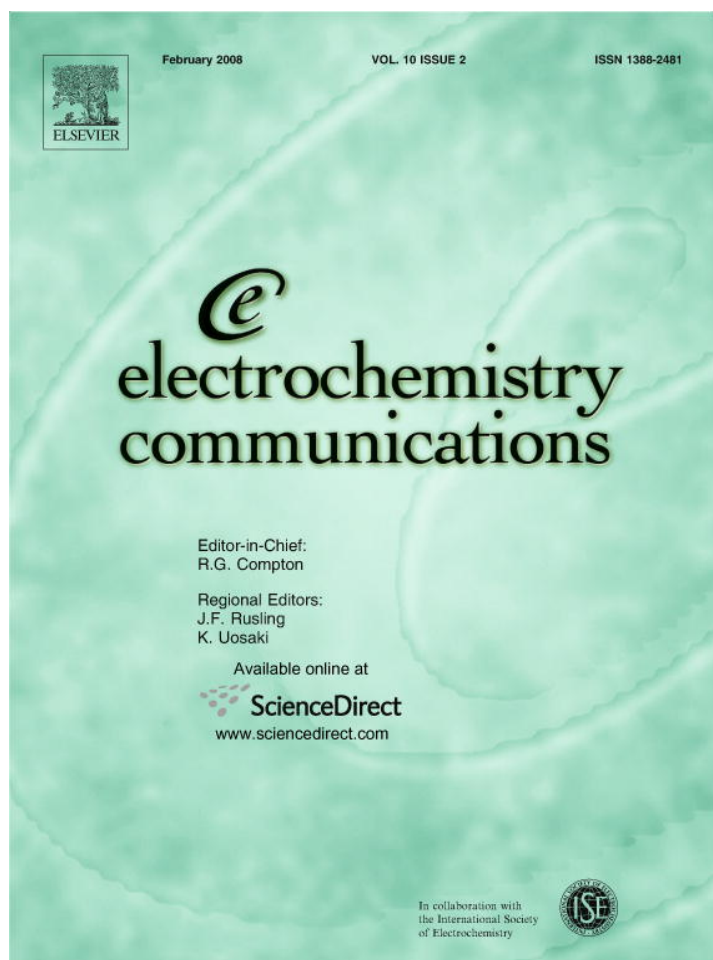


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Hydrogen oxidation reaction: Evidences of different electrocatalytic activity between α and β Pd–H

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Abstract

The hydrogen oxidation reaction (hor) was studied in steady state conditions on a palladium thin film electrode supported on a gold rotating disc. The electrode surface was characterized by cyclic voltammetry and SEM observation. The hydrogen absorption process was analysed by open circuit potential decay in an acid solution saturated with hydrogen and the kinetic measurements were carried out potentiostatically in the same solution. The results obtained show a marked change on the dependence of the current density on overpotential due to the transition between the α and β phases of the Pd–H system. These results were correlated with appropriate kinetic expressions and the corresponding electrocatalytic activity of both phases was estimated.

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1. Introduction

The hydrogen oxidation reaction (hor) has been recently studied on a variety of metals and bimetallic surface alloys such as Pt (*hkl*) [1–3], polycrystalline Pt [4–6], Pt–M (M: Sn, Sb, Mo, etc.) [6,7], Ru (0001) [8], Au (111)–Pd [9], Pt (111)–Pd [10]. Besides, there are only two studies reported in the literature of the hor on pure palladium, both of them carried out on Pd particles dispersed on carbon black [11] and polythiophene [12]. Palladium, unlike the rest of the mentioned metals, is a hydrogen absorbing electrode with a hydride phase transition in the range of overpotentials where the hor is displayed [13,14]. The transition is between α -Pd/H, a solid solution with a low hydrogen concentration, and β -Pd/H, a hydride form with a high hydrogen content [13,14]. This behaviour has prevented the study of the hor on a bulk Pd electrode and

therefore it has not been established yet if this reaction displays different electrocatalytic activity for the α and β phases.

In this context, the aim of the present work is the experimental study of the hor on a Pd thin film deposited on a gold rotating disc under steady state conditions and the analysis of the results under the Tafel–Heyrovsky–Volmer kinetic mechanism.

