Study of hydrogen evolution reaction in acid medium on Pt microelectrodes

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Abstract

This work describes the utilization of a Pt UME in the study of the hydrogen evolution reaction in 0.5 M H₂SO₄. A non-linear fitting procedure was employed in order to analyze polarization curves obtained at several temperatures (25–75 °C). The results revealed that the traditionally accepted model described by a Volmer–Tafel route fails to fit the obtained experimental data. In this sense, a new model was proposed involving the Volmer–Heyrovsky mechanism, being the Heyrovsky reaction rate determining step. To achieve the best fit between experimental and calculated data, the kinetic equations had to be proposed with a small value of the transfer coefficient (β < 0.2). This unusual value was associated with an activationless process, which can also justify the limiting kinetic current (not diffusional) observed. Trying to get further insight into this possibility, the polarization studies were also performed on a surface modified by underpotentially deposited copper. With a degree of coverage as high as 0.8, the only observed effect on the polarization curves was a shift towards minor current values. This shift can be completely justified by the blocking of surface area. A change in mechanism was not observed albeit the Cu UPD eliminated the pairs of neighbor active sites necessary to the Volmer–Tafel pathway. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogen evolution reaction; Microelectrodes; Platinum; Underpotential deposition; Polarization curves

1. Introduction

The hydrogen evolution reaction (HER) has been extensively studied mainly due to peculiarities based on the strong interaction observed between adsorbate and substrate. The nature of the electrocatalytic surface plays a decisive role in the kinetics and mechanism of this reaction. Platinum, among several metals usually employed as a substrate, is one of the more active for the HER, mainly in acid media. However, studies on the mechanism of this reaction in such conditions are, until now, sparse, and insufficient to allow definitive conclusions.

One intriguing feature in such a mechanism is the experimentally observed Tafel slope of ca. 30 mV dec⁻¹ [1–5]. As analyzed by Vetter [5], theoretically a small but exponentially potential-dependent coverage, θₜₐ, must be postulated to account for the recombination Tafel slope of 30 mV dec⁻¹. However, platinum surfaces are completely covered with a full monolayer of underpotentially adsorbed hydrogen in a potential region less negative than that for hydrogen evolution [1,2,6–8]. Such UPD species are easily studied by cyclic voltammetric techniques. Nevertheless, based on the previous analysis [5], they cannot be postulated as the adsorbed intermediate in Volmer–Tafel route of the
HER since their coverages is potential independent in the hydrogen evolution region. Nichols and Bewick [9] and Martins et al. [10] have even identified a new type of adsorbed hydrogen on platinum in the potential range of the HER employing in-situ IR spectroscopy. Despite all efforts made in this area, the identification of such intermediate is, to date, the subject of many controversies [1].

Another possibility to explain the Tafel slope of 30 mV dec\(^{-1}\) was proposed by Breiter [11] as a new mechanism to account for this slope at highly active electrodes and involves diffusion of molecular \(\text{H}_2\) from the surface. This possibility was also discussed by Yeger et al. [12].

Another aspect that has to be carefully controlled in such studies is the conditioning of the Pt surface. As stressed by Conway et al. [1,13,14], the state of the surface and the presence or absence of chemisorbed impurities determine the electrochemical behavior of Pt to a much greater extent than for other metals. Thus, even a concentration level as low as \(10^{-10}\) mol dm\(^{-3}\) can significantly poison the electrode reaction [1]. This behavior can explain the discrepancy of several results of the HER on Pt reported in the literature [1,3,5]. The importance of reproducible surfaces practically imposes the need of digital programming of potentials.

In order to minimize diffusional contributions, some authors worked with rotating disk electrodes (RDE) at high rotational speeds [1,2,12,15]. An interesting novelty in the study of gas evolving reactions, however, is the utilization of microelectrodes (UME) [16,17]. UMEs are electrodes that present at least one of their dimensions in the order of 1–50 \(\mu\)m. A usual shape is microdisks having the diameter of few tens of micra. This small dimension has the same size of the diffusion layer and, in this sense, it promotes a spherical form of diffusion to, or from, the electrode surface. This is a process of mass transportation much faster than the linear diffusion. In fact, a 10 \(\mu\)m diameter UME shows a diffusion rate equivalent to a RDE with a diameter of 1 cm at 5000 rpm [18]. In addition, the enhanced mass transportation away from the electrode surface allows the UME to operate at very high current densities (up to 2 A cm\(^{-2}\)) without nucleation of bubbles on the surface [17]. Moreover, due to the small magnitude of current (\(I\)) that flows through a UME, the product IR (ohmic drop) is usually very low for a large range of resistances (\(R\)). In this way, UME is a unique tool in the study of electrochemical reactions in highly resistive media where the ohmic drop plays an important role.

