Analysis of the applicability of short time chronoamperometry for the kinetic study of the hydrogen oxidation reaction

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ABSTRACT

This work analyses the applicability of the chronoamperometric method for the evaluation of the kinetic parameters of the hydrogen oxidation reaction. It consists in the application of an overpotential step and the subsequent plot of the current density response against the square root of time. The extrapolation of the resulting straight line at short times is assigned to the kinetic current density (j_k) at such overpotential (η). Then, from the polarization curve obtained after the evaluation of j_k at different η, the parameters exchange current density and Tafel slope are evaluated. This method is only strictly valid for simple reactions without adsorbed intermediates. Therefore, a complete analysis that takes into account all the phenomena involved, including the effect of the pseudocapacitive current due to the adsorbed hydrogen, is carried out. The results obtained confirm the inapplicability of the chronoamperometric method for the kinetic study of the hydrogen oxidation reaction.

1. Introduction

The evaluation of the kinetic parameters of the hydrogen oxidation reaction (HOR) can be carried out from the experimental dependence of the current density (j) on overpotential (η). This dependence can be obtained under different experimental conditions (transient or steady state). One of the methods usually employed consists in the determination of the experimental dependences $j(\eta)$ on steady state at different rotation rates (ω) and then the evaluation of the corresponding kinetic or activated contribution to the current density (j_k), free of mass transport effect, at different overpotentials. From these values and through the application of a basic kinetic analysis, the kinetic parameters are calculated [1–3]. The most frequently used method for the calculation of the kinetic current density is the Levich-Koutecky method, which consists in the plot of the reciprocal of the current density versus the reciprocal of the square root of the rotation rate (j^{-1} vs. $\omega^{-1/2}$) at a given overpotential. From the intercept of this plot ($\omega \to \infty$), the corresponding supposed value of j_k at such overpotential is obtained. However, this method was critically analyzed [4,5], having been demonstrated that even though this procedure is applicable to simple reactions, it cannot be applied when the reactions involve adsorbed intermediates. Moreover, it was

unequivocally proved that its application to the HOR leads to wrong results [4–6].

Another commonly used method is the analysis of the transient dependence of the current resulting from a potential step (chrono-amperometry). The step is applied from the reversible potential to a given overpotential value and the resulting current is recorded in the short time range ($t < 0.01$ s) and then plot against the square root of time. The extrapolation at $t \to 0$ of the resulting straight line is assigned to the kinetic current density at such overpotential [7]. This technique is also clearly justified for simple reactions that do not involve adsorbed species [7–9]. On the other hand, the application of this method for the kinetic study of reactions where there is a marked variation of the surface coverage of the adsorbed reaction intermediates on overpotential, such as hydrogen oxidation, has not been verified as a valid procedure yet. Moreover, the pseudocapacitive current produced by the adsorbed species introduces a strong contribution to the measured current value, which was not taken into account in the theoretical derivation of the current–time dependence [7–9]. However, it is commonly applied for the kinetic study of the HOR [10,11].

On this context, the present work proposes to analyze the applicability of the chronoamperometric method to the kinetic study of the hydrogen oxidation reaction. The system of equations needed for the calculation of the transient response of the current density resulting from a potential step beginning at the equilibrium state to a given overpotential will be derived and solved, considering that the reaction takes place under the Tafel-Heyrovsky-Volmer kinetic mechanism. Then, the time region where the relationship j
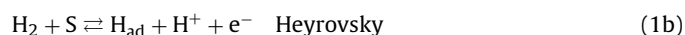
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vs. $t^{1/2}$ is linear will be established and the kinetic current density corresponding to such overpotential will be obtained. This chronoamperometric value (j_k^{ca}) will be compared with that corresponding to the kinetic current density on steady state (j_k^{ss}), obtained from the rigorous resolution of the kinetic mechanism on such conditions for the same overpotential value [6].

