



# Analysis of the hydrogen electrode reaction mechanism in thin-layer cells. 3. Study of hydrogen electro-oxidation by scanning electrochemical microscopy



Mariela A. Brites Helú, José L. Fernández \*

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, (S3000AOM) Santa Fe, Santa Fe, Argentina

## ARTICLE INFO

### Article history:

Received 1 September 2016  
Received in revised form 31 October 2016  
Accepted 28 November 2016  
Available online 5 December 2016

### Keywords:

Hydrogen oxidation reaction  
Scanning electrochemical microscopy  
Kinetic analysis  
Thin-layer cell  
Reaction mechanism

## ABSTRACT

Scanning electrochemical microscopy (SECM) in the feedback mode was used to analyze the complete mechanism of the hydrogen oxidation reaction (*hor*). A general SECM equation was proposed to carry out the kinetic analysis of the dependences of the tip current ( $i_T$ ) on the substrate potential ( $E_S$ ) and on the tip-substrate distance ( $d$ ). This SECM equation involves the contribution of a thin-layer cell (TLC) with no aprioristic restrictions about the reaction mechanism. A dependence of the TLC current on  $E_S$  previously developed for the *hor* operating through the Tafel-Heyrovsky-Volmer mechanism was included in the proposed SECM model. The domain of conditions where the equation properly reproduces the SECM responses was determined by contrasting the calculated  $i_T(E_S, d)$  dependences with simulated curves obtained by a numerical method using varied kinetic and geometric parameters. The experimental conditions where the model can be used were explored by analyzing the *hor* on Pt. The present treatment provides a versatile tool for the application of SECM to the kinetic and mechanistic analysis of the *hor*, which can be easily adapted for the analysis of any multi-step electrocatalyzed reaction on infinite substrates.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Scanning electrochemical microscopy (SECM) is a powerful electrochemical technique for the analysis of reaction mechanisms of electrocatalyzed reactions [1–3]. The great spatial resolution of this technique allows to restrict the kinetic analysis over confined submicrometer-sized domains of a macroelectrode and to achieve high mass transport rates (equivalent to those attained with micro- and nanoelectrodes). These properties make SECM (and its variants) an exceptional tool to analyze the effects of the surface state on reactions electrocatalyzed by heterogeneous electrode surfaces (i.e. structural [4–6], conformational [7,8], and compositional [9–11] effects). The technique has already been employed to study mechanistic aspects of a number of emblematic reactions in Electrocatalysis, which in general involve several elementary steps and the participation of one or more adsorbed intermediates, as are the hydrogen electrode reaction (HER) and the oxygen electrode reaction (OER) [1,2]. More specifically, the HER was studied by SECM in different operation modes, both to analyze its cathodic branch, the hydrogen evolution reaction (*her*) [12–17], and its anodic branch, the hydrogen oxidation reaction (*hor*) [7,10,17–27]. This last one (which is defined in acid media by Eq. (1)), is

technologically important in energy conversion systems such as hydrogen-based fuel cells [28] where it operates on the anode under mixed control in the highly demanding mass-transport optimized conditions of real devices. Thus, the *hor* mechanism and kinetics play important roles in the anode performance. Besides, the knowledge of mechanisms related with poisoning by CO or impurities in the fuel, and with the tolerance to poisoning by cooperative effects still requires deeper investigations.



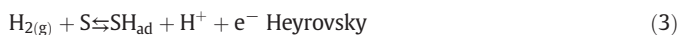
Under these premises, the *hor* on different types of electrodes was analyzed using both feedback-based and generation collection modes. Bard and co-workers [18] were the first to analyze the *hor* by SECM pointing to understand the metal oxidation and adsorption of anions at high overpotentials. Contemporarily, Hillier and co-workers reported a kinetic analysis of the *hor* in the presence of CO on polycrystalline Pt [19,21], on Pt nanoparticle ensembles [20], and on combinations of Pt, Ru and Mo through combinatorial studies [22]. Furthermore, Zoski [23] carried out a kinetic study of the *hor* on polycrystalline Pt, Ir and Rh using feedback-based approach curves to obtain the exchange current densities on these metals. More recently, studies of the *hor* on multimetallic catalysts [10,24], supported nanoparticle arrays [17,25] and single nanoparticles [7] were reported. These works proved the

\* Corresponding author.  
E-mail address: [jlfernan@fiq.unl.edu.ar](mailto:jlfernan@fiq.unl.edu.ar) (J.L. Fernández).

usefulness of SECM to reveal mechanistic details of this reaction even though they used approximate models to describe the *hor* mechanism (single step irreversible reaction [29]).