Aiming to overcome most of the problems discussed above, in this work the HER will be studied in 0.5 M sulfuric acid solutions on Pt UME (\(\phi = 25 \mu\)m). The experiments will be computer controlled to assure an identical surface conditioning and to improve the reproducibility of the results. The Tafel curves obtained will be simulated using a non-linear regression routine [19] employing kinetic equations derived for different mechanisms and selecting the one most appropriate to describe the experimental results. In order to verify the validity of the Volmer–Tafel mechanism proposed for the HER in acid media [1,2,5], the polarization measurements were also performed on a 40 \(\mu\)m Pt surface previously modified by the underpotential deposition of Cu adsorbed atoms (ad-atoms). This procedure was previously developed [20–22] to produce different degrees of coverage on the Pt surface with Cu ad-atoms. In this work, the aim is to eliminate pairs of neighbor active sites, which are essential to the recombination step of the Volmer–Tafel mechanism and analyze the influence of such modification on the polarization measurements response.

2. Experimental

2.1. Cell

A one-compartment Pyrex cell with Teflon cover was used. The small size of the cell (volume of 25 ml), cover and electrodes were advantageous to work with highly purified electrolyte. It facilitates the cleanness of the task. The solutions were deaerated exhaustively with purified \(\text{N}_2\) in order to eliminate the interference of the oxygen reduction reaction.

2.2. Electrodes

The working electrode was two disk-shaped platinum microelectrodes with diameter of 25 or 40 \(\mu\)m. The electrodes were constructed by sealing a Pt wire (Johnson and Matthey 99.95%) in Pyrex glasses followed by polishing the tips with emery paper grid 600 until the exposure of a microdisk. The final polishing was then performed with aqueous 0.3 \(\mu\)m alumina suspension. The geometric area was then checked by optical microscopy and the electrochemical area calculated from the charges under the hydrogen UPD peaks [6] determined by cyclic voltammetry in the same electrolyte at 25 °C.

The reference/auxiliary electrode was a reversible hydrogen electrode in the same solution. A Luggin capillary was used though the ohmic drop was always depreciable in the polarization experiments.

2.3. Solutions

The electrolyte used in this work was prepared with Merck suprapur sulfuric acid and water purified by a Milli-Q system from Millipore Inc.
2.4. Equipments

The electrochemical measurements were performed in an EGG&PARC model 174A Polarographic Analyzer device controlled by an IBM compatible 386 microcomputer. Potential programming was imposed by an AD/DA converter interface linked to the microcomputer and commanded by software written in BASIC, both developed in this laboratory. The state of the UME surface was observed by an Olympikus metallographic microscope. Polarization data were analyzed with a non-linear regression method that is included in the commercial software “MATLAB” (Matlab INC.).

3. Results

3.1. Surface state, electrolyte purity and real area determination

The levels of purity of the electrolyte and the cleanliness of the electrode surface were tested by cyclic voltammetry. Presented in Fig. 1 is one typical voltammogram of the 25 μm Pt UME in 0.5 M H₂SO₄ solution at room temperature and a scan rate of 0.2 V s⁻¹. The usual shape of this voltammogram, presenting well-defined peaks for hydrogen adsorption–desorption and oxide formation–reduction is evidence of the electrolyte purity and the adequate state of the surface. Adsorption of impurities should promote inhibition of those voltammetric peaks [7]. Another problem occurring in home-made UME is the infiltration of electrolyte between the microwire and the insulating layer, by capillarity, which promotes the inclination of voltammograms around the x-axis, an effect that is absent in Fig. 1.

