

The evaluation of the polarization resistance in a tubular electrode and its application to the hydrogen electrode reaction

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Abstract

An alternative method for the determination of the kinetic parameters involved in the elementary steps of the reaction mechanism of the hydrogen electrode reaction is proposed. It is based on the determination of the variation of the polarization resistance in a tubular platinum electrode with a laminar flow of electrolyte as a function of the activity of protons of the electrolyte solution. A theoretical expression that relates the experimental variables and the equilibrium polarization resistance is developed, which takes into account the current distribution along the electrode surface. The results are compared with others obtained previously, contributing to the verification of the kinetic mechanism through a completely different experimental procedure.

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1. Introduction

The experimental determination of the kinetic parameters involved in the elementary steps of the reaction mechanism of the hydrogen electrode reaction (HER) is generally carried out through the evaluation of the dependence of the current density (j) with the overpotential (η), for the high η region ($|\eta| > 0.050$ V). This relationship has been obtained more frequently from the study of the hydrogen evolution reaction (her) [1–3], which is usually considered that operates without mass transfer restrictions. With the same objective several kinetic studies have been carried out recently for the hydrogen oxidation reaction (hor) [4–6], although in this case the diffusion of the molecular hydrogen makes difficult the direct calculations of the kinetics constants. Two facts are common to all these studies, one is that the $j(\eta)$ curves correspond to a unique value of the activity of the proton ion and the other is the predominance of the forward reaction upon the backward one for all the elementary steps involved.

On the other hand, an alternative method for the determination of the kinetic parameters of the HER has been already proposed, which carries out the evaluation in a potential region where the rates of the direct and inverse reaction of an elementary step are very similar [7]. In this method, the experimental polarization resistance (R_p^{exp}) is determined from the dependence $j^{\text{exp}}(\eta)$ measured in the overpotential region $-0.005 \leq |\eta| \leq 0.005$ V, being R_p^{exp} the corresponding slope in the origin $R_p^{\text{exp}} = \partial \eta / \partial j^{\text{exp}}|_{\eta=0}$. Then, the variation of R_p^{exp} with the activity of protons (a_{H^+}) and/or the hydrogen partial pressure (P_{H_2}) was analysed [7]. In this case, the potential region as well as the experimental variables, R_p^{exp} , a_{H^+} , P_{H_2} , are different from the conventional method. However, as it has been demonstrated later [8], the dependence $j^{\text{exp}}(\eta)$ has a mass transfer contribution due to the molecular hydrogen, yet at these very low overpotential values. This aspect was not taken into account in the data analysed in our previous work [7]. On this sense, it has been found on steady state conditions a linear relationship between R_p^{exp} and the inverse of the limiting diffusion current density (j_L) [7]:

$$R_p^{\text{exp}}(j_L) = R_p^0 + \frac{RT}{nFj_L} \quad (1)$$

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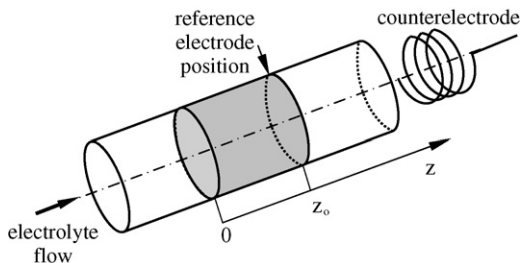


Fig. 1. Schematic representation of the tubular electrode.

where R_p^0 is the equilibrium polarization resistance, which represents the condition of absence of mass transfer contribution. This equation is strictly valid only when the reaction is taking place on electrodes where j_L is uniform in the whole surface, that is in absence of any type of current distribution. Then, the kinetic parameters can be obtained from the correlation of the dependence $R_p^0(a_{H^+})$ or $R_p^0(P_{H_2})$. The corresponding analytical expression $R_p^0(a_{H^+}, P_{H_2})$ has been already derived [7] for the Volmer–Heyrovsky–Tafel (VHT) mechanism, which is generally accepted for this reaction on metallic electrodes [1–8], being the reaction steps in acid solutions:



where H_{ad} is the reaction intermediate.

In this context, the present work studies the application of the method described above for the case of a tubular electrode with a laminar flow of electrolyte, oriented to the evaluation of the kinetic parameters of the HER. As Eq. (1) is not directly applicable to this case because j_L varies along the electrode surface (tertiary current distribution) [9,10], the theoretical expression that relates the experimental variables and the equilibrium polarization resistance is developed. Then, the kinetic parameters will be evaluated from the correlation of the relationship $R_p^0(a_{H^+})$.

