

# Analysis of the effect of surface hydrogen concentration on the hydrogen oxidation reaction: Voltammetry vs. steady state

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## ABSTRACT

Starting from the modelling of the processes involved in the hydrogen oxidation reaction, the present work provides an explanation about the origin of the differences observed between the polarization curves obtained by voltammetric sweeps and those corresponding to the steady state measurements. It was demonstrated that the dependence of molecular hydrogen concentration at the electrode surface on overpotential plays a key role in the current density profile. These concepts are illustrated and discussed on the basis of the voltammetric response of the reaction on platinum.

**KEYWORDS:** hydrogen oxidation reaction, voltammetric sweeps, steady state, surface hydrogen concentration

## 1. INTRODUCTION

The kinetics of the hydrogen electrode reaction (HER) has been widely studied, with the hydrogen oxidation reaction (*hor*) receiving less attention than the hydrogen evolution reaction (*her*). This fact can be understood if it is taken into account that historically the *her* has been considered as a purely faradaic reaction [1] while the *hor* was assessed as a diffusion-controlled reaction [2, 3]. Although this point of view has changed, there are still some who sustain the idea that *hor* on

platinum in acid solutions is controlled by pure diffusion [4], implying that the surface concentration of molecular hydrogen ( $C_{H_2}^s$ ) varies with overpotential ( $\eta$ ) through the following relationship,

$$\frac{C_{H_2}^s}{C_{H_2}^e} = e^{-\frac{2F}{RT}\eta} \quad (1)$$

where  $C_{H_2}^e$  is the equilibrium concentration of molecular hydrogen [4]. This point of view has changed in the last few decades, as it was demonstrated to be incorrect [5, 6]. Its main inconsistency comes from the experimental current-potential dependence near the equilibrium condition, which shows a clear diffusion contribution [6, 7]. This result puts into evidence a strong uncertainty in the way in which the values of the exchange current density were evaluated [8]. The statement about the completely different behaviours of both branches of the HER turns to be meaningless, as it has been demonstrated previously [9]. Hydrogen evolution operates under faradaic control only in strong acid (or alkaline) solutions at high cathodic potentials, meanwhile hydrogen oxidation reaches the limiting diffusion condition only at high anodic potentials [9]. At intermediate potential range a mixed control takes place, obviously more pronounced at *hor* than *her* [9]. These results raise the need to review the way in which the experimental current-potential dependences are interpreted, including the diffusion contribution in the whole range of overpotentials of the HER.

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Although the analysis of the experimental curves is usually carried out through kinetic expressions derived in steady state, the use of voltammetric sweeps is quite common, under the argument that low sweep rates give a current response similar to that corresponding to the steady state [4, 10-16]. However, recent studies demonstrate that such approximation could be inadequate if certain precautions in the experimental design are not taken into account [17]. One of the main problems is that the responses of the anodic and cathodic sweeps in the voltammetric scan are not coincident due to the contribution of the double layer capacity and the pseudocapacitive current originated from the variation of the surface coverage of the reaction intermediate ( $H_{ad}$ ). Moreover, the adsorption of the so-called underpotentially deposited hydrogen ( $H_{UPD}$ ) on noble metals (Pt, Ir, Rh, etc.) also takes place. Although  $H_{UPD}$  does not participate in the HER, it strongly influences the potentiodynamic response [18]. Therefore, the interpretation of the experimental potentiodynamic response ( $j_{exp}^{vs}$ ) must consider both, the voltammetric current density ( $j^{vs}$ ) and the pseudocapacitive current density due to  $H_{UPD}$  ( $j_{upd}^{vs}$ ),

$$j_{exp}^{vs}(\eta, \omega, v_s) = j^{vs}(\eta, \omega, v_s) + j_{upd}^{vs}(\eta, v_s) \quad (2)$$

The term  $j^{vs}$  is a function of overpotential ( $\eta$ ), sweep rate ( $v_s$ ) and electrode rotation rate ( $\omega$ ), while  $j_{upd}^{vs}$  is only a function of  $\eta$  and  $v_s$ . If we take into account that the contribution due to  $H_{upd}$  defines current peaks at well-defined potentials, then  $j_{exp}^{vs}$  should only show these peaks, as the current density on steady state does not display peaks. However, voltammetric studies [15, 19-20] of the *hor* have shown peaks that cannot be assigned to the  $H_{upd}$ , which were not explained or their interpretation was confusing.