2. Experimental

The working electrode was a Pd thin film electrodeposited on a gold rotating disc (0.07 cm²). The electrodeposition was carried out in a 0.056 M PdCl₂–0.10 M H₂SO₄ solution, at 80 °C and 400 rpm, applying a current density of 400 μ A cm⁻² during 30 min. The Pd film was characterized by cyclic voltammetry and the morphology was analysed by SEM.

The study of the hor was carried out in a 0.5 M H₂SO₄ solution prepared with triply distilled water at 30 °C, ensuring a continuous saturation of the electrolyte with

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molecular hydrogen. A Pt counterelectrode and a hydrogen bubble reference electrode in the same solution were used and therefore potentials (E) are coincident with overpotentials (η). A potential program was applied for the evaluation of the experimental dependence $I(\eta)$ at a rotation rate of 8100 rpm. The electrode was held at 1.2 V during 4 s, where takes place the oxidation of any surface polluting substances and besides a reproducible initial condition is ensured. It was followed by a reduction step at 0.0 V during 30 s and the final step to the desired overpotential during 30 s. In this period, lectures of the current value were made each 1 s and the mean value of the last 10 s was assigned to this overpotential.

3. Results

3.1. Electrode characterization

Fig. 1 illustrates the voltammogram of the Pd electrode, which displays a profile similar to that already published [13–16]. It can be clearly observed the potential region of the adsorption/desorption of H_{UPD} ($0.10 < E/V < 0.30$), as well as the hydrogen absorption ($E/V < 0.1$). This process is shown through the anodic peak at 0.09 V corresponding to the electrooxidation of the absorbed hydrogen that emerges from the metallic matrix.

Fig. 2a–c illustrates the scanning electron micrographs of the electrodeposited Pd films. It can be observed (Fig. 2a) that the electrode surface is uniform, although at higher magnifications a granular morphology and a certain degree of porosity are revealed (Figs. 2b and c).

3.2. Hydrogen absorption on the Pd thin film

The behaviour of the Pd film in the presence of hydrogen was analysed through the variation of the electrode

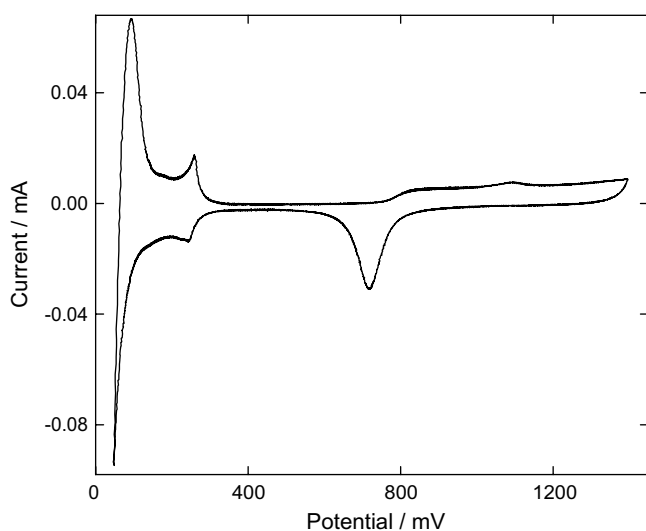


Fig. 1. Cyclic voltammogram for the Pd film electrode recorded at 0.05 V s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$.