2. Theoretical basis

It is considered a tube of inner radius r_0 with isolated walls except an intermediate region of length z_0 that is an electronic conductor (Fig. 1). A H_2SO_4 aqueous solution saturated with hydrogen gas at 1 atm. flows in laminar conditions (Reynolds number less than 2000 [9,10]) inside the tube at a volume flow rate $Q = \pi r_0^2 v_f$, where v_f is the mean fluid velocity. When a small electric current (I^{exp}) flows between the electronic conductor (tubular electrode) and a counter electrode (located upstream), the HER is verified at the electrode with a local current density $j(z)$. The resulting experimental current density (j^{exp}) is the mean value of $j(z)$:

$$j^{exp} = \frac{I^{exp}}{2\pi r_0 z_0} = \frac{1}{z_0} \int_0^{z_0} j(z) dz \quad (3)$$

Furthermore, increasing the current, a limiting value is reached when the concentration of the molecular hydrogen is annulled

in the whole electrode surface. In this condition the limiting local current density (j_L) is defined, which depends on z and on the maximum fluid velocity of the electrolyte $v_m = v(r=0)$ as follows [9,10]:

$$j_L(z, v_m) = 0.6782nFC^0 D \left(\frac{v_m}{r_0 Dz} \right)^{1/3} \quad (4)$$

being D the diffusion coefficient and C^0 the concentration of H_2 and the other constants have the usual meaning. Taking into account that in conditions of laminar flow $v_m = 2v_f$, Eq. (4) can be written as

$$j_L(z, v_f) = K \left(\frac{v_f}{z} \right)^{1/3} \quad (5)$$

where K is

$$K = 0.8548nFC^0 \frac{D^{2/3}}{r_0^{1/3}} \quad (6)$$

On the other hand, when the tubular electrode is operated at very low overpotentials ($|\eta| < 0.005$ V), the following linear dependence is verified at any position z [11]:

$$\eta(z, v_f) = R_p(z, v_f) j(z, v_f); \quad j(z, v_f) \ll j_L(z, v_f) \quad (7)$$

where $R_p(z, v_f)$ is the local polarization resistance, which is defined as [11]:

$$R_p(z, v_f) = \left. \frac{\partial \eta(z)}{\partial j(z)} \right|_{\eta=0, v_f} = \lim_{\eta \rightarrow 0} \frac{\eta(z)}{j(z)} \Big|_{v_f} \quad (8)$$

$R_p(z, v_f)$ can be expressed by Eq. (1) at a given value of the z coordinate and consequently, substituting it into Eq. (7), the following expression is obtained at constant v_f :

$$\eta(z) = \left[R_p^0 + \frac{RT}{nFj_L(z)} \right] j(z) \quad (9)$$

being $j_L(z)$ described by Eq. (5). As the current I^{exp} is measured at the overpotential corresponding to the position $z_0(\eta_0)$, an expression similar to Eq. (7) can be always written:

$$\eta_0(v_f) = R_p^{*exp}(v_f) j^{exp}(v_f) \quad (10)$$

where $R_p^{*exp}(v_f)$ is the experimental polarization resistance for the present case:

$$R_p^{*exp}(v_f) = \left. \frac{\partial \eta_0}{\partial j^{exp}} \right|_{\eta=0, v_f} = \lim_{\eta \rightarrow 0} \frac{\eta_0}{j^{exp}} \Big|_{v_f} \quad (11)$$

and j^{exp} is given by Eq. (3). Then, applying the condition $z = z_0$ to Eq. (8) and substituting it into Eq. (11), the following relationship can be easily obtained:

$$R_p(z_0, v_f) = R_p^{*exp}(v_f) \lim_{\eta \rightarrow 0} \frac{j^{exp}}{j(z_0)} \Big|_{v_f} = R_p^{*exp}(v_f) \psi_0 \quad (12)$$

At $\eta \rightarrow 0$, the experimental current density (a mean value) and the local current density (in this case at z_0) tend simultaneously to zero. Therefore, the diffusion effect disappears and the relationship between both current densities (ψ_0) can be considered

