



# Sensing electroadsorption reactions and surface mobility of electroadsorbed species by scanning electrochemical induced desorption



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## ABSTRACT

A theoretical analysis of electro-adsorption reactions and of the surface diffusion of electro-adsorbed species based on scanning electrochemical microscopy (SECM) in the feedback mode, usually known as scanning electrochemical induced desorption (SECMID), is presented. Numerical simulations of the classical feedback process were carried out by including in the model a potential-dependent electro-adsorption reaction from the mediator at the substrate and allowing the adsorbed species ( $A_{ad}$ ) to diffuse over the substrate surface affecting the mediator loop. As in classical SECMID, the local variation of the mediator concentration underneath the tip causes a potential-dependent gradient of the  $A_{ad}$  surface coverage at the substrate over the tip-affected region, which drives the  $A_{ad}$  surface diffusion toward this area and the consequent positive feedback of mediator, reaching a steady state. The simulated steady-state dependences of the tip current ( $i_T$ ) on the substrate potential ( $E_S$ ) show the presence of a peak over the potential range affected by the electro-adsorption reaction, whose amplitude at a given tip-substrate distance is mostly influenced by the surface diffusion coefficient of  $A_{ad}$  and the density of adsorption sites at the substrate. When this surface process is parallel to an electrode reaction of the mediator that proceeds over the same potential range, the adsorption/diffusion peak is overlapped with the typical Butler-Volmer type response of the electrode reaction, affecting the  $i_T(E_S)$  shape and interfering with the determination of kinetic parameters from this dependence. These phenomena were experimentally observed when using the  $H^+/H_2$  mediator loop on Au and Pt, where  $H_{ad}$  is electro-adsorbed from  $H^+$ , a process that in the case of Pt is parallel to the oxidation of the tip generated  $H_2$ .

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## 1. Introduction

Scanning electrochemical microscopy (SECM) is nowadays a well-established powerful electrochemical technique thoroughly used to gain information on a great number of surface processes [1]. Among the many variants of the technique created to address different applications, one that emerged almost with the introduction of the technique is the so-called scanning electrochemical microscopy induced desorption (SECMID) [2]. This operation approach, which is based on the conventional feedback mode of SECM, allows measuring kinetics of adsorption/desorption reactions and rates of surface diffusion of adsorbed species [2]. SECMID and its variants were employed to study the behavior (i.e. the surface mobility) of species such as proton and others that were adsorbed on single-crystalline oxide surfaces [2] and on self-assembled monolayers [3–5]. As it was theoretically and experimentally demonstrated in these studies, the feedback of a mediator that involves an adsorbed participant is locally affected by the gradient of surface concentration of adsorbed species (or gradient of surface coverage) that

develops on the substrate surface around the tip-affected area [2]. Thus, both the transient and the steady-state feedback approach curves contain information on the adsorption process and on the surface transport of the adsorbate. However, this operation mode was only barely considered in studies of electro-adsorption reactions and electro-adsorbed species [5]. The analysis of steady-state dependences of the feedback tip current on the substrate potential and on the tip-substrate distance could be potentially useful for measuring electro-adsorption parameters such as surface density of sorption sites, surface diffusion coefficient of an adsorbate, rate constant of an electro-adsorption reaction, among others. Moreover, the potential effects of adsorption processes on SECM voltammetric responses is lately receiving increasing attention due to the great deviation from the expected model behaviors that can be caused by this type of processes [6]. Thus, such analysis should also be important to understand the effect that an electro-adsorption reaction could have on the feedback loop of a redox mediator in solution that is used to investigate the kinetics of an electrode reaction at the substrate.

Electro-adsorption reactions are common reactions in electrocatalytic processes. An emblematic example is the electro-adsorption of atomic hydrogen ( $H_{ad}$ ) from  $H^+$  through reaction (1), which proceeds along with the hydrogen electrode reaction (HER).

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In fact, this is an important surface process with many implications in fundamental and technological electrochemical topics including not only electrocatalysis [7], but also corrosion [8], modified electrodes (for example with self-assembled monolayers [9]), among many others. Most conductive materials are capable to electro-adsorb atomic hydrogen through reaction (1), and the resulting  $\text{H}_{\text{ad}}$  could have different roles in a given electrocatalytic process depending on the particular situation. For example, the species  $\text{H}_{\text{ad}}$  may be simple spectators during the course of an electrochemical reaction, as are the under-potential deposited H ( $\text{H}_{\text{UPD}}$ ) on Pt during the HER [7,10,11], which are electro-adsorbed over a potential range anodic respect to the equilibrium potential of the HER. These  $\text{H}_{\text{UPD}}$  may also participate as inhibitors of reaction sites of other reactions, as it happens during the  $4 - \text{e}^-$  oxygen reduction on noble metals at cathodic potentials [12,13]. Moreover, the species  $\text{H}_{\text{ad}}$  may also participate as key intermediate species in the mechanism of an electrode reaction, as for example the over-potential deposited H (or  $\text{H}_{\text{OPD}}$ ) in the HER [10,11], and as an important reactant in electrochemical hydrogenation of organic molecules [14]. Thus, the surface behavior of  $\text{H}_{\text{ad}}$  is likely to significantly affect the performance of many electrode reactions.

In the described context, this communication reports a theoretical study of the expected steady-state potential-dependent feedback responses of SECMID when an electro-adsorption reaction proceeds at the substrate affecting the mediator loop. The importance of this type of analysis is exemplified with SECM results measured on gold and platinum electrodes for the electro-adsorption of  $\text{H}_{\text{ad}}$  from  $\text{H}^+$  through the reaction (1) and its surface diffusion.