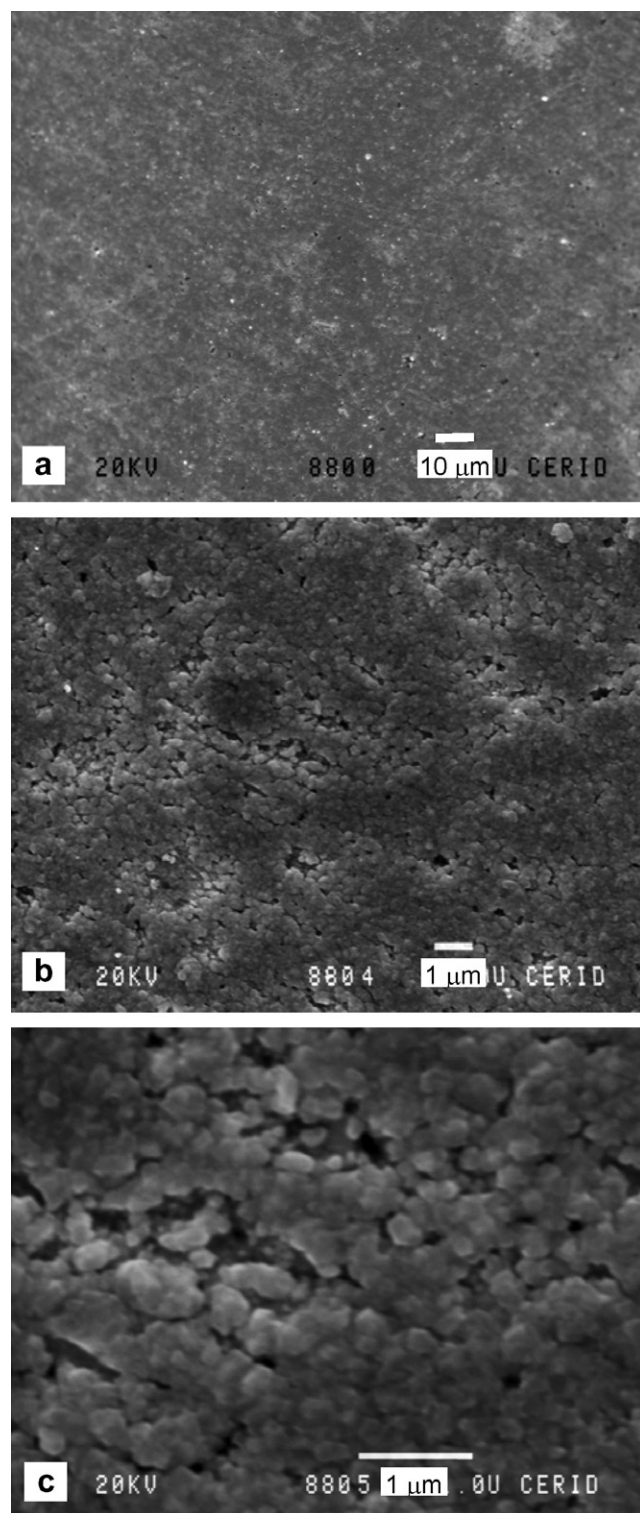


Fig. 2. SEM micrographs of the Pd film. Magnifications: (a) 780 \times ; (b) 7800 \times ; (c) 24000 \times .

potential at open circuit. The electrode was polarized at 1.2 V during 30 s, then the circuit was opened and the transient potential dependence was registered (Fig. 3). It can be appreciated a fast decrease, reaching $E \cong 0.055 \text{ V}$ in less than 1 s, which is the mean value of the plateau corresponding to the transition $\alpha \rightarrow \beta$ [13,14]. The potential

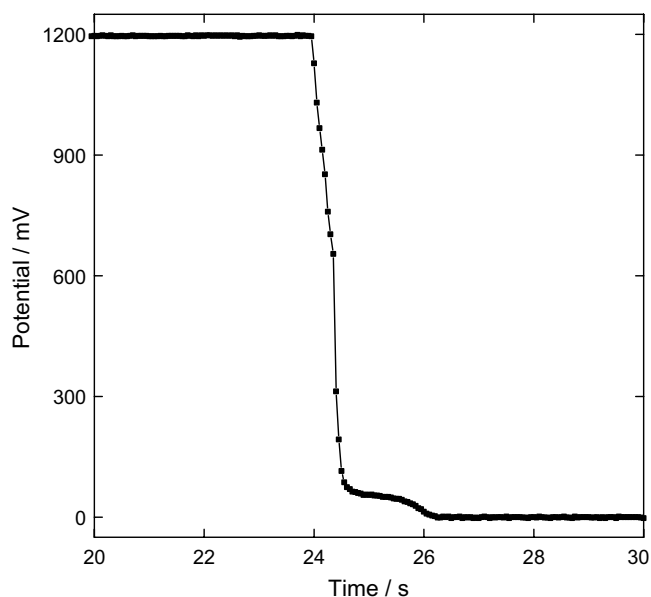


Fig. 3. Potential vs. time at open circuit for the Pd film electrode recorded in 0.5 M H₂SO₄.

remains at this value for less than 2 s and immediately after it falls to the equilibrium state. This experiment demonstrates that in the present conditions the hydrogen sorption inside the metal lattice is very fast.