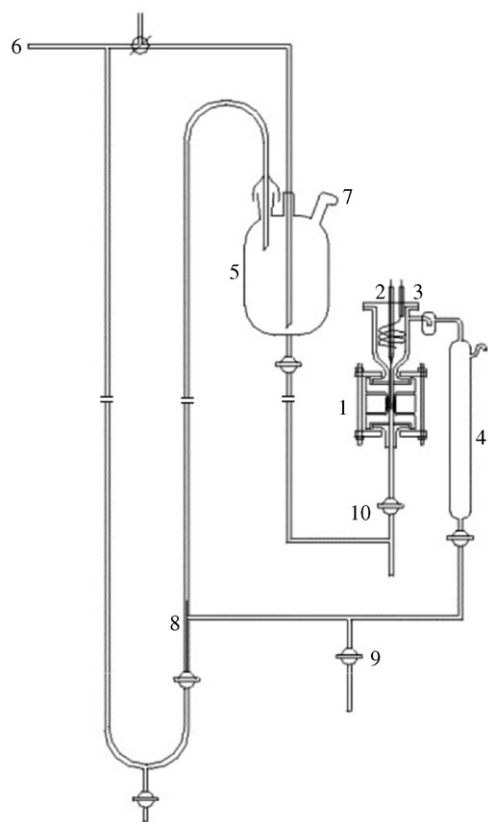


Fig. 2. Experimental device (cell and solution circulation system). (1) tubular Pt electrode and support; (2) reference electrode; (3) counter electrode; (4) test tube; (5) solution reservoir; (6) hydrogen inlet; (7) hydrogen outlet; (8) drive system for electrolyte circulation (hydrogen-lift); (9) sampler; (10) flow regulation valve.

invariant with the flow rate. Then, reordering Eq. (12) and taking into account Eqs. (5) and (9):

$$R_p^{*exp} = \frac{R_p^0}{\psi_0} + \frac{RTz_0^{1/3}}{nFK\psi_0} \frac{1}{v_f^{1/3}} \quad (13)$$

Eq. (13) predicts a linear relationship between R_p^{*exp} and the inverse of the cube root of the mean fluid velocity:

$$R_p^{*exp} = A + B v_f^{-1/3} \quad (14)$$

This equation will be used to evaluate R_p^0 from the experimental results on a tubular electrode.

3. Experimental

3.1. Flow cell details

A device consisting in a platinum tubular electrode and an electrolyte circulation system has been design and constructed (Fig. 2). The main body consists in a tubular platinum electrode of 3 mm length and 1.8 mm inner diameter. It was anchored in a carbon graphite holder of 10 mm thickness and 38 mm external diameter, which is also used for the electric contact. The supporting device is completed with two Teflon rings of 45 mm

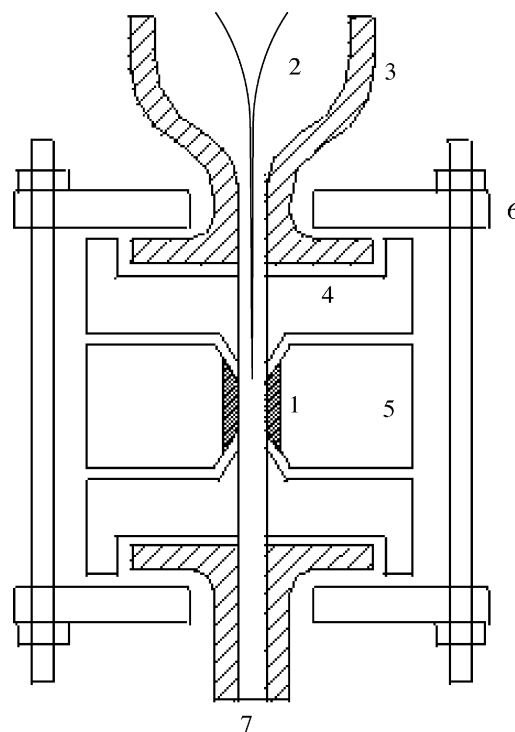


Fig. 3. Scheme of the working electrode and holder. (1) tubular Pt electrode; (2) Luggin capillary; (3) upper part of the cell; (4) Teflon rings; (5) graphite holder; (6) bridles; (7) electrolyte inlet.

diameter and a central hole of the same diameter of the working electrode. These rings have a conical terminal seated on the ends of the electrode and of the graphite holder, so that it is defined a cylindrical hole of 1.8 mm diameter and 15 mm length, 3 mm of which correspond to the platinum electrode, located at 7 mm from the entrance. A detailed scheme of this part can be observed in Fig. 3.

Above and below the main body there are two glass tubes that finish in grinded planes of 27 mm external diameter, which are firmly held to the main body through a system of acrylic bridles. The upper body gets wider to give place to the cell that contains the platinum counter electrode and the Luggin capillary with the reference electrode (reversible hydrogen electrode), which end is located in the external edge of the tubular electrode. To avoid fluid dynamic problems, the Luggin capillary was located upstream with respect to the working electrode. It was built stretching a tube until the external diameter was less than 0.1 mm (Fig. 3). A lateral outlet allows the discharge of the electrolytic solution in a test tube for the measurement of the volume flow rate (Q). A flow regulation valve below the main body is used to control the electrolyte circulation from the cell toward the upper part in a closed loop. The solution reservoir, located one meter above the discharge of the cell, have a hydrogen bubbler and it is constantly fed by the electrolyte that leaves the flow cell. It was filled with Raschig rings to improve the interfacial contact between the gas and the liquid, allowing a quicker and more efficient saturation of the solution. After passing through the test tube, the electrolyte is impelled to the reservoir by means of a “hydrogen-lift” system. This device allows the elevation of

the electrolyte and contributes to the saturation of the solution with hydrogen gas.