2. Theoretical analysis

Consider a non-porous flat (or cylindrical) electrode in contact with a stagnant acid solution saturated with molecular hydrogen at 1 atm, where the hydrogen oxidation reaction is taking place. The kinetic steps of the Tafel-Heyrovsky-Volmer mechanism are,

$$H_2 + 2S \rightleftarrows 2H_{ad} \quad \text{Tafel} \tag{1a}$$

$$H_2 + S \rightleftarrows H_{ad} + H^+ + e^- \quad \text{Heyrovsky} \tag{1b}$$

$$H_{ad} \rightleftarrows H^+ + e^- + S \quad \text{Volmer} \tag{1c}$$

where S is an adsorption site and H_{ad} is the adsorbed hydrogen (reaction intermediate). The corresponding expressions of the rates of the elementary steps, considering a Frumkin type adsorption for H_{ad}, are [6],

$$v_T = v_T^e \left[\frac{C_{H_2}^s (1-\theta)^2}{C_{H_2}^e (1-\theta^e)^2} e^{-2\lambda u(\theta - \theta^e)} - \frac{\theta^2}{\theta^{e2}} e^{2(1-\lambda)u(\theta - \theta^e)} \right] \tag{2a}$$

$$v_H = v_H^e \left[\frac{C_{H_2}^s (1-\theta)}{C_{H_2}^e (1-\theta^e)} e^{-\lambda u(\theta - \theta^e)} e^{\alpha_H f\eta} - \frac{\theta}{\theta^e} e^{(1-\lambda)u(\theta - \theta^e)} e^{(\alpha_H - 1)f\eta} \right] \tag{2b}$$

$$v_V = v_V^e \left[\frac{\theta}{\theta^e} e^{(1-\lambda)u(\theta - \theta^e)} e^{\alpha_V f\eta} - \frac{(1-\theta)}{(1-\theta^e)} e^{-\lambda u(\theta - \theta^e)} e^{(\alpha_V - 1)f\eta} \right] \tag{2c}$$

where θ is the surface coverage, C_{H_2} the concentration of the molecular hydrogen in solution, α_i ($i = V, H$) the symmetry factor of the reaction step i, λ the symmetry factor of adsorption and u (in RT units) is the energy of interaction between the adsorbed hydrogen atoms. Superscripts e and s indicate equilibrium and electrode surface, respectively, and $f = F/RT$.

When the electrode at equilibrium is subjected to an anodic potential step, the current response in the first few microseconds corresponds to the double layer charging, followed immediately by that of the hydrogen oxidation reaction. This current is the sum of the contributions of the two steps with electronic transfer (Heyrovsky and Volmer),

$$j = F(v_H + v_V) \tag{3}$$

Moreover, the surface coverage of the adsorbed intermediate will vary according to the following differential equation [12],

$$\frac{d\theta}{dt} = \frac{F}{\sigma}(2v_T + v_H - v_V) = -\frac{j_{pc}}{\sigma} \tag{4}$$

where σ is the charge corresponding to one monolayer of adsorbed hydrogen and j_{pc} is the pseudocapacitive current density. Meanwhile, the electrode reaction produces a decrease of the surface concentration of the molecular hydrogen, being the concentration profile governed by the Fick's law,

$$\frac{\partial C_{H_2}}{\partial t} = D_{H_2} \nabla^2 C_{H_2} \tag{5}$$

where the concentration of the molecular hydrogen in the electrolytic solution (C_{H_2}) is a function of time and of the distance

Table 1
Kinetic parameters and constants used in the calculations.

Parameters and constants values	
T	303.15 K
$\alpha_V = \alpha_H$	0.50
λ	0.50
u	0.50
θ^e	0.28
v_T^e	10^{-7} mol cm^{-2} s^{-1}
v_H^e	2×10^{-8} mol cm^{-2} s^{-1}
v_V^e	4×10^{-7} mol cm^{-2} s^{-1}
σ	2.2×10^{-4} C cm^{-2}
D_{H_2}	5×10^{-5} cm^2 s^{-1}
$C_{H_2}^e$	10^{-7} mol cm^{-3}

perpendicular to the electrode surface (x), and D_{H_2} is the diffusion coefficient of the molecular hydrogen in the solution.

The simultaneous resolution of Eqs. (2)–(5) leads to the evaluation of the dependence of the current density on time resulting from the application of a potentiostatic step. Starting from this dependence, the corresponding value of the kinetic current density at such overpotential will be calculated.