## 2. Theory

The electrode reaction of a generic species O in solution that is electro-reduced at the substrate to an adsorbed species  $\text{A}_{\text{ad}}$  through reaction (2) was considered, where  $k_a^{\text{app}}$  and  $k_d^{\text{app}}$  are the potential dependent apparent electro-adsorption and electro-desorption rate constants [15].



The two scenarios that are schematized in Fig. 1 were theoretically analyzed by mean of simulations.

The situation shown in Fig. 1a was proposed to explore the effect that the surface process by itself produces on the dependences of the tip current ( $i_T$ ) vs. substrate potential ( $E_S$ ) and tip-substrate distance ( $d$ ), usually known as “working curves”. A complete analysis of this case would permit to have a good overview on the potentiality of using  $i_T(E_S, d)$  dependencies for measuring kinetic or equilibrium parameters of electro-adsorption reactions and of surface diffusion of the electro-adsorbed species. The second situation schematized in Fig. 1b was proposed to analyze the possible effects on the working curves of the surface processes occurring parallel to an electrode reaction with dissolved species. This should be useful to understand to what extent this phenomenon may interfere with the determination of kinetic parameters of the studied electrode reaction from fitting the feedback  $i_T(E_S, d)$  dependences. The configuration shown in Fig. 1b is more general and includes the case of Fig. 1a as a particular condition where the rate of the electrode reaction at the substrate is null. Thus, the general model presented in Fig. 1b is developed below.

The theoretical model of Fig. 1a is essentially identical to that initially proposed by Unwin and Bard for the SECMID studies [2], but an  $E_S$ -dependent adsorption rate is involved in this case. Besides, in order to complete the model described in Fig. 1b, both the diffusion in solution of tip-generated species R and the electrode reaction at the substrate

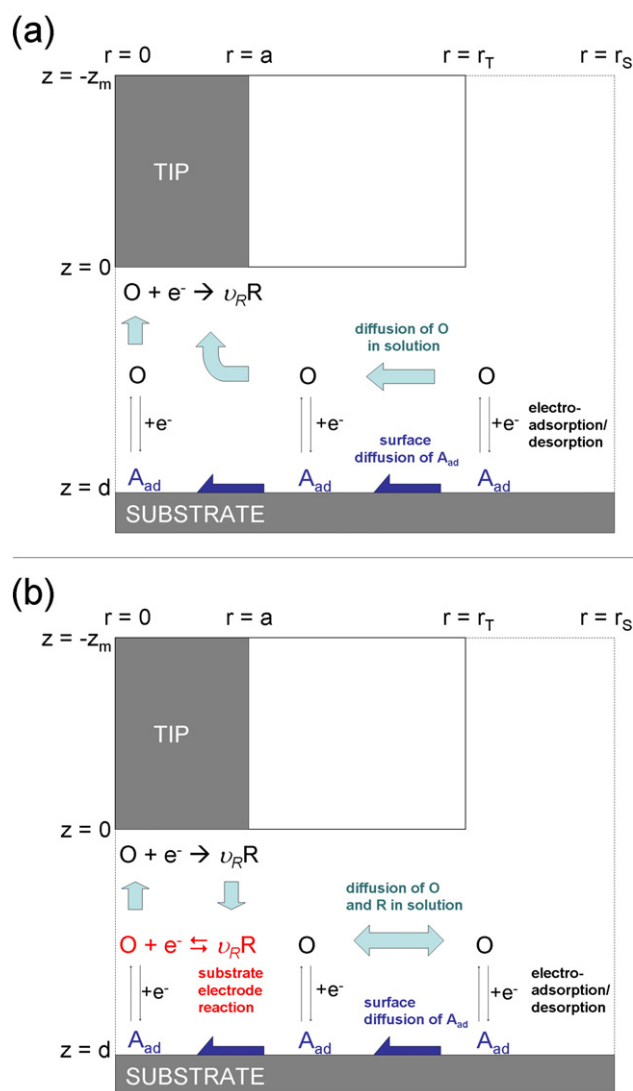


Fig. 1. Schematics of the two SECMID situations that were analyzed in this work.

indicated in Eq. (3) should be taken into account. Then, the dependences of the concentrations of species O ( $c_O$ ) and R ( $c_R$ ) with time ( $t$ ) and position ( $r$  and  $z$  in cylindrical coordinates) are given by Eqs. (4) and (5), where  $D_i$  (in  $\text{cm}^2 \text{s}^{-1}$ ) is the diffusion coefficient of species  $i$  (O or R) in solution.

$$\nu_R \text{R}_{(\text{dis})} \rightleftharpoons \text{O}_{(\text{dis})} + \text{e}^- \quad (3)$$

$$\frac{\partial c_O}{\partial t} = D_O \left( \frac{\partial^2 c_O}{\partial r^2} + \frac{\partial c_O}{r \partial r} + \frac{\partial^2 c_O}{\partial z^2} \right) \quad (4)$$

$$\frac{\partial c_R}{\partial t} = D_R \left( \frac{\partial^2 c_R}{\partial r^2} + \frac{\partial c_R}{r \partial r} + \frac{\partial^2 c_R}{\partial z^2} \right) \quad (5)$$

Furthermore, assuming Langmuir isotherm for modeling the electro-adsorption reaction (15), the initial and boundary conditions are defined by Eqs. (6) to (11).

$$t = 0: \quad 0 \leq z \leq d \text{ and } 0 \leq r \leq r_s, \quad -z_m \leq z \leq 0 \text{ and } r_t \leq r \leq r_s: \quad c_O(r, z) = c_O^*; \quad c_R(r, z) = 0 \quad (6)$$

$$z = d \text{ and } 0 \leq r \leq r_s: \quad \theta = \frac{c_O^* K_{\text{ad}}(E_S)}{1 + c_O^* K_{\text{ad}}(E_S)} \quad (7)$$

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