3.2. Cleaning of the device

The presence of extremely small amounts of contaminants is immediately detected because the reversible potential of the working electrode cannot be achieved. Therefore, a high level of purity is needed in both the electrolytic solution and the hydrogen gas. A thorough cleaning process of the experimental device is also needed. It was carried out through the circulation of chromic-sulphuric solution followed by a strong rinsing with triply distilled water and finally with the electrolyte solution.

3.3. Methodology

The electrochemical experiences were carried out with a potentiostat-galvanostat Wenking POS2, controlled through an interface Advantech PCI1710HG and the software Labview 6i. The experimental determination of the current–potential dependence around the equilibrium potential was carried out by the application of a program of current pulses at different electrolyte velocities and different pH values. In the first anodic pulse with a duration of 7 s, a potential of 1.75 V was reached oxidizing any substance that could have been accumulated by adsorption on the electrode surface. A layer of platinum oxide is also formed at this potential, which is reduced in the following cathodic pulse generating a reproducible surface state. In the following pulse, the current is annulled during 30 s, reaching the potential the corresponding reversible value. Finally, a third pulse is applied to a given (anodic or cathodic) current during 45 s. Then, the program is repeated changing only the third pulse in order to obtain the dependence $j^{\text{exp}}(\eta_0, a_{\text{H}^+}, v_f)$. The selected current values produce an apartment with respect to the reversible potential less than 5 mV, which correspond to the linear region of the current–potential dependence. The volume flow rate Q ($\text{cm}^3 \text{s}^{-1}$) was measured as the time needed to fill a given volume in the test tube. The corresponding mean fluid velocity (v_f) was calculated as $v_f = Q/\pi r_0^2$.

3.4. Evaluation of a_{H^+}

The determination of the activity of protons was carried out starting from the corresponding pH of the H_2SO_4 solutions ($a_{\text{H}^+} = 10^{-\text{pH}}$). A calibration curve of the pH meter was made with buffer solutions of 25 cm^3 0.2 M KCl + $X \text{ cm}^3$ 0.2 M HCl [12]. This curve was used for the lower concentrations. For the most concentrated solutions ($\text{pH} < 1$), the relationship pH versus concentration obtained from the literature was employed [13].

4. Results

4.1. Dependence $j^{\text{exp}}(\eta_0)$

Fig. 4a illustrates the potential response corresponding to the applied program of current pulses shown in Fig. 4b, for the case of a pH value equal to 1.50 and a mean fluid velocity

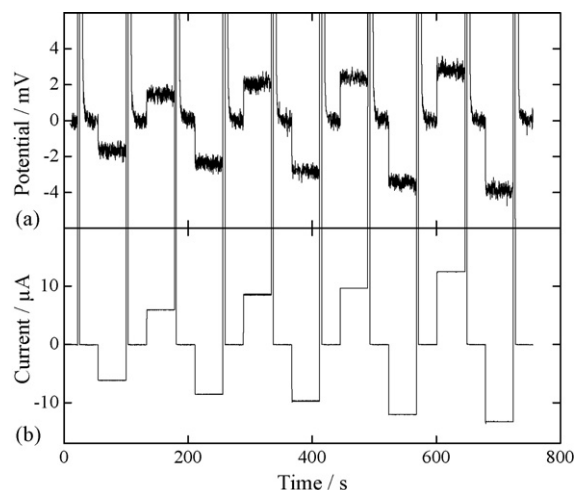


Fig. 4. Potential transient (a) obtained from the application of the current program (b). pH 1.50, $v_f = 21.13 \text{ cm s}^{-1}$.

$v_f = 21.13 \text{ cm s}^{-1}$. For each current pulse, 400 potential readings were obtained and the 2/3 ends were averaged to assure that the system has reached the stationary state. Then, the mean value ($\bar{\eta}$) was calculated and the corresponding standard error of the mean (S.E.) was always less than 0.02 mV ($\eta = \bar{\eta} \pm 0.02$). Starting from these averages the current–potential plots around the equilibrium potential were obtained, one of those is shown in Fig. 5. It should be taken into account that the measured potentials correspond to the point where the electrolyte leaves the tubular electrode.