In this context, the present work deals with a theoretical study of the kinetics of the hydrogen oxidation reaction in order to evaluate the role of  $C_{H_2}^s$  on the potentiodynamic profiles and to establish the differences with the steady state conditions.

## 2. THEORETICAL ANALYSIS

In order to obtain the theoretical dependence  $j^{vs}(\eta, \omega, v_s)$  for the hydrogen oxidation reaction, the kinetic mechanism of Tafel-Heyrovsky-Volmer must be solved,



where  $S$  is the active site for the adsorption of the reaction intermediate  $H_{ad}$ . The reaction must be verified in conditions that enable the comparison with the steady state. Thus, a rotating disc electrode of radius  $r_e$  operating at a rotation rate  $\omega$  is considered. This electrode ensures a hydrodynamic condition that enables a current stable on time as well as a fixed value of the limiting diffusion current density ( $j_L$ ). A brief description of the formalism, which was derived recently by the authors, will be given here. More details can be found elsewhere [17].

The voltammetric current density can be described as a sum of two contributions, one corresponding to the electrode reaction  $j^r(\eta, \omega, v_s)$  and the other originated in the double layer capacitance  $j^c(\eta, v_s)$  [17, 21],

$$j^{vs}(\eta, \omega, v_s) = j^r(\eta, \omega, v_s) + j^c(\eta, v_s) \quad (4)$$

$j^r(\eta, \omega, v_s)$  involves the charge required for the electrochemical reaction (faradaic) and the charge required for the adsorption of the reaction intermediate (pseudocapacitive). It is the sum of the contributions of the two elementary steps with electronic transfer (Heyrovsky and Volmer) of the THV mechanism [5, 22-24],

$$j^r(\eta, \omega, v_s) = F(v_H + v_V) \quad (5)$$

The reaction rates of these elementary steps,  $v_i$  ( $i: T, H, V$ ), described on the basis of a Frumkin-type adsorption, are given by the following expressions [5],

$$v_T = v_T^e \left[ \frac{C_{H_2}^s}{C_{H_2}^e} \left( \frac{1-\theta}{1-\theta^e} \right)^2 e^{-2u(\theta-\theta^e)\lambda} - \left( \frac{\theta}{\theta^e} \right)^2 e^{2u(\theta-\theta^e)(1-\lambda)} \right], \quad (6a)$$

$$v_H = v_H^e \left[ \frac{C_{H_2}^s}{C_{H_2}^e} \left( \frac{1-\theta}{1-\theta^e} \right) e^{-u(\theta-\theta^e)\lambda} e^{\alpha_H f \eta} - \left( \frac{\theta}{\theta^e} \right) e^{u(\theta-\theta^e)(1-\lambda)} e^{-(1-\alpha_H) f \eta} \right] \quad (6b)$$

and

$$v_V = v_V^e \left[ \left( \frac{\theta}{\theta^e} \right) e^{u(\theta-\theta^e)(1-\lambda)} e^{\alpha_V f \eta} - \left( \frac{1-\theta}{1-\theta^e} \right) e^{-u(\theta-\theta^e)\lambda} e^{-(1-\alpha_V) f \eta} \right] \quad (6c)$$

where  $\theta$  is the surface coverage of the adsorbed hydrogen  $H_{ad}$ ,  $C_{H_2}$  is the concentration of the molecular hydrogen in solution,  $\alpha_i$  and  $\lambda$  are the symmetry factors of the step  $i$  ( $i = V, H$ ) and adsorption, respectively,  $u$  is the interaction parameter (in  $RT$  units) of the Frumkin adsorption isotherm, and  $f = F/RT$ . The superscripts 'e' and 's' indicate equilibrium and electrode surface, respectively. Finally the expressions (6a-c) define a positive (negative) value for  $\eta$  in the anodic (cathodic) direction.

