electrode reactions with the electroactive reactant and/or product adsorbed obeying both Henry and Langmuir isotherms [44,49]. It was assumed for Langmuir adsorption, the system current was spent only on the adsorbed molecular and correspondingly, the theory was extended to study the electrochemical behavior of the electrodes coated with electroactive molecular films [45–47]. In this work, we consider that the flux by both diffusion and

adsorption contributes to the charge transfer for electrode reaction coupled with Langmuir adsorption, which contains non-linear boundary condition. A more generalized model of the electrode process is presented based on the following assumptions:

(i) The reversible electrode process considered is given by $\text{Ox} + n\text{e} = \text{Red}$. The schematic of the electrode process and the symmetrical programmed current applied of the form $I_1(t) = I_0$, $I_2(t) = -I_0, \dots, I_m(t) = (-1)^{m+1}I_0$ are illustrated in Scheme 1. For the Nernstian featured process, the charge transfer rate is much faster than that of the diffusion. Meanwhile, the rates of adsorption and desorption of both Ox (oxidized species) and Red (reduced species) are sufficiently rapid and adsorption equilibrium is always maintained. Consequently, the limiting step of the electrode process is the diffusion rate; (ii) planar electrode is employed and the theoretical model follows one dimensional space system. The solution remains unstirred throughout. Only Ox exists at the beginning of the electrolysis, with the initial concentration noted by C_{Ox}^* ; (iii) adsorption of the solvent and the electric double-layer effect is neglected; (iv) in general, competitive adsorption of Ox and Red on electrode surface is considered and the Langmuir isotherm is given by [9]

$$\Gamma_{\text{Ox}}(t) = \frac{\Gamma_{\text{Ox},s}\beta_{\text{Ox}}C_{\text{Ox}}(0,t)}{1 + \beta_{\text{Ox}}C_{\text{Ox}}(0,t) + \beta_{\text{Red}}C_{\text{Red}}(0,t)} \quad (1)$$

$$\Gamma_{\text{Red}}(t) = \frac{\Gamma_{\text{Red},s}\beta_{\text{Red}}C_{\text{Red}}(0,t)}{1 + \beta_{\text{Ox}}C_{\text{Ox}}(0,t) + \beta_{\text{Red}}C_{\text{Red}}(0,t)} \quad (2)$$

where $C_i(0,t)$ (in mol L^{-1}) is the surface concentration ($x=0$) of electroactive species i ($i = \text{Ox}$ and Red , respectively) at time t . $\Gamma_i(t)$ (in mol cm^{-2}) is the surface excess and $\Gamma_{i,s}$ is the corresponding maximum surface excess of species i and is in relationship with the adsorption site of the electrode surface, the geometry of the adsorbent molecular and the adsorption orientation. $\Gamma_{i,s}$ depends on the electrode potential, since in these cases the adsorption orientation is affected by the potential applied [67,68]. The Langmuir adsorption coefficient β_i (in L mol^{-1}), which reflects the affinity between the adsorbate and the electrode surface, is related to the adsorption free energies. In fact, according to the assumption of the Langmuir adsorption model, the Langmuir adsorption coefficient β_i depends on the energy and the surface state of the electrode, and therefore, varies with the electrode potential [68,69]. In this paper, for mathematical feasibility, we suppose that $\Gamma_{i,s}$ and β_i is invariable at the whole potential range.

The initial and boundary conditions describing the electrode process are expressed by,

$$C_{\text{Ox}}(x,t)|_{x=0,t=0} = C_{\text{Ox}}^*, \quad C_{\text{Red}}(x,t)|_{x=0,t=0} = 0 \quad (3)$$

$$C_{\text{Ox}}(x,t)|_{x \rightarrow +\infty} = C_{\text{Ox}}^*, \quad C_{\text{Red}}(x,t)|_{x \rightarrow +\infty} = 0 \quad (4)$$

$t > 0, x = 0$:

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