![Fig. 1. Steady-state cyclic voltammogram for the 25 μm Pt UME in 0.5 M H₂SO₄ solution at v = 0.20 V s⁻¹. The shaded area corresponds to the desorption charge of one monolayer of H (2.4 nC) and was used to evaluate the electrochemical area of the electrode (1.1 × 10⁻⁵ cm⁻²).](image)

The electroactive area of Pt was calculated using the H desorption charge (dashed area in the voltammogram of Fig. 1). Considering that the oxidation of one monolayer of Hₐds on polycrystalline Pt surfaces is associated with a charge of 210 μC cm⁻² [6], and the calculated value of 2.4 nC in Fig. 1, one can find an electroactive area of 1.1 × 10⁻⁵ cm⁻². This value corresponds to a roughness factor of 2, a usual value for surfaces polished with 0.3 μm alumina suspension. The same procedure adopted for the 40 μm diameter UME yielded a similar roughness factor.

3.2. Surface conditioning and polarization experiments

In order to achieve an adequate reproducibility of the experimental results it is indispensable to establish a specific procedure to ensure the same initial surface conditioning prior to each measurement. The importance of this matter has already been discussed by Conway and Bai [1]. In this work, a potential programming was applied to the Pt surface before each point in the polarization curves aiming to minimize the influence of the impurities adsorption in the electrochemical response of the HER. In this way, the electrode was initially polarized at 1.55 V for 1 s to create a PtO layer on the surface. After this period, the potential was jumped to 0.05 V during 50 ms to reduce the oxide and expose a clean Pt surface free from adsorbed species others than Hₐds. Finally the potential was driven to the several values in the range of interest to analyze the HER. The resulting currents were then collected after 10 ms of polarization and analyzed. Fig. 2 represents a series of potentiostatic transients with the potential incursion on the range over study. The constant values of currents in the plateau displayed in Fig. 2 for different potential jumps indicate that, after the polarization time above, the HER currents present a stationary-state character and also that no inhibition promoted by the adsorption of eventual impurities could be detected.

This procedure has been applied in the 25 μm Pt UME on 0.5 M H₂SO₄ electrolyte on a temperature range between 25 and 75 °C. All the currents were corrected for back reaction contribution by [1]:

\[
i_{\text{cor}} = \frac{i}{1 - \exp\left(-\frac{-2Fe}{RT}\right)}
\]

where \(i\) is the current density, \(F\) the Faraday constant, \(R\) the gas constant, \(T\) the absolute temperature and \(\eta\) the overpotential. The polarization curves obtained are shown in Fig. 3. The general shapes of these curves are very similar to those reported in the literature [1], i.e. a linear region at low overpotentials showing a Tafel slope of ca. 40 mV dec⁻¹ at 25 °C followed by a non-linear segment almost independent of \(\eta\). This last
Fig. 2. Multiple potentiostatic transients related to the following processes occurring on the 25 µm Pt UME in 0.5 M H₂SO₄ solution: (A) from −1000 to 0 ms-formation of PtO layer at 1.55 V; (B) from 0 to 50 ms-reduction, at 0.05 V, of the PtO previously formed exposing a clean Pt surface to the HER; and (C) from 50 to 100 ms the transient due to the hydrogen reduction on the newly exposed Pt surface. Such transients were performed from 0.05 V to the potentials indicated as $E_{\text{step}}$.

region cannot be associated with a diffusion control because, for a 25 µm UME in the conditions of this work, it would correspond to a current density of ca. 7 A cm⁻².

The extrapolation of the linear region of the curve at 25 °C yielded an $i_0$ value of $2.4 \times 10^{-2}$ A cm⁻², higher than that reported for the same solution, that is $3.2 \times 10^{-3}$ A cm⁻² [1]. This higher value can be justified by the effect of the activation procedure, which is more effective here because the anodic polarization is performed before the measurement of each point, compare to Ref. [1] where it is done previously to each polarization curve.