3. Results and discussion

The simultaneous resolution of Eqs. (2)–(5) was carried out with the following boundary conditions,

$$\eta(t = 0) = 0 \tag{6a}$$

$$\eta(t > 0) = \eta \tag{6b}$$

$$C_{H_2}^s(t = 0, x = 0) = C_{H_2}^e \tag{6c}$$

$$C_{H_2}(t, x \to \infty) = C_{H_2}^e \tag{6d}$$

It should be noted that the classical treatment, without an adsorbed intermediate, considers a Butler–Volmer type kinetics, which leads to an analytical expression for the time dependence of the current [7–9]. Such expression cannot be obtained in the present case, where the Butler–Volmer equation is replaced by Eqs. (2a)–(2c) and Eqs. (3) and (4) are added. Thus, the system of Eqs. (2)–(5) was numerically solved with the boundary conditions set in (6a)–(6d). In order to carry out the calculations and to get the final comparison with the kinetic response in steady state, values of the kinetic parameters corresponding to the Tafel-Heyrovsky-Volmer mechanism are needed (θ^e, v_T^e, v_H^e, v_V^e, α_H, α_V, λ, u). These values were taken from the correlation of experimental results obtained on a Pt electrode in 0.5 M H$_2$SO$_4$ solution [13]. The values of the diffusion coefficient (D_{H_2}) and bulk concentration ($C_{H_2}^e$) of molecular hydrogen are those corresponding to this solution. The value of the charge of one monolayer of adsorbed hydrogen (σ) is that of Pt. Calculations were carried out at 30 °C. All these values are given in Table 1.

The calculations were carried out on both a plane electrode (linear diffusion) and a cylindrical electrode (radial diffusion). Even though it is known that at long times the transient dependences are different for linear and for radial diffusions, in the analyzed region (short times) no difference was observed between both cases. Consequently, only the figures corresponding to linear diffusion will be shown. The system of Eqs. (2)–(5), with the boundary conditions set in Eqs. (6a)–(6d), was solved through numerical calculations for 22 overpotential values ranging between 0.01 V and 0.40 V. The corresponding dependences $j(t)$ are illustrated in part (a) of Figs. 1–4. It can be observed the typical transient responses, where the value of the current density immediately after the application of the step
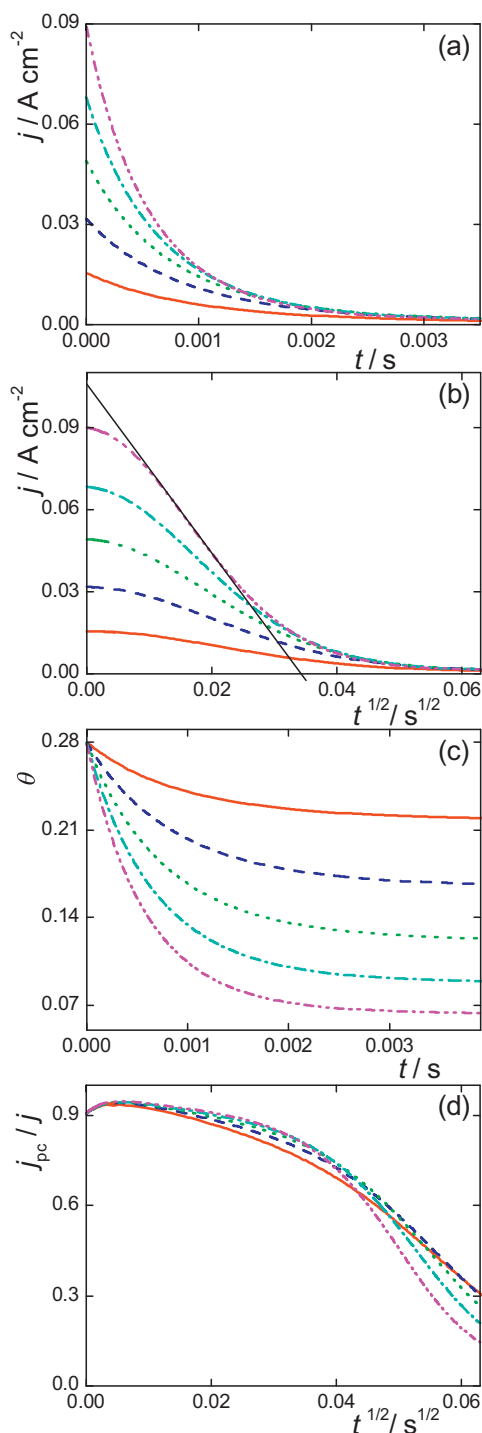
Fig. 1. Transient responses to the potential step: (a) j vs. t, (b) j vs. $t^{1/2}$, (c) θ vs. t, (d) j_{pc}/j vs. $t^{1/2}$. Overpotentials: (—) 0.01 V, (– –) 0.02 V, (·····) 0.03 V, (–·–·–·) 0.04 V, (–···–) 0.05 V.

increases as the overpotential value increases. Meanwhile, current density decays faster as the overpotential increases.

