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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 (chronoamperometry). 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,

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

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

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

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

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

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

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

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

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}
$D_{\mathrm{H_2}}$	5×10^{-5} cm^2 s^{-1}
$C_{\mathrm{H_2}}^e$	10^{-7} mol cm^{-3}

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,

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

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

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

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

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 $\mathrm{H_2SO_4}$ solution [13]. The values of the diffusion coefficient (D_{H_2}) and bulk concentration ($C_{\mathrm{H_2}}^e$) 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