3.3. Polarization curves analysis

Previous analyses of the HER on Pt in acid media using polarization data similar to those obtained in this work have been performed based on the following mechanism [1]:

1. a primary discharge step (Volmer Reaction):

$$M + H_3O^+ + e^- \leftrightarrow MH_{\text{ADS}} + H_2O \quad (2)$$

Fig. 3. Polarization curves for the HER on the 25 µm Pt UME in 0.5 M H₂SO₄ solution at several temperatures: (A) 25, (B) 30, (C) 35, (D) 40, (E) 45, (F) 50, (G) 55, (H) 60, (I) 65, (J) 70 and (K) 75 °C. Details of polarization measurements were discussed in the text. Current densities were corrected by the electrochemical area of the electrode and for the back-reaction contribution.
2. an electrochemical-desorption step (Heyrovsky Reaction):

\[ \text{MH}_{\text{ADS}} + \text{H}_3\text{O}^+ + e^{-} \underset{k_2}{\Rightarrow} \text{M} + \text{H}_2\text{O} + \text{H}_2 \]  

(3)

3. and a recombination step (Tafel Reaction):

\[ \text{MH}_{\text{ADS}} + \text{MH}_{\text{ADS}} \underset{k_3}{\Rightarrow} 2\text{M} + \text{H}_2\text{O} \]  

(4)

with the overall mechanism being a combination of two [5] or even three [1,2] of these steps. The main discussion is related to the evaluation of the rate determining step (rds). The steady-state condition for the material balance for the adsorption of intermediates in the scheme described by Eqs. (2)–(4) is [4]:

\[ \frac{d\theta}{dt} = 0 = V_1 - V_2 - 2V_3 \]  

(5)

where \( \theta \) is the coverage with H ads, \( \lambda = q_{\text{max}}/F \) and

\[ V_1 = k_1C_{\text{H}^+}(1 - \theta) \exp(\beta_1f_1) \exp(-\beta_1g\theta) \]  

\[ -k_{-1}\theta \exp(-(1 - \beta_1)f_1) \exp((1 - \beta_1)g\theta) \]  

(6)

\[ V_2 = k_2C_{\text{H}^+}\theta \exp(\beta_2f_2) \exp(\beta_2g\theta) \]  

\[ -k_{-2}(1 - \theta) \exp(-(1 - \beta_2)f_2) \exp((1 - \beta_2)g\theta) \]  

(7)

\[ V_3 = k_3\theta^2 \exp(2g\theta) - k_{-3}(1 - \theta)^2 \exp(2g\theta) \]  

(8)

where \( \beta = F/RT \) and \( C_{\text{H}^+} \) is the concentration of H\(^+\) ions. In Eqs. (6)–(8) \( V_i \) refers to the reaction rates of Eqs. (1)–(3), \( k_i \) to the rate constants for the step noted in the subscript, \( \eta \) to overpotentials and \( \beta_1 \) and \( \beta_2 \) to the symmetry factors for the forward step of Reactions (1) and (2), respectively. The parameter \( g \) in Eqs. (6)–(8) measures, in RT units, the change of free energy of adsorption with coverage under Temkin conditions of adsorption [4,23].

In the conditions above, the total faradaic current density, \( i \), can be expressed as [4,24]:

\[ \frac{i}{F} = V_1 + V_2 = 2(V_2 + V_3) \]  

(9)

depending on the adopted mechanism, simplifications can be made to Eq. (9). In this sense, Conway and Bai proposed [1]:

\[ \frac{i}{2F} = k_1C_{\text{H}^+} \exp(\beta_2f_2) \exp(k_2g\theta) + k_3\theta^2 \]  

(10)

This relationship accounts for a mechanism where the Tafel and Heyrovsky reactions are involved in parallel paths but the Tafel reaction makes the greater contribution to the reaction at low \( \eta \), while the Heyrovsky reaction becomes predominant at high \( \eta \). These reactions also neglect the repulsion parameter of the Temkin isotherm. The authors proposed that numerical simulations using Eq. (10) can justify the experimentally obtained Tafel slope of ca. 30 mV dec\(^{-1}\) at low overpotentials, thus confirming the proposed mechanism.

A non-linear fitting method [19] was used here to calculate the current densities values with Eq. (10) and to compare with experimental data. The adjustment procedure between calculated and experimental curves allow us to obtain the values for the rate constant of the determining step. However, to assume that the kinetic equation used describes precisely the experiment, the calculated current densities values have to agree very well with the data points. The polarization results obtained at 25 °C are shown in Fig. 4. It can be seen that the fitting is very poor, mainly in the shape of the calculated curve.