The kinetic analysis of electrode reactions by SECM in the feedback mode was recently comprehensively reviewed [30]. This type of study is usually carried out by correlation of experimental dependences of the tip current ( $i_T$ ), or of its normalized value ( $I_T$ ) respect to the current at infinite tip-substrate distance ( $i_{T,\infty}$ ), on the normalized tip-substrate distance ( $L = d/a$ , where  $a$  is the tip radius) and on the substrate potential ( $E_S$ ). The theoretical dependences to perform the correlations were generated by solving the diffusion equations for the SECM geometry and assuming a particular reaction mechanism for the substrate electrode reaction. On this sense, numerically simulated  $I_T$ - $L$ - $E_S$  curves for a single Butler-Volmer type electrode reaction at the substrate were earlier reported [31] and can be used to analyze single-step electrode reactions. Moreover, an analytical equation is available for an irreversible first-order reaction [29]. For the case of electrode reactions whose mechanisms involve more than one elementary step, these theoretical formalisms can be applied only in restricted potential ranges where one step becomes the rate determining step and a first-order dependence of the reaction rate on the reactant surface concentration is accomplished [32]. Thus, the rate constant (or the exchange current density) measured under these conditions is only an apparent indicator of the electrocatalytic activity and can hardly be related to the complete set of elementary kinetic parameters.

The *hor* operates by a three-step mechanism known as Tafel-Heyrovsky-Volmer (THV) mechanism, which in acid media involves steps (2) to (4) [32] (where S denotes an active site). The reaction proceeds simultaneously by two independent routes, which are the Tafel-Volmer and the Heyrovsky-Volmer routes, respectively [33]. The contribution of each of these routes to the whole reaction rate depends on the relative values of the elementary kinetic parameters. Thus for example, experiments carried out on Pt rotating disk electrodes (RDEs) [34,35], nanoelectrode arrays [36,37], and ultramicroelectrodes (UMEs) [38, 39] in acid media demonstrated that the *hor* operates principally through the Tafel-Volmer route at low overpotentials (<0.2 V) and it reaches a kinetic limiting current (current plateau) before the Heyrovsky-Volmer route becomes significant. For a direct observation of the transition between both routes, the diffusion limiting current density must be large enough (for example that verified on sub-micrometer UMEs [38] or highly-dispersed ensemble electrodes [36]) to become significantly different to the kinetic limiting value.



Taking into account the advantageous mass-transport properties of SECM, it is clear that this technique is particularly useful for the examination of the *hor* mechanism and for the determination of its elementary kinetic parameters on any substrate material, but a proper theoretical model to correlate the experimental  $I_T(E_S, L)$  curves should be used. On that sense, there were a few attempts to generate more general models by applying corrections to the ideal thin-layer cell (TLC) configuration [40,41], which can be rigorously solved for the particular mechanism of the analyzed reaction. Moreover, a formalism to analyze the *hor* on an ideal TLC was already reported [42]. Thus, by incorporating this formalism in the TLC-based SECM theoretical equations, it should be possible to develop a model to carry out the mechanistic analysis of this reaction and the quantification of the complete set of elementary rate constants. In this context, this work reports a general equation for the analysis of  $I_T(E_S, L)$  dependences, which introduces the TLC contribution in such a way that any reaction mechanism occurring at the substrate can be accounted. This equation is applied to describe the SECM

feedback both for a typical quasi-reversible reaction (to test it against a well-known case) and for analyzing the THV mechanism of the *hor*, and contrasted with results of numerical simulations to verify its descriptive capabilities. The use of this equation to correlate experimental results is shown and discussed.