Then, in order to obtain the kinetic current density for a given overpotential value, the current density must be plotted against the square root of time. These dependences are shown in part (b) of Figs. 1–4. It should be interesting to note the absence of a true linear region in the j vs. $t^{1/2}$ plot, there is only an approximately linear region with a point of inflection. Consequently, the tangent line at this inflection point was taken as representative of the approximately linear region in order to obtain the value
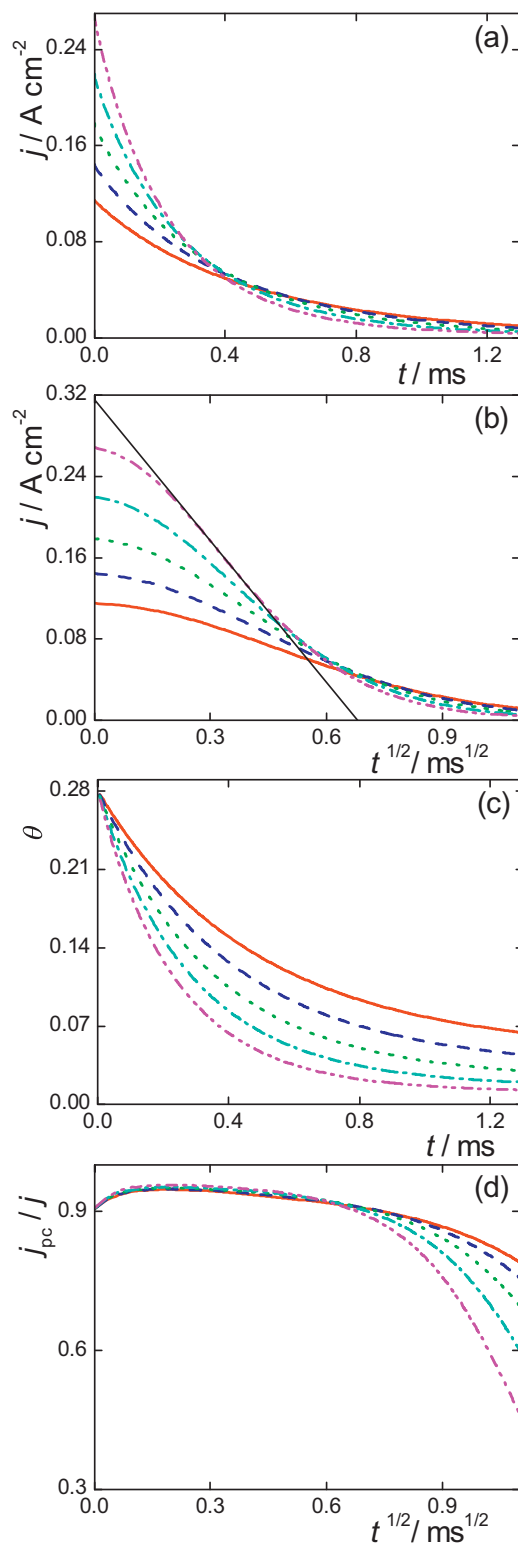

Fig. 2. Transient responses to the potential step: (a) j vs. t, (b) j vs. $t^{1/2}$, (c) θ vs. t, (d) j_{pc}/j vs. $t^{1/2}$. Overpotentials: (—) 0.06 V, (– –) 0.07 V, (·····) 0.08 V, (–·–·–·) 0.09 V, (–···–) 0.10 V.