![Fig. 4. Non-linear fitting of the experimental data (Curve (A) in Fig. 3) at 25 °C with the points calculated using Conway's equation (Eq. (10) in the text) [1].](image-url)
Alternatively, if a Volmer–Heyrovsky (rds) mechanism is operating, the theoretical kinetic equation becomes:

\[ i = 2Fv_{\text{H}^+}k_2\theta \exp(\beta_2 f\eta) \exp(\beta_2 g\theta) \] (11)

where \( g \) is the repulsion parameter of a Temkin-type isotherm:

\[ \theta = \frac{1}{1 + (K^{-1}c_{\text{H}^+} \exp(g\theta) \exp(-f\eta))} \] (12)

with \( K \) being the equilibrium constant for the (fast) Volmer reaction. The fittings for curves at 30, 50 and 70 °C are shown in Fig. 5. The curves at the other temperatures showed similar results. The adjustment is almost perfect and indicates that Eqs. (11) and (12) describe the experiment very well. The calculation procedure also allows simulation of the adsorption isotherm for \( \text{H}^+ \). The results are presented in Fig. 6 for the temperatures of 30, 50 and 70 °C indicating that surface coverage is \( \sim 0.1 \) at the beginning of the polarization curve, approaching 1 at high overpotentials. These results disregard the first monolayer of adsorbed H as the reaction intermediate because, as pointed out in Section 1, at potentials more anodic than those explored in the polarization curves, a full monolayer is already present.

The non-linear fitting procedure yielded the values of \( K, k_2, g \) and \( \beta_2 \) that are shown in Table 1 for all sets of temperatures, together with the experimental and calculated value of the exchange current density and the statistical parameters for each line fitting. An analysis of the values displayed in Table 1 points to the following observations: (a) The direct dependence of the rate constant \( k_2 \) with temperature is expected since it involves a desorption step, which is fastened by \( T \). An Arrhenius plot in the form of \( \ln k_2 \) versus \( 1/T \) is shown in Fig. 7. From the slope of this straight line \( (r^2 = 0.99411 \text{ and SD = 0.05967}) \), the apparent activation energy was calculated as 17.9 kJ mol\(^{-1}\). This value is very close to that obtained by Conway et al. for the HER on Pt in 1 M CF\(_2\)SO\(_3\)H, that is 19.7 kJ mol\(^{-1}\) [25]. (b) The values of the equilibrium constant \( K \), for the Volmer Reaction, are almost independent of the temperature. This fact suggests that both the forward and the backward reactions have the same dependence on \( T \). The values were close to 0.1 that was used by Conway and Bai to simulate the polarization curves for the Volmer–Heyrovsky–Tafel mechanism [1]. (c) The \( g \) values have oscillated a little but are always near to one, pointing to a very weak lateral interaction between adsorbed intermediates. (d) The values found for the symmetry factor, \( \beta_2 \), for the Heyrovsky Reaction were very small, when compared with the 0.5 expected. This fact deserves special attention and will be analyzed in Section 3.4. (e) The exchange current values obtained...
Table 1
Parameters extracted from the non-linear fitting for the HER on Pt UME

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$k_2 \times 10^6$ (cm$^2$ s$^{-1}$)</th>
<th>$K$</th>
<th>$g$</th>
<th>$\beta$</th>
<th>$i_{o,exp} \times 10^{-2}$ (A cm$^{-2}$)</th>
<th>$i_{o,calc} \times 10^{-4}$ (A cm$^{-2}$)</th>
<th>$\chi^2 \times 10^{-5}$</th>
<th>$r^2$</th>
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<td>0.70</td>
<td>0.14</td>
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<td>4.0</td>
<td>4</td>
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<td>4.1</td>
<td>3</td>
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<tr>
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by extrapolation of the polarization curves are higher than those obtained from the fitting procedure, by considering $i_o = 2Fz_{Cl + k_2}$. Of course, direct comparison of the two values is not straightforward since HER, in this condition, cannot be considered to be a simple reaction. The calculation from the fitting procedure is not directly related to the low overpotential (and coverage) conditions, but a mean value which includes the dependence of coverage with overpotential and the small value for the transfer coefficient. In literature, the $i_o$ value for HER on Pt in different acid media has been reported to be in the order of $10^{-3}$ A cm$^{-2}$, for 25 °C [26–28]. The extrapolated values of $i_o$ is one order of magnitude higher than the literature one. This may be attributed to the microelectrode characteristics.