In order to solve Eqs. (6a-c), the corresponding dependences of the surface coverage on overpotential, on rotation rate and on sweep rate,  $\theta = \theta(\eta, \omega, v_s)$ , must be known. Thus, the following differential equation must be solved [22-24],

$$\frac{d\theta(\eta, \omega, v_s)}{d\eta} = F \frac{(2v_T + v_H - v_V)}{v_s \sigma} \quad (7)$$

where  $\sigma$  is the electric charge per unit area corresponding to a  $H_{ad}$  monolayer and  $F$  is the Faraday constant. An expression for the dependence  $C_{H_2}^e(\eta, \omega, v_s)$  is needed for Eqs. (6a,b), which is obtained from the resolution of the general equation for the molecular hydrogen mass transport, comprising the diffusion and convective terms [17],

$$\frac{\partial C_{H_2}}{\partial t} = D_{H_2} \nabla^2 C_{H_2} - v \nabla C_{H_2} \quad (8)$$

where  $t$  is time,  $D_{H_2}$  is the hydrogen diffusion coefficient and  $v$  is the fluid flow velocity vector

in cylindrical coordinates (Figure 1). The components ( $v_r$ ,  $v_\phi$  and  $v_y$ ) of the fluid velocity vector  $v$  are [25],

$$v_r = r \omega \left( a \gamma - \frac{\gamma^2}{2} - b \frac{\gamma^3}{3} + \dots \right), \quad (9a)$$

$$v_\phi = r \omega \left( 1 + b \gamma + \frac{\gamma^2}{2} - a \frac{\gamma^3}{3} + \dots \right) \quad (9b)$$

and

$$v_y = (v\omega)^{1/2} \left( -a \gamma^2 + \frac{\gamma^3}{3} + b \frac{\gamma^4}{6} + \dots \right) \quad (9c)$$

Eqs. (9a-c) involve the dimensionless variable  $\gamma$ ,

$$\gamma = \left( \frac{\omega}{v} \right)^{1/2} y \quad (10)$$

where  $v$  is the kinematic viscosity of the electrolyte solution. Following the V. G. Levich theoretical approach [25] the first term of each series is considered, corresponding to  $a = 0.51023$  and  $b = -0.6159$ . The resolution of the Eqs. (8-10) requires the following appropriate boundary conditions,

$$C_{H_2}(\eta, \omega, v_s, y) \Big|_{y \rightarrow \infty} = C_{H_2}^e \quad (11)$$

and

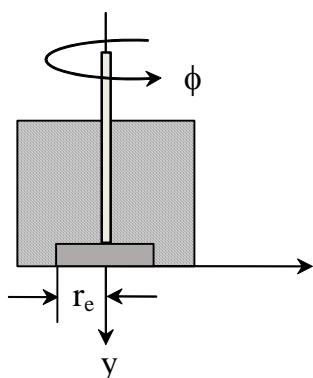
$$\left. \frac{\partial C_{H_2}}{\partial t} \right|_{y=0} =$$

$$\lim_{\Delta y \rightarrow 0} \left[ \frac{D_{H_2} \frac{\partial C_{H_2}}{\partial y} \Big|_{\Delta y} + v_y(\Delta y) C_{H_2}(\Delta y) - v_T + v_H}{\Delta y} \right] \quad (12)$$

as well as the following initial condition,

$$C_{H_2}(\eta, \omega, v_s, y) \Big|_{t=0} = C_{H_2}^e \quad (13)$$

Finally, the double layer capacitance contribution to the current density,  $j^c(\eta, v_s)$ , can be evaluated from the following equation:



**Figure 1.** Scheme of a rotating electrode indicating the cylindrical coordinates.

$$j^c(\eta, v_s) = c v_s \quad (14)$$

where  $c$  represents the double layer capacitance, which was considered constant on the range of potentials used in this study.