4.2. Verification of Eq. (14)

The experimental determinations were carried out in the following range of the electrolyte velocity $6 < v_f$ (cm s^{-1}) < 53 . Six different pH values of the H_2SO_4 solutions comprised in the range $0.2 < \text{pH} < 2$ were used, being the corresponding range of the activity of protons $0.01 < a_{\text{H}^+} < 0.65$. A total amount of forty three measurements of the dependence $j^{\text{exp}}(\eta_0, a_{\text{H}^+}, v_f)$ were made.

The experimental polarization resistance was evaluated for each relationship $i^{\text{exp}}(\eta_0)$, according to Eq. (11). The values

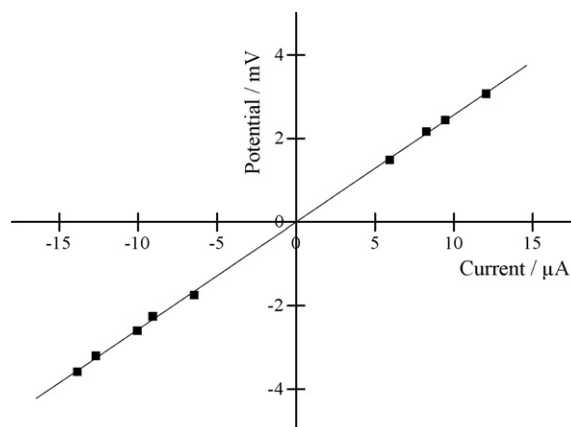


Fig. 5. Potential vs. current plot. pH 1.50, $v_f = 13.55 \text{ cm s}^{-1}$.

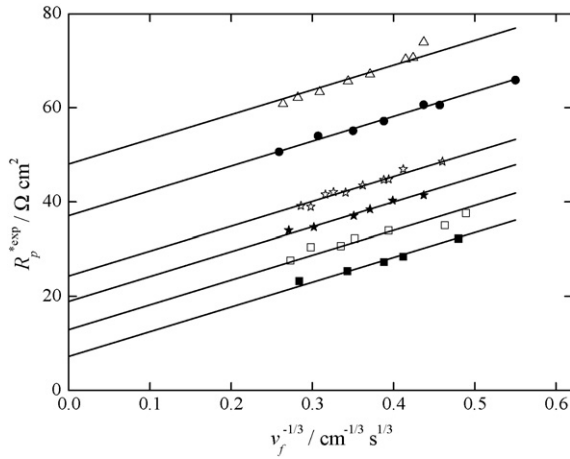


Fig. 6. Experimental dependence R_p^{*exp} vs. $v_f^{-1/3}$. a_{H^+} : (Δ) 0.0105; (\bullet) 0.0148; (\star) 0.0313; (\star) 0.0490; (\square) 0.0676; (\blacksquare) 0.6456.

of R_p^{*exp} obtained from the 43 experiments were plotted as a function of the inverse of the cube root of the mean fluid velocity (Fig. 6). It can be appreciated that R_p^{*exp} increases linearly with $v_f^{-1/3}$ as it was predicted by Eq. (14) and also the independence of ψ_0 with v_f was verified.

In order to evaluate $R_p^0(a_{H^+})$, it is necessary to calculate the ψ_0 value. The following expression can be obtained from Eqs. (13) and (14):

$$\psi_0 = \frac{RTz_0^{1/3}}{nFKB} = \frac{B_0}{B} \quad (15)$$

Starting from the straight lines in Fig. 5, the value $B = 51.3 \Omega \text{ cm}^{7/3} \text{ s}^{-1/3}$ was obtained for all the pH values analysed. On the other hand, B_0 can be evaluated from the constants included in its definition (Eq. (15)). The solubility and the diffusion coefficient of the molecular hydrogen in the H_2SO_4 solutions are needed. They can be considered approximately constant in the range of pH analysed, being $C^0 = 7.14 \times 10^{-6} \text{ mol cm}^{-3}$ and $D = 3.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [4]. With $r_0 = 0.09 \text{ cm}$, $z_0 = 0.3 \text{ cm}$, $n = 2$ and $T = 298 \text{ K}$, the value $B_0 = 2.95 \Omega \text{ cm}^{7/3} \text{ s}^{-1/3}$ was obtained and consequently $\psi_0 = 0.0575$. Finally, taking into account that $R_p^0 = A\psi_0$ (Eqs. (13) and (14)), the corresponding values of the equilibrium polarization resistance were calculated for each pH. The dependence $R_p^0(a_{H^+})$ is illustrated in Fig. 7 (square dots).