The statistical parameters included in Table 1 show the good agreement between experimental and calculated values of the polarization curves.

3.4. Study of the HER on Pt UME modified by UPD Cu

The electrodeposition of some metals in amounts up to one monolayer onto foreign substrates is known as underpotential deposition of metals (UPD) [29–31]. This kind of electrochemical deposition is an apparent violation to the Nernst law and is basically associated with the difference in work functions between the depositing metal and the surface, which generates a residual positive charge on the ad-atom. These dipoles formed on the surface promote a random deposition, with the next ad-atom depositing at the larger possible distance from the previous one. In this sense, the UPD technique has been defined to be an excellent tool to modify the surface on electrocatalysts, in a totally controlled way, by blocking the neighbor active sites and avoiding the adsorption of poisoning species.

The UPD of copper on the Pt UME was used here to take advantage of the elimination of pairs of neighbors active sites on the surface, by depositing amounts larger than a half-monolayer and analyzing the effect of such modification in the HER. The Tafel Reaction proposed in literature for the HER on Pt in acidic media requires neighboring adsorbed hydrogen ad-atoms to undergo chemical recombination. In this way, a half-layer of Cu adsorbed (that inhibits the hydrogen adsorption) should promote a profound effect in the HER pathway by changing the whole mechanism.

Previous studies of Cu UPD have shown that one Cu atom blocks one active site of Pt surface for hydrogen adsorption [20–22]. Besides, the coverage with Cu ad-atom is a function that depends directly on deposition time and inversely on the hydrogen coverage.

The effect of the addition of $5 \times 10^{-5}$ M CuSO$_4$ on the Pt UME steady-state voltammogram in 0.5 M H$_2$SO$_4$ at 6 V s$^{-1}$ is shown in Fig. 8. The deposition potential was chosen as 0.38 V, a value slightly more positive than the Nernst potential for the Cu/Cu$^{2+}$ pair (0.34 V [32]). This is necessary to avoid the formation
of a massive Cu layer in more active regions of the UME, like the border, thus hindering the homogeneous access of Cu$^{2+}$ to the whole disc surface [31]. The formation of an outer massive Cu ring could leave the center of the disk free from Cu$_{ads}$ allowing the HER to occur on a bare surface.

As can be seen in the first-cycle voltammograms displayed in Fig. 8, the charge of desorption for Cu ad-atoms increases with the deposition time up to 80 s, when the anodic branch of the voltammogram presents three oxidation peaks associated with the desorption of the Cu monolayer, in total agreement with previously published results [20–22]. The maximum charge value obtained for the three peaks was 420 $\mu$C cm$^{-2}$, which corresponds to a complete monolayer of Cu$_{ads}$ [22]. The dependence of Cu$_{ads}$ and H$_{ads}$ coverages on the deposition time is presented in Fig. 9.

The effect of the surface modification on HER at 25 °C in 0.5 M H$_2$SO$_4$ + 1 x $10^{-5}$ M CuSO$_4$ solution is shown in Fig. 10. Here the deposition times for Cu UPD are 0, 5 and 30 s for curves (A), (B) and (C), respectively. The surface was initially conditioned at 1.55 V during 1 s and after that the deposition potential of 0.38 V was imposed to the electrode by the specified interval of time aiming to deposit a given amount of Cu. As can be seen in Fig. 9, with the deposition time of 5 s, the coverage with Cu rises to approximately 30% while for 30 s it reaches 80%. After that, the potential was jumped to the cathodic values of the HER and the current measured in 10 ms, as before. Prior to the measurement of each point, the surface was reconditioned at 1.55 V during 1 s and the procedure repeated for the next potential. This methodology allows us to obtain excellent reproducibility in the experiments.

The behavior of the HER either on smooth surfaces or on that modified by deposition of ca. 0.3 and 0.8 monolayer of Cu ($t_{dep}=30$ s) are similar. The only observable effect in Fig. 10 is the shift of the whole curve towards minor values of current as the Cu deposition times increase. This shift can be readily associated to the diminution in the number of active sites for the HER on the surface area, which are partially blocked by the Cu$_{ads}$. With the coverage of 30% the mean values of HER currents in curve (B) are 71% of that on curve (A), while for 80% the current values diminish to approximately 17%. These results show that the blocking of a major amount of allowable surface area was not sufficient to change the mechanism of the HER (given by the slope and the shape of the curves).
In this sense, it is easy to see that the Tafel Reaction is improbable on Pt UME in H$_2$SO$_4$ solutions and that a Volmer–Heyrovsky (rds) mechanism is more convincing. This result agrees with the non-linear fitting and is discussed in the items above.