of the kinetic current density of the chronoamperometric method $[j_k^{ca} = \lim_{t \to 0} j(t^{1/2})]$. As an example, it was plotted the tangent line for the curve corresponding to the highest overpotential value in each figure. Therefore, the values of j_k^{ca} for all the overpotentials were calculated.
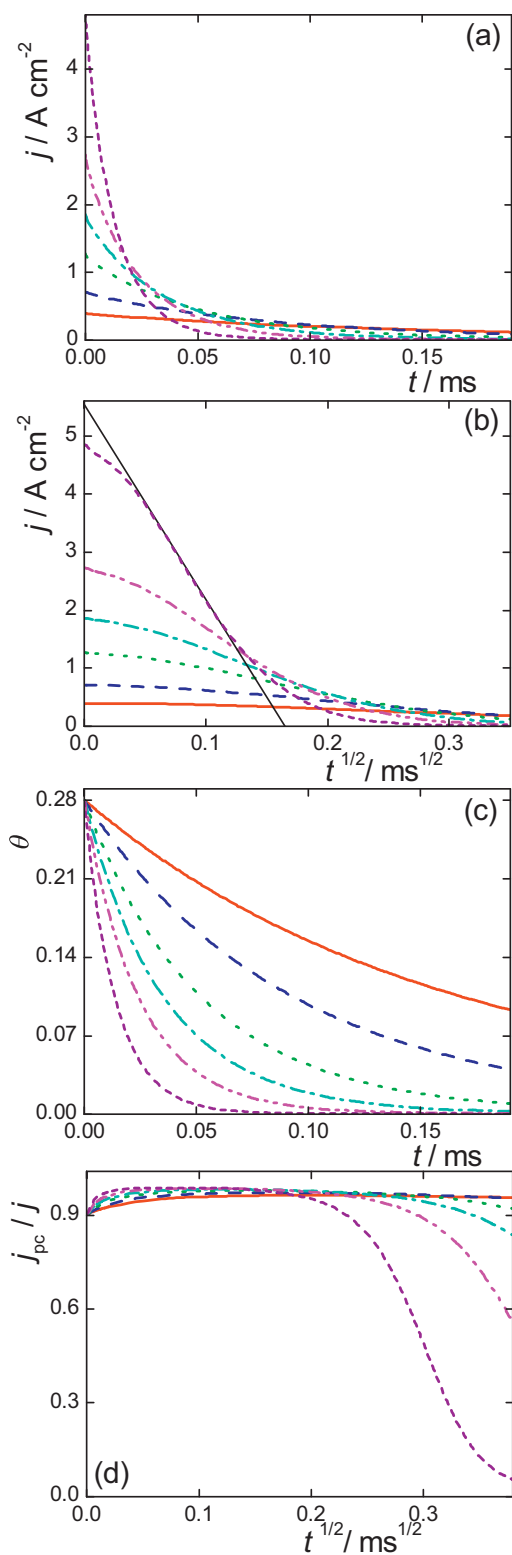
Fig. 3. Transient responses to the potential step: (a) j vs. t, (b) j vs. $t^{1/2}$, (c) θ vs. t, (d) j_{pc}/j vs. $t^{1/2}$. Overpotentials: (—) 0.12 V, (− −) 0.15 V, (······) 0.18 V, (−·−·−·) 0.20 V, (−··−) 0.22 V, (—) 0.25 V.

Fig. 4. Transient responses to the potential step: (a) j vs. t, (b) j vs. $t^{1/2}$, (c) θ vs. t, (d) j_{pc}/j vs. $t^{1/2}$. Overpotentials: (—) 0.28 V, (− −) 0.30 V, (······) 0.32 V, (−·−·−·) 0.35 V, (−··−) 0.38 V, (—) 0.40 V.