The parameters involved in the system of eqs. (4-14) are the hydrogen concentration in solution ( $C_{H_2}^e$ ), the kinematic viscosity ( $\nu$ ), the hydrogen diffusion coefficient ( $D_{H_2}$ ), the kinetic parameters ( $\nu_i^e$  and  $\theta^e$ ), the symmetry factors ( $\alpha_i$  and  $\lambda$ ) and the Frumkin interaction parameter ( $u$ ). The dependences  $j^{vs}(\eta, \omega, v_s)$ ,  $\theta(\eta, \omega, v_s)$ ,  $C_{H_2}^s(\eta, \omega, v_s)$ , and  $C_{H_2}(\eta, \omega, v_s, y)$ , resulting from the application of a potentiodynamic sweep on a rotating disc electrode, can be simulated for a given set of these parameters. Moreover, the steady state current density  $j^{ss}(\eta, \omega)$  can be also determined. In this case eq. (7) is equal to zero and the following expression is accomplished for the ratio  $C_{H_2}^s / C_{H_2}^e$  [5, 7, 9],

$$\frac{C_{H_2}^s}{C_{H_2}^e} = 1 - \frac{j^{ss}}{j_L} \quad (15)$$

where  $j_L$  is the limiting diffusion current density, which was in turn calculated with the Levich equation [25],

$$j_L(\omega) = 0.62 n F D_{H_2}^{3/2} \nu^{-1/6} C_{H_2}^e \omega^{1/2} \quad (16)$$

where  $\omega$  is expressed in  $\text{rad s}^{-1}$  and  $n$ , the number of electrons in the global reaction, is equal to 2.

### 3. RESULTS AND DISCUSSION

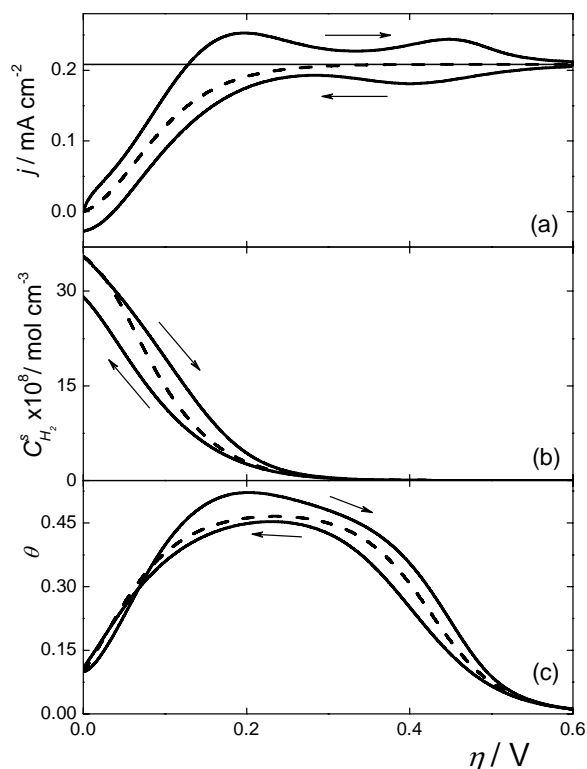
#### 3.1. Selection of parameters

The system of eqs. (4-14), numerically solved by the method of finite increments, enables the evaluation of the variables current density ( $j^{vs}$ ), surface coverage of the adsorbed intermediate ( $\theta$ ) and surface concentration of molecular hydrogen ( $C_{H_2}^s$ ), as a function of overpotential ( $\eta$ ), electrode rotation rate ( $\omega$ ) and voltammetric sweep rate ( $v_s$ ). Moreover, the variables  $j^{vs}$ ,  $\theta$  and  $C_{H_2}^s$  were also simulated under the steady state condition by the resolution of the system of eqs. (5-7, 15-16). Each variable is in this case only a function of  $\eta$  and  $\omega$ . Finally, the dependence of  $C_{H_2}^e$  under the consideration of pure diffusion control was evaluated from eq. (1).