4.3. Evaluation of the kinetic parameters

The theoretical expression that relates the equilibrium polarization resistance with the kinetic constants of the elementary steps corresponding to the Volmer–Heyrovsky–Tafel mechanism of the hydrogen electrode reaction was derived previously [7],

$$R_p^0 = \frac{RT}{4F^2} \frac{(K_T^{1/2} + P_{H_2}^{1/2})\{4k_{+T}P_{H_2} + (K_T^{1/2} + P_{H_2}^{1/2}) \times [k_{+V}a_{H^+}^{\alpha_V} K_T^{1/2} P_{H_2}^{(1-\alpha_V)/2} + k_{+H}a_{H^+}^{\alpha_H} P_{H_2}^{(2-\alpha_H)/2}]\}}{\{(K_T^{1/2} + P_{H_2}^{1/2})k_{+V}k_{+H}a_{H^+}^{(\alpha_V+\alpha_H)} K_T^{1/2} P_{H_2}^{(3-\alpha_V-\alpha_H)/2} + k_{+H}k_{+T}a_{H^+}^{\alpha_H} P_{H_2}^{(4-\alpha_H)/2} + k_{+V}k_{+T}a_{H^+}^{\alpha_V} K_T^{1/2} P_{H_2}^{(3-\alpha_V)/2}\}} \quad (16)$$

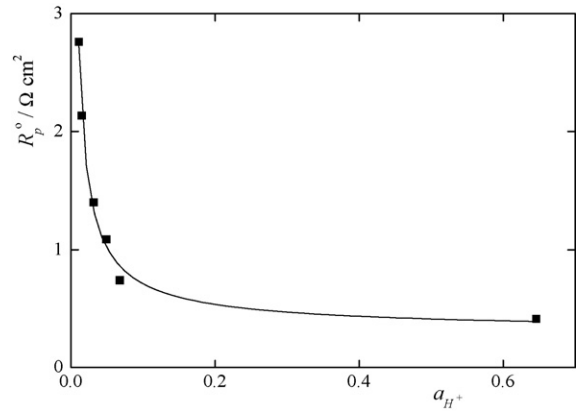


Fig. 7. Dependence R_p^0 vs. a_{H^+} . (\blacksquare) Experimental data and (—) simulation.

Table 1

Kinetic constants from the correlation of the experimental data

k_{+V}	3.9×10^{-6}
k_{-V}	1.3×10^{-7}
k_{+H}	$<10^{-10}$
k_{-H}	$<10^{-10}$
k_{+T}	2.578
k_{-T}	2.25×10^{-7}
α_V	0.787
α_H	0.50

where k_{+i} and k_{-i} are, respectively, the kinetic constants of the forward and backward reactions of the elementary step i ($i = V, H, T$), α_i ($i = V, H$) is the symmetry factor of the step i and K_T is the equilibrium constant of the Tafel step ($K_T = k_{+T}/k_{-T}$). Eq. (16) allows the evaluation of the independent kinetic parameters k_{+V} , k_{+H} , k_{+T} , $K_T^{1/2}$, α_V , α_H from the correlation of the experimental dependence of R_p^0 on a_{H^+} or P_{H_2} . In the present case, the data shown in Table 1 were obtained from the regression of the experimental points shown in Fig. 7. It has been found a high sensitivity for all the correlated parameters. This is due to the shape of the function, which has a very high derivative for $a_{H^+} < 0.1$ and very low for $a_{H^+} > 0.2$. Therefore, it can be considered that the calculated values of the kinetic parameters are reasonably accurate. The continuous line in Fig. 7 is the corresponding simulation with them.

The other parameters k_{-V} , k_{-H} and k_{-T} were also evaluated starting from the following relationships [7]:

$$k_{-V} = K_T^{1/2} k_{+V} \quad (17)$$

$$k_{-H} = \frac{k_{+H}}{K_T^{1/2}} \quad (18)$$

$$k_{-T} = \frac{k_{+T}}{K_T} \quad (19)$$

Table 2
Calculated elementary kinetic parameters

Pt electrode	v_V^e	v_H^e	v_T^e	θ^e
Polyc. ^a	2.10×10^{-6}	$<10^{-12}$	2.25×10^{-7}	2.94×10^{-4}
Polyc. [7]	5.21×10^{-7}	$<10^{-12}$	1.37×10^{-6}	1.46×10^{-7}
Polyc. [8]	8.12×10^{-6}	6.78×10^{-12}	6.13×10^{-9}	1.08×10^{-4}
Polyc. [14]	1.48×10^{-5}	$<10^{-12}$	2.97×10^{-7}	8.40×10^{-3}
(1 0 0) _{S_I} [15]	7.82×10^{-7}	–	3.16×10^{-8}	1.01×10^{-1}
(1 0 0) _{S_{II}} [15]	1.49×10^{-5}	–	1.83×10^{-7}	1.29×10^{-1}
(1 1 1) _I [15]	2.35×10^{-6}	–	1.82×10^{-7}	9.8×10^{-2}
(5 1 1) [15]	3.40×10^{-5}	–	2.75×10^{-7}	5.9×10^{-2}
(1 1 1) [15]	6.11×10^{-5}	–	2.38×10^{-7}	2.47×10^{-1}
Polyc. [16]	6.73×10^{-7}	2.64×10^{-8}	1.24×10^{-6}	9.1×10^{-2}

^a This work.