On the other hand, it should be of interest also to analyze the variation of the surface coverage of the adsorbed reaction intermediate during the transient. Such dependences can be observed in part (c) of Figs. 1–4, calculated for the different overpotentials. They clearly indicate the existence of a strong influence of the pseudocapacitive contribution to the total current density. Moreover,
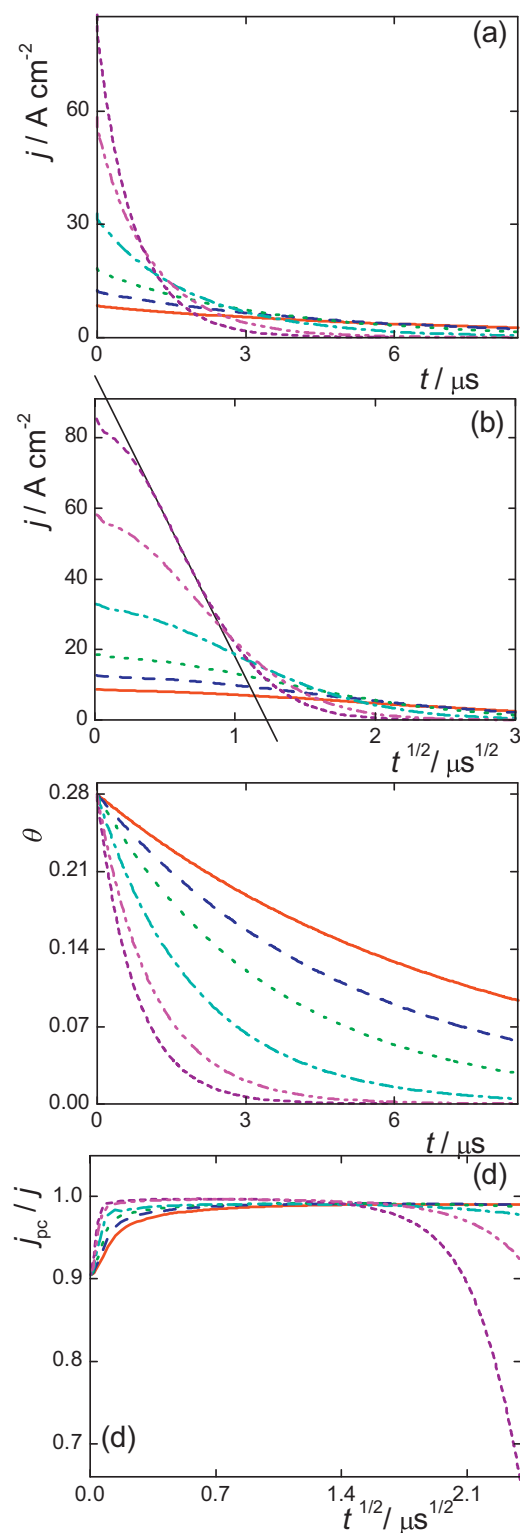
the ratio between the pseudocapacitive current density, evaluated from Eq. (4), and the total current density (j_{pc}/j) is illustrated against $t^{1/2}$ in part (d) of Figs. 1–4. It can be appreciated that in the time region where the plot j vs. $t^{1/2}$ (part (b) of Figs. 1–4) is approximately linear, the pseudocapacitive contribution notoriously prevails. Therefore, the value obtained from the extrapolation
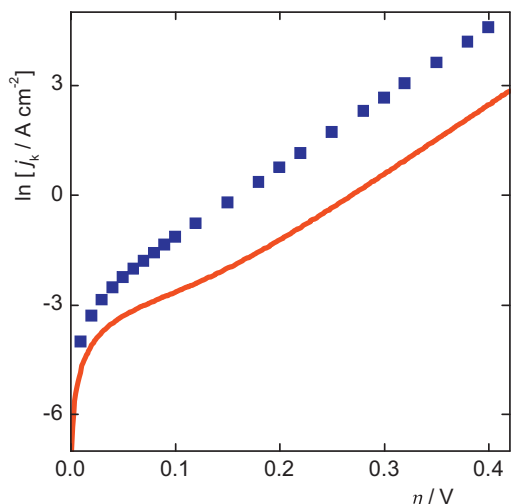
Fig. 5. Comparison between the polarization curves: (■) ln j_k^{ca} vs. η (chronoampe-rometry), (—) ln j_k^{ss} vs. η (steady state).

of this line (j_k^{ca}) is mainly the pseudocapacitive current density and not the kinetic current density.

Taking into account the results described above, the kinetic current density was calculated in conditions of strict activated control. It is obtained when two conditions are accomplished simultaneously. The first one is the steady state condition (absence of pseudocapacitive contribution), which applied to Eq. (4) leads to,

$$2v_T + v_H - v_V = 0 \tag{7}$$

The other is the absence of mass transport phenomena, which implies that $C_{H_2}^s = C_{H_2}^e$ in Eqs. (2a)–(2c). Substituting these equations into Eq. (7) an implicit expression is obtained, which describes the dependence of the surface coverage on overpotential on steady state under activated conditions,

$$2v_T^e e^{-2\lambda u(\theta - \theta^e)}\left[\frac{(1-\theta)^2}{(1-\theta^e)^2} - \frac{\theta^2}{\theta^{e2}}e^{2u(\theta-\theta^e)}\right] + v_H^e e^{-\lambda u(\theta-\theta^e)}e^{\alpha_H f\eta}$$