As the number of possible combinations of kinetic and experimental parameters is almost infinite, one set of parameters that are most representative of the objective of the present work is presented here. They are also compared with voltammetric results obtained from the literature. In this sense, the most interesting results are those where both anodic and cathodic potentiodynamic sweeps are included, which are unfortunately scarce [26, 27]. The values of the parameters will be specified in each case, while the following will be maintained constant: the Frumkin parameters:  $\lambda = u = 0.5$ ; the electric charge per unit area:  $\sigma = 2.2 \times 10^{-4} \text{ C cm}^{-2}$ ; the double layer capacitance:  $c = 2 \times 10^{-5} \text{ F cm}^{-2}$ ; temperature:  $T = 303 \text{ K}$  and the radius of electrode:  $r_e = 0.1 \text{ cm}$ . The mass transport parameters were the kinematic viscosity:  $\nu = 8.01 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ ; the molecular hydrogen diffusion coefficient  $D_{H_2} = 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and the molecular hydrogen solubility  $C_{H_2}^e = 3.547 \times 10^{-7} \text{ mol cm}^{-3}$ , corresponding to a hydrogen pressure of 1 atm. From these values, the parameter  $B$  of the Levich equation ( $B = 0.62 n F D_{H_2}^{3/2} \nu^{-1/6} C_{H_2}^e$ ) is  $B = 1.2876 \times 10^{-4} \text{ A cm}^{-2} \text{ s}^{1/2}$  (or  $B = 4.1667 \times 10^{-5} \text{ A cm}^{-2} \text{ rpm}^{-1/2}$ ). Finally, the voltammetric initial state was always the equilibrium condition ( $\eta = 0 \text{ V}$ ,  $\theta = \theta^e$ ,  $C_{H_2}^s = C_{H_2}^e$ ). A voltammetric sweep is applied from this condition up to 0.6 V and then back to the initial value.

### 3.2. Simulation of $j^{vs}$ , $\theta$ and $C_{H_2}^s$

The simulation of current density, surface hydrogen concentration and  $H_{ad}$  surface coverage resulting from the application of a voltammetric sweep in the overpotential range corresponding to the hydrogen oxidation reaction is illustrated in figure 2a-c. The sweep rate was  $0.05 \text{ s}^{-1}$ , with  $v_V^e = 1.0 \times 10^{-13} \text{ A cm}^{-2} \text{ s}^{-1}$ ,  $v_H^e = 1.0 \times 10^{-9} \text{ A cm}^{-2} \text{ s}^{-1}$ ,  $v_T^e = 3.80 \times 10^{-11} \text{ A cm}^{-2} \text{ s}^{-1}$ ,  $\theta^e = 0.1$ ,  $\alpha_V = \alpha_H = 0.5$  and  $\omega = 25 \text{ rpm}$ . The potentiodynamic profile of the current density  $j^{vs}$  is shown in figure 2a (continuous line), where two anodic peaks located at 0.18 and 0.45 V can be observed. The cathodic sweep shows a peak at 0.4 V. The curve corresponding to the current density at steady state condition  $j^{ss}$  (dashed line) is also shown. It should be important to note that in the present analysis the adsorption of  $H_{upd}$  was not considered, which implies that the observed peaks are due to the dynamics of the *hor* when the interphase is perturbed by a potentiodynamic sweep. It should be also worth mentioning that at the inversion potential (0.6 V) the anodic and cathodic current densities are equidistant from the value corresponding to the limiting diffusion current density, which at 25 rpm is  $j_L = 0.2083 \text{ mA cm}^{-2}$ , value obtained from eq. (16). The behaviour of the  $j^{vs}(\eta)$  dependence can be explained from the corresponding curves of the surface concentration of molecular hydrogen  $C_{H_2}^s(\eta)$  (Figure 2b) and the surface coverage  $\theta(\eta)$  (Figure 2c). It can be inferred from Eqs. (5) and (6a-c) that the current density of the *hor* increases (or decreases) as  $C_{H_2}^s$  is higher (or lower) than that corresponding to the steady state. Consequently, the voltammetric response is determined by the dynamics of the surface concentration resulting from the coupling of two processes, the transference of the molecular hydrogen towards the electrode surface and its consumption due to the oxidation reaction, which is governed by eq. (12). These processes lead to the hysteresis observed in both  $C_{H_2}^s(\eta)$  (Figure 2b) and  $\theta(\eta)$  (Figure 2c), which depends on the rotation rate, the sweep rate and the kinetics of the reaction. Moreover, it also depends on the sign of