The resulting values are also shown in Table 1. This way all the kinetic constants of the forward and backward reactions of the elementary steps could be known. Finally, the equilibrium surface coverage (θ^e) was calculated through Eq. [7]:

$$\theta^e = \frac{P_{H_2}^{1/2}}{K_T^{1/2} + P_{H_2}^{1/2}} \quad (20)$$

The equilibrium reaction rates of the elementary steps v_i^e ($i = V, H, T$) can be also evaluated through their respective expressions as a function of P_{H_2} and a_{H^+} [7]:

$$v_V^e = \frac{k_{+V} a_{H^+}^{\alpha_V} K_T^{1/2} P_{H_2}^{(1-\alpha_V)/2}}{K_T^{1/2} + P_{H_2}^{1/2}} \quad (21)$$

$$v_H^e = \frac{k_{+H} a_{H^+}^{\alpha_H} P_{H_2}^{(1-\alpha_H)/2}}{K_T^{1/2} + P_{H_2}^{1/2}} \quad (22)$$

$$v_T^e = \frac{k_{+T} P_{H_2}}{(K_T^{1/2} + P_{H_2}^{1/2})^2} \quad (23)$$

The values of θ^e , v_V^e , v_H^e and v_T^e for $a_{H^+} = 0.455$ (0.5 M H₂SO₄) and $P_{H_2} = 1$ atm. are shown in Table 2. This condition was chosen in order to compare the present results with previously obtained data, also shown in Table 2. It can be appreciated that the kinetic parameters obtained by the present method have an adequate agreement with those obtained through the study of the HER [7], hor [8] and the simultaneous correlation of the her and hor with a Frumkin-type adsorption [14]. This agreement can be also observed in the comparison with the results reported by Conway et al. [15] and Bai [16] (Table 2), with the exception of the equilibrium surface coverage where our results are significantly less.

5. Discussion

For the experimental determination of the dependence $j(\eta)$ for the hydrogen electrode reaction on steady state it is necessary to fix the thickness of the diffusion layer of the molecular hydrogen. The rotating disc electrode is usually employed for this purpose. The present work proposes an alternative, consisting in the use of a flow cell with a tubular electrode. The device was design to operate without mobile elements and with an

efficient capacity to saturate the electrolyte solution with hydrogen gas. Two basic aspects must be taken into account in order to ensure a laminar flow. The first one is that the mean fluid velocity must be $v_f < 10^3 \sigma r_0^{-1}$ [10], where σ is the kinematic viscosity in cm² s⁻¹. Being $\sigma = 0.01$ cm² s⁻¹ and $r_0 = 0.09$ cm, then $v_f < 111$ cm s⁻¹, which is verified in all the experiments ($6 < v_f$ (cm s⁻¹) < 53). The other refers to the existence of large insulating tubular sections located before the electrode. Besides, the inner surface must be very smooth in the whole length.

Furthermore, the present study demonstrates that the kinetic parameters of the HER can be evaluated by the use of the experimental current–potential dependence near equilibrium under appropriate fluid dynamic conditions. This alternative method is based on the determination of the relationship between the polarization resistance and the activity of protons in the electrolyte solution. It should be emphasized that in this method the kinetic constants are calculated through a procedure that cannot be applied to the experimental data obtained in the cathodic or anodic potential region. Therefore, the comparison of the present results with others obtained at $|\eta| > 0.050$ V constitutes a test of consistency due to the important differences between each method. The reasonable agreement in the parameters values (Table 2) indicates that the kinetic mechanism used to describe the HER is consistent. An exception is the equilibrium surface coverage, which is different from the values reported by other authors [15,16]. In relation to this parameter, it should be useful to discuss the participation or not of the under potential deposited hydrogen (H_{UPD}) as the reaction intermediate of the HER. The analysis can be done on a voltammogram recorded on a platinum electrode in acid solution [17]. It shows that the potential range of H_{UPD} adsorption is $0.03 < E$ versus RHE (V) < 0.35 . Due to the absence of molecular hydrogen in the solution, the reversible potential of the platinum electrode is located at high anodic values (near infinite) with respect to the reference electrode (RHE). Therefore if the H_{UPD} would be the reaction intermediate, the Tafel and/or Heyrovsky steps should be verified immediately after its adsorption (Volmer step) and lead to the dissolution of molecular hydrogen, the nucleation of hydrogen bubbles and the gas evolution, but these processes are not observed up to potentials very closed to that of the electrode reference ($E \leq 0.02$ V). This behaviour can be due to the high values of the energy involved in the H_{UPD} adsorption process, which turn negligible