3.5. Analysis of the symmetry factor values

Low values of $\beta$ can be associated with the so-called activationless process [33–35], as depicted in Fig. 11. The full lines on Fig. 11 represent a normal behavior of electrochemical processes in the absence of transport limitation. The symmetry factor here is close to 1/2. Now, if the cathodic potential is increased, the initial state curve, with the potential dependent energy of the initial state and the energies of several vibrational states, is shifted upward with respect to vacuum, towards less negative potential energy. This new state is represented by the dotted line in Fig. 11. During almost the whole course upward of the initial state curve, the slopes of both initial and final states curves at the intersection point change but $\beta$ remains practically constant. However, with a sufficiently negative shift in the potential, obtainable for fast electrode reactions, there will come a diminution in $\beta$, and in the limiting case the activation energy will be reduced to zero [34], as can be seen in the dotted line in Fig. 11.

The activationless state is difficult to reach experimentally. It needs very high current densities and measurement times shorter than transition times. As stated by Bockris and Khan [34], UME must facilitate such observation. Kriksunov and Krishtalik [36] have discussed the opposite process, i.e. the barrierless process for the hydrogen discharge from 6 M HCl solutions on a conventional Hg electrode.

![Fig. 10. Polarization curves for the HER on the 40 µm Pt UME in 0.5 M H$_2$SO$_4$ + 1 x 10$^{-5}$ M CuSO$_4$ solutions. Curve (A) represents the smooth surface, curve (B) the surface modified with UPD Cu ($\theta_{Cu} = 0.3$) and curve (C) with Cu ($\theta_{Cu} = 0.8$). All the current densities were corrected for the electrochemical area and for the back-reaction contribution.](image1)

![Fig. 11. Plot of potential energy vs. reaction coordinates for a normal process (full lines) and an activationless processes (dotted line).](image2)
It seems very reasonable to associate the low $\beta$ value obtained for the HER with the activationless process discussed above. The HER is a fast reaction with low activation energy ($\Delta G^r = 17.9$ kJ mol$^{-1}$). At very high current densities (near 1 A cm$^{-2}$) polarization curves show the beginning of a limiting current region. Those current density values are still far from the calculated one for diffusion limited current, i.e. 7 A cm$^{-2}$, as mentioned before.

4. Conclusions

The utilization of UME in the study of the HER on Pt in acidic medium brings some novelties in relation with those previously published. First, the non-linear fitting procedure was unable to adjust the kinetic equations of the accepted Volmer–Tafel or Volmer–Heyrovsky–Tafel mechanism to the experimental results obtained using UME. On the other hand, it gave very good agreement between the kinetic equations of the Volmer–Heyrovsky (rds) route and experimental data but with small values for the transfer coefficient $\beta$ ($\sim 0.14$). This unusual result was associated with an activationless process. In this case, the ground state of the reagents is so activated by potential that it can go direct to products, without further chemical activation. There is no activated state and, in the limit case, $\beta$ can be equal to zero. The main consequence of such processes is the appearance of one limiting current without being a diffusional one. This effect seems to be represented in the curves of Fig. 3.

Another attempt to clarify the HER mechanism on such conditions was the experiment with the Pt UME surface modified by Cu UPD. As discussed above, the deposition of Cu blocks the surface active sites and inhibits the H adsorption. In this sense, at high coverage (in this case $\theta_{Cu} = 0.8$) the randomly distributed ad-atoms would eliminate the pairs of neighbors’ active sites on the surface. As in the Volmer–Tafel route, the H ad-atoms need a neighbor to undergo chemical combination, this pathway should be inhibited on the modified surface. However, the results pointed out only a shift of the whole polarization curve to minor current values. The shift was completely justified by the diminishing in the surface area of the electrode.

From the discussions above it seems clear that the utilization of UME in the study of the HER can bring some new information about one of the most studied reactions in electrochemistry.

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References

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