**Figure 2.** Dependences of current density (a), surface hydrogen concentration (b) and surface coverage (c) on overpotential for the *hor* simulated at  $0.05 \text{ V s}^{-1}$  (continuous line) and at steady state (dashed line).

$\left. \frac{\partial C_{H_2}}{\partial y} \right]_{y=0}$ . It should be taken into account that this partial derivative evaluated at  $y = 0$  is a measure of the diffusion flow (Fick's law) to or from the electrode surface. It can be positive, when hydrogen is consumed due to the *hor*, or negative, which means that hydrogen is being produced through the inverse reaction (*her*). These different situations are illustrated in figure 3, where the molecular hydrogen concentration is plotted as a function of the distance  $y$  from the electrode surface at a given overpotential. It not only shows different values for the anodic and cathodic sweep, but also a change of the derivative sign at low overpotential values and consequently the hydrogen generation (curves d'' and e'' in figure 3). These results show that the behaviour of the current density in the voltammetric response, unlike that corresponding to the steady state, strongly depends on the sweep

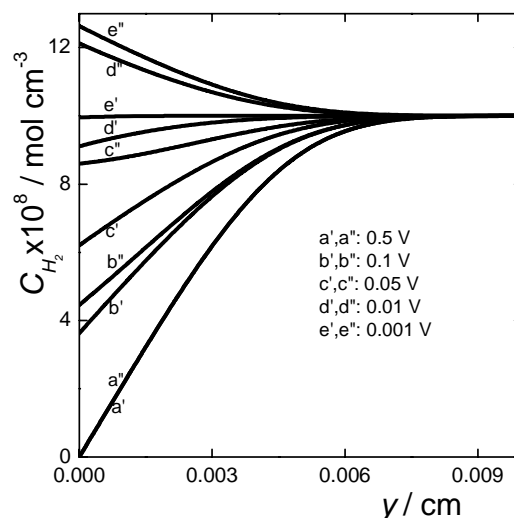
direction. Moreover, the potentiodynamic behaviour of  $C_{H_2}^s$  also results in the modification of the dependence of the surface coverage of the adsorbed intermediate with respect to that at steady state (Figure 2c).

On the other hand, as it is described by Eq. (2), the voltammetric response of electrodes where the  $H_{\text{upd}}$  adsorption is produced presents a pseudocapacitive contribution ( $j_{\text{upd}}^{\text{vs}}$ ). In order to illustrate this behaviour a platinum electrode is considered, subjected to a voltammetric sweep at  $0.05 \text{ V s}^{-1}$  in acid solution. Figure 4a shows the well-known potentiodynamic profile in the potential range where the  $H_{\text{upd}}$  adsorption takes place. At the same time figure 4b corresponds to the combination of this contribution with the potentiodynamic response given in figure 2a. Thus, figure 4b is the representation of the experimental current density  $j_{\text{exp}}^{\text{vs}}$  (eq. 2). It should be of interest to note that this curve is very similar to that obtained by H. Kita *et al.* [26].