the corresponding desorption through the Heyrovsky or Tafel steps. Then, it can be concluded that the reaction intermediate of the HER is a more weakly form of adsorbed hydrogen than the H_{UPD} . In this sense, there is a quite widespread acceptance of the Conway's proposal about that the reaction intermediate of the HER is a different form of adsorbed hydrogen called H_{OPD} (over potential deposited) [3,18]. Therefore, the equilibrium surface coverage should be $\theta^e < \theta_{H(UPD)}$ ($E = 0.0$). In the present work, it was found $\theta^e \cong 10^{-4}$, which although is consistent with our previous results [8,14], it is significantly less than other values reported in the literature or that can be evaluated from the reported values of the specific kinetic constants [7]. Some of them, obtained from the correlation of the experimental dependence $j(\eta)$ corresponding to the her, were included in Table 2 [15,16]. As in all cases there was a fitting process, it should be important to find another independent way to analyse the magnitude of θ^e . It can be considered that the HER is verified mainly through the Volmer–Tafel route [8,16,19,20], which is characterised by the existence of a finite limiting kinetic current j_L^{kin} . Under Langmuir adsorption conditions j_L^{kin} is given by [21],

$$j_L^{kin}(her) = \frac{2Fv_T^e}{\theta^e} \quad (24)$$

$$j_L^{kin}(hor) = \frac{2Fv_T^e}{(1 - \theta^e)^2} \quad (25)$$

and the corresponding relationship between Eqs. (24) and (25) can be used for the estimation of θ^e :

$$\frac{j_L^{kin}(her)}{j_L^{kin}(hor)} = \frac{(1 - \theta^e)^2}{\theta^e} \quad (26)$$

Experimental determinations carried out in our laboratory indicates that the her on Pt reaches values of $j = 7 \text{ A cm}^{-2}$ without any indication of a limiting value [14]. Furthermore, studies made on other metals much less active than Pt such as Ni [22] or Hg [23] found $j_L^{kin}(her) > 10 \text{ A cm}^{-2}$. Consequently, it can be considered reasonable that for platinum $j_L^{kin}(her) \gg 10 \text{ A cm}^{-2}$. On the other hand, the analysis of the hor on rotating Pt disc electrode gave $j_L^{kin}(hor) \cong 0.24 \text{ A cm}^{-2}$ [8], while for the hor on Pt microelectrodes was obtained $j_L^{kin}(hor) \cong 0.26 \text{ A cm}^{-2}$ [24]. Therefore, substituting these values into Eq. (26) it can be concluded that the equilibrium surface coverage is $\theta^e \ll 0.14$. On this context, the data available in the literature can be analysed. In absence of kinetic approximations, such as when the backward contributions of the Heyrovsky and Tafel steps are neglected, the values are less than 0.14 (see Table 2) with the exception of Pt(111) and Pt(100) S_{II} . Nevertheless, in all cases, these values were obtained through the correlation of the her under Langmuirian adsorption, which is not appropriate because the variation of $\theta(\eta)$ is large, even more if a high θ^e value is considered. It is likely that a kinetic analysis including interactions between adatoms will produce θ^e values less than those reported. Therefore, the value of the equilibrium surface coverage is still an open subject that would need new independent evaluations.

Other interesting aspect of the present methodology related to the adsorption behaviour of the reaction intermediate is that it is not necessary to propose an expression for the Gibbs free energy

of adsorption on terms of the surface coverage (Frumkin, etc.) because all the parameters that are functions of θ are evaluated at the equilibrium value θ^e [11]. This fact is very important because for the evaluation of the kinetic parameters at high overpotentials is necessary to propose not only a kinetic mechanism but also the description of the adsorption process. Consequently, if the kinetic parameters are already known by this method, then the experimental $j(\eta)$ curves at high $|\eta|$ would be used only for the characterization of the adsorption process (e.g. the calculation of the Frumkin interaction parameter).

6. Conclusions

A method for the evaluation of the kinetic parameters of the hydrogen electrode reaction is proposed using an experimental procedure completely different to the usual methodology, which can contribute to verify the kinetic mechanism. It consists basically in the determination of the variation of the polarization resistance in a tubular platinum electrode as a function of the activity of protons of the electrolyte solution. Besides, an advantage of this method is that the description of the adsorption behaviour of the reaction intermediate is not needed. The results obtained confirm that the hydrogen electrode reaction on platinum in acid solutions operates, basically, under the Volmer–Tafel route.

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