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

$$\left[\frac{\theta}{\theta^e}e^{u(\theta-\theta^e)} - \frac{(1-\theta)}{(1-\theta^e)}e^{-f\eta}\right] = 0 \tag{8}$$

The value of θ for a given η was calculated from Eq. (8), with the parameters given in Table 1. Then, v_H and v_V were calculated from Eq. (2b) and Eq. (2c) respectively in activated control condition. Finally, from Eq. (3) the kinetic current density on steady state (j_k^{ss}) was obtained. This calculation was carried out in the same range of overpotentials used in the chronoamperometric method.

The dependence of the logarithm of both, j_k^{ca} and j_k^{ss}, on overpotential is illustrated in Fig. 5. It can be clearly observed that the values of the kinetic current density calculated from the potential step method are different from those evaluated under pure activated control conditions. The overestimation of about one order of magnitude is basically due to the pseudocapacitive contribution caused by the adsorbed reaction intermediate, which was not included in the original derivation of the chronoamperometric method.

On the other hand, it can be observed in Fig. 5 the existence of an inflection point in the dependence of ln j_k^{ss} vs. η. This is a clear indication of the participation of the Tafel step in the kinetics of the hydrogen oxidation reaction. Meanwhile, the absence

of such inflection point in the polarization curve corresponding to j_k^{ca} evidences that the effect of the Tafel step would be in this case less significant. In order to verify this assertion, the dependence ln j_k^{ca} vs. η was correlated. The resulting values of the equilibrium reaction rates were: $v_T^e = 1.58 \times 10^{-8}$ mol cm^2 s^{-1}, $v_H^e = 1.62 \times 10^{-7}$ mol cm^2 s^{-1}, $v_V^e = 8.74 \times 10^{-6}$ mol cm^2 s^{-1}. The comparison of these values with those used in the calculations gives an increase of one order of magnitude in the equilibrium reaction rates of the Heyrovsky and Volmer steps and a decrease of the same magnitude in that of the Tafel step, which confirms the asseveration.

It should be noticed that although the results shown correspond to a given set of kinetic parameters, in order to ensure that the observed behavior is valid, more calculations were carried out with different values of the parameters. The results obtained demonstrate that the difference between the value evaluated from the extrapolation and the real kinetic current density is basically due to the variation of the surface coverage of the reaction intermediate on time (Eq. (4)). This difference increases as $d\theta/dt$ increases. In other words, the pseudocapacitive contribution is the responsible of the inability of the chronoamperometric method to evaluate the kinetic current density of the hydrogen oxidation reaction.

Finally, as the two most usually employed methods for the determination of the kinetic current densities of the hydrogen oxidation reaction, Levick-Koutecky and potential step, are not accurate, a question arises about a reliable method to be applied in order to evaluate the kinetic parameters. Actually, the correlation of the experimental current–overpotential curves obtained on steady state conditions is the simplest way, although an alternative method is the use of electrochemical impedance spectroscopy [14,15]. The analytical expressions needed for the correlation were derived under the Tafel-Heyrovsky-Volmer mechanism on steady state, including the diffusion of the molecular hydrogen and considering a Langmuir [4] or Frumkin [6] type adsorption for the adsorbed hydrogen. Different experimental methods can be applied in order to obtain the experimental $j(\eta)$ curves on steady state with defined diffusion conditions such that the limiting diffusion current density can be determined. Some of them are the use of rotating disk electrodes [6,16,17], the evaluation of the electrolyte flow rate through a tubular electrode [18] and the use of microelectrodes of different diameters [19,20]. In all these cases the analytical expressions can be used for the rigorous calculation of the kinetic parameters.

4. Conclusions

The applicability of the chronoamperometric method for the evaluation of the kinetic current density for the hydrogen oxidation reaction was analyzed. The method was originally derived for simple reactions with no adsorbed reaction intermediates. However, the presence of such species introduces a pseudocapacitive contribution in the transient current response to the applied potential step. It was demonstrated that such contribution leads to erroneous values of the kinetic current density evaluated from the extrapolation of the linear plot of the experimental current density against the square root of time. Thus, the values of the kinetic parameters calculated from this method are not reliable.

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