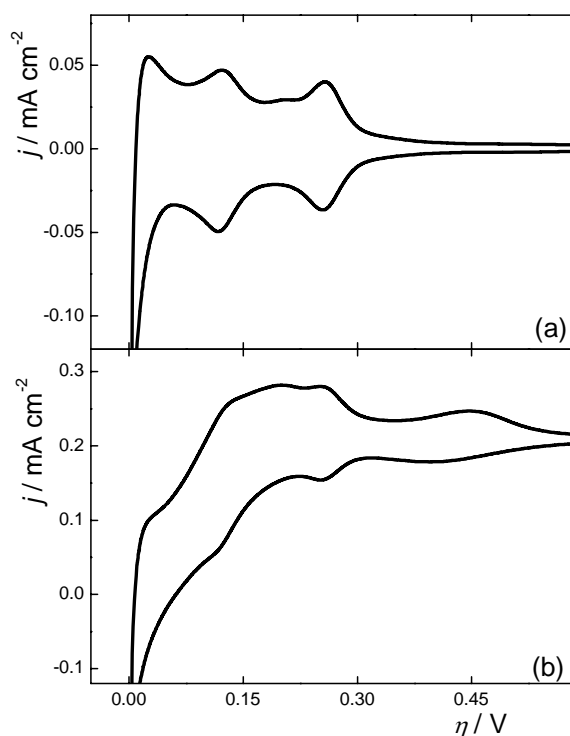
A final aspect that should be mentioned is the use of the term concentration overpotential, which is originated from eq. (1). This is the potential difference of a hydrogen concentration primary cell constituted by two hydrogen electrodes, one at the concentration  $C_{H_2}^s$  and the other at  $C_{H_2}^e$ . As it has been already mentioned, sometimes it is considered that the *hor* on Pt in acid solution operates under purely diffusion control [4]. The results obtained in the present work demonstrate that if it would be the case, the response  $j^{\text{vs}}(\eta, \omega, v_s)$  must be coincident to that given by the expression,

$$j^{\text{vs}}(\eta, \omega) = j_L(\omega) \left( 1 - e^{-\frac{2F}{RT}\eta} \right) \quad (17)$$

It is obvious that eq. (17) cannot describe the hysteresis between the anodic and cathodic sweep, as well as the influence of the sweep rate and the inflection point in the  $C_{H_2}^s(\eta)$  curve [6, 9, 28, 29]. Therefore, it cannot be used to interpret the current density-overpotential response of the hydrogen oxidation reaction.



**Figure 3.** Profiles of the hydrogen concentration as a function of the axial coordinate for the *hor* simulated at different overpotentials indicated in the figure. (') anodic sweep; (') cathodic sweep.



**Figure 4.** (a) Voltammogram of a Pt electrode in 0.5 M  $H_2SO_4$  solution under  $N_2$  bubbling run at  $0.05 \text{ V s}^{-1}$  showing the  $H_{\text{upd}}$  adsorption; (b) Experimental current density as sum of the contributions  $j_{\text{upd}}^{\text{vs}}$  and  $j^{\text{vs}}$  (Figure 2 continuous line).

#### 4. CONCLUSION

The hydrogen oxidation reaction was studied theoretically in order to find an explanation for the experimental results that show the presence of peaks in the current density - overpotential dependence when these polarization curves are obtained by the application of a voltammetric sweep, which are not observed on steady state. From the expressions previously derived, the dependences on overpotential of the surface concentration of the molecular hydrogen and the surface coverage of the adsorbed intermediate were obtained. It was observed that all these responses strongly depend on the way in which the system reaches a given state. This fact explains the existence of current peaks different from those corresponding to  $H_{upd}$ . Consequently, the use of potentiodynamic sweeps for mechanistic studies of the *hor* is not advisable. On the other hand, it was also demonstrated that the use of approximated equations as well as usual considerations such as pure diffusion control are far from being verified experimentally, even more when the reaction involves adsorbed intermediates.