## 2. Theory

### 2.1. Analytical model

#### 2.1.1. General model

A recent model that incorporates the TLC contribution as a TLC current ( $i_{\text{TLC}}$ ) into the dependence of  $I_T$  on  $E_S$  and on  $L$  was reported by Zoski et al. [40] to carry out SECM tip voltammetry experiments on reversible reactions. On the basis of this model, the analytical expression for  $I_T$  given by Eq. (5) is proposed here.

$$I_T(E_S, L) = I_{\text{TLC}}(E_S, L)\varphi(L) + I_{\text{disk}}(E_S, L, t) \quad (5)$$

The core of this equation is the dependence of the normalized TLC current ( $I_{\text{TLC}} = i_{\text{TLC}}/i_{T,\infty}$ ) for the reaction under study (for example the *hor*) on  $E_S$  and on  $L$ . This is affected by a parameter  $\varphi(L) = (4/\pi)L\beta(I_T^{\text{PF}} - I_T^{\text{NF}})$ , which guarantees the attainment of the positive and negative feedback normalized limiting currents ( $I_T^{\text{PF}}$  and  $I_T^{\text{NF}}$ , respectively), where  $\beta$  is the correction factor due to the finite tip-sheath radius ( $r_g$ ), which depends on the ratio  $R_g = r_g/a$  [29].

The reaction at the microelectrode tip is the backward reaction of the substrate operating under diffusion control. Then, Eq. (5) also involves the term  $I_{\text{disk}}$  defined by Eq. (6), which incorporates the contribution of the diffusion-limiting current at the microelectrode tip at a distance  $L$  ( $i_{T,L}$ ) normalized respect to  $i_{T,\infty}$ .

$$I_{\text{disk}}(E_S, L, t) = \left( \frac{i_{T,L}(E_S, L, t)}{i_{T,\infty}} \right) I_T^{\text{NF}}(L) = c(E_S, L, t) I_T^{\text{NF}}(L) \quad (6)$$

Note that  $i_{T,L}$  can be approximated by  $i_{T,L} = 4\beta\text{FDC}(L)a$  [40], where  $D$  is the diffusion coefficient of the tip reactant,  $C(L)$  is the local concentration at the distance  $L$  of the tip reactant, which could depend on  $E_S$  and time ( $t$ ), and  $F$  is the Faraday constant. Moreover,  $i_{T,\infty} = 4\beta\text{FDC}^*a$ , where  $C^*$  is the bulk concentration of the tip reactant. Thus,  $i_{T,L}/i_{T,\infty}$  results equal to the dimensionless reactant concentration ( $c = C(L)/C^*$ ) at the distance  $L$ . In fact, the radial diffusion toward the disk tip is affected by the blocking effect that the substrate causes at a certain distance  $L$ . In Eq. (6) this effect is accounted by  $I_T^{\text{NF}}$  [40]. Over the  $E_S$  interval where the substrate reaction proceeds in the studied direction (opposite to the tip reaction) the tip reactant concentration should not be modified ( $C = C^*$  for all  $L$ ), so  $c = 1$ . However, over the  $E_S$  interval where the reaction proceeds at the tip and at the substrate in the same direction, the reactant concentration is modified by the substrate, producing a time-dependant concentration profile (so called “shielding effect” [43]). As the substrate is infinite, the mass transport of the reactant toward its surface is carried out by linear diffusion. Then, under shielding conditions the value of  $c$  depends on  $E_S$ , on  $L$ , and on  $t$ . Such  $c(E_S, L, t)$  dependence is determined by the reaction rate at the substrate, which is governed by the kinetics of the reaction.

The mechanism and kinetics of the studied reaction defines the  $I_{\text{TLC}}(E_S, L)$  and  $c(E_S, L, t)$  dependences. Two different cases are presented in this work. The first case is the quasireversible single-step reaction, which is very well known and can be used as a model-system for testing Eq. (5). The second case, which is the actual focus of this work, is the *hor* operating through the THV mechanism (Eqs. (2)–(4)). In both cases, reported expressions for  $I_T^{\text{PF}}$ ,  $I_T^{\text{NF}}$  and  $\beta$  [29] were used.

#### 2.1.2. Quasi-reversible single-step reaction

For a quasi-reversible single step oxidation reaction ( $\text{R} \rightleftharpoons \text{O} + \text{e}^-$ ) operating at the substrate, the  $I_{\text{TLC}}(E_S, L)$  and  $c(E_S, L, t)$  dependences

Download English Version:

<https://daneshyari.com/en/article/4908044>

Download Persian Version:

<https://daneshyari.com/article/4908044>

[Daneshyari.com](https://daneshyari.com)