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#### CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

#### REFERENCES

1. Krishtalik, L. I. 1986, Charge Transfer Reactions in Electrochemical and Chemical Processes, Plenum Press, New York.
2. Harrison, J. A. and Khan, Z. A. 1971, J. Electroanal. Chem., 30, 327.
3. Bagotsky, V. S. and Osetrova, N. V. 1973, J. Electroanal. Chem., 43, 233.
4. Sheng, W., Gasteiger, H. A. and Shao-Horn, Y. 2010, J. Electrochem. Soc., 157, B1529.
5. Gennero de Chialvo, M. R. and Chialvo, A. C. 2004, Phys. Chem. Chem. Phys., 6, 4009.
6. Quaino, P. M., Gennero de Chialvo, M. R. and Chialvo, A. C. 2004, Phys. Chem. Chem. Phys., 6, 4450.
7. Gennero de Chialvo, M. R. and Chialvo, A. C. 2006, Current Topics in Electrochem., 11, 1.
8. Gennero de Chialvo, M. R. and Chialvo, A. C. 2012, Currents Topics in Electrochem., 17, 41.
9. Quaino, P. M., Gennero de Chialvo, M. R. and Chialvo, A. C. 2007, Electrochim. Acta, 52, 7396.
10. Sun, Y., Dai, Y., Liu, Y. and Chen, S. 2012, Phys. Chem. Chem. Phys., 14, 2278.
11. Lukaszewski, M., Hubkowska, K. and Czerwinski, A. 2010, Phys. Chem. Chem. Phys., 12, 14567.
12. Hoshi, N., Asaumi, Y., Nakamura, M., Mikita, K. and Kajiwara, R. 2009, J. Phys. Chem. C, 113, 16843.
13. Zeng, J., Zhuang, Z., Xu, B. and Yan, Y. 2015, ACS Catal., 5, 4449.
14. Esparbe, I., Brillas, E., Centellas, F., Garrido, J. A., Arias, R. M., Arias, C. and Cabot, P. 2009, J. Power Sources, 190, 201.
15. Durst, J., Simon, C., Hasche, F. and Gasteiger, H. A. 2015, J. Electrochem. Soc., 162, F190.
16. Kajiwara, R., Asaumi, Y., Nakamura, M. and Hoshi, N. 2011, J. Electroanal. Chem., 657, 61.
17. Marozzi, C. A., Gennero de Chialvo, M. R. and Chialvo, A. C. 2015, J. Electroanal. Chem., 748, 61.
18. Strmcnik, D., Tripkovic, D., van der Vlied, D. and Markovic, N. M. 2008, Electrochem. Commun., 10, 1602.
19. Wesselmarm, M., Wickman, B., Lagergren, C. and Lindbergh, G. 2010, Electrochem. Commun., 12, 1585.
20. Zalitis, C. M., Sharman, J., Wright, E. and Kucernak, A. R. 2015, Electrochim. Acta, 176, 763.
21. Harrington, D. A. and Conway, B. E. 1987, Electrochim. Acta, 32, 1703.

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22. Gennero de Chialvo, M. R. and Chialvo, A. C. 1996, *J. Electroanal. Chem.*, 415, 97.
  23. Marozzi, C. A., Gennero de Chialvo, M. R. and Chialvo, A. C. 2013, *Electrochim. Acta*, 112, 68.
  24. Marozzi, C. A., Canto, M. R., Costanza, V. and Chialvo, A. C. 2005, *Electrochim. Acta*, 51, 731.
  25. Levich, V. G. 1962, *Physicochemical Hydrodynamics*, Prentice Hall, Englewood Cliffs.
  26. Kita, H., Gao, Y. and Hattori, H. 1994, *J. Electroanal. Chem.*, 373, 177.
  27. Herrero, E., Clavilier, J., Feliu, J. M. and Aldaz, A. 1996, *J. Electroanal. Chem.*, 410, 125.
  28. Quaino, P. M., Fernandez, J. L., Gennero de Chialvo, M. R. and Chialvo, A. C. 2006, *J. Mol. Catal. A: Chemical*, 252, 156.
  29. Rau, M. S., Gennero de Chialvo, M. R. and Chialvo, A. C. 2013, *J. Power Sources*, 229, 210.