3.3. Hor on Pd thin film

Fig. 4 illustrates the current response to the pulse at $\eta = 0.14$ V, where it can be observed the achievement of the equilibrium condition ($I = 0$) and that the steady state current is reached very fast. The experimental dependence $j(\eta)$, shown in Fig. 5 (dots), exhibits an un-

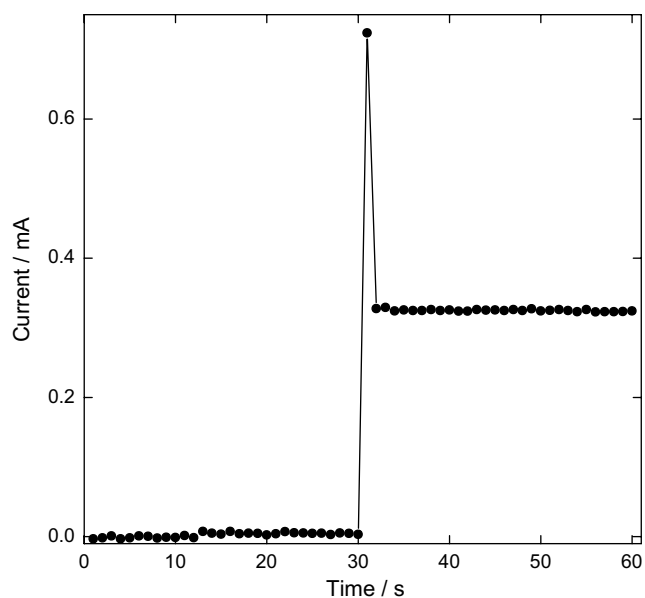


Fig. 4. Current vs. time response to a pulse at 0.14 V for the Pd film electrode recorded in 0.5 M H₂SO₄ at $\omega = 8100$ rpm.

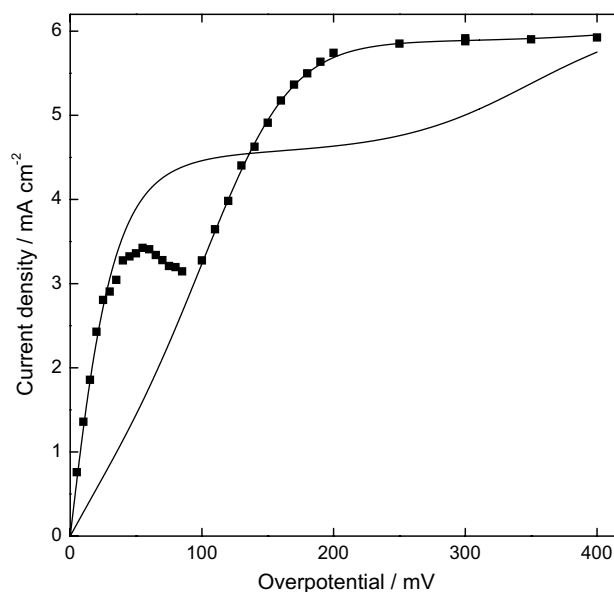


Fig. 5. Current vs. potential dependence for the hor on the Pd film electrode recorded in 0.5 M H₂SO₄ at $\omega = 8100$ rpm. (■) Experimental; (—) simulation.

sual behaviour. At first, in the range $0 < \eta/V < 0.04$, it can be observed the usual increase of the current density. Then, it is interrupted by an irregular apparent current plateau ($0.04 \leq \eta/V \leq 0.10$), where the points are rather spread. At $\eta > 0.1$ V, the current density increases again with a well defined response, reaching a constant value (5.88×10^{-3} A cm⁻²). It should be noticed that this value is less than that corresponding to a Pt electrode in the same conditions (6.09×10^{-3} A cm⁻²), which is as well slightly smaller than the limiting diffusion current density at 8100 rpm ($j_L = 6.19 \times 10^{-3}$ A cm⁻²) [5]. Therefore, this constant current density is not due to a pure diffusion control [17,18].

4. Discussion

The behaviour of the Pd thin film electrode towards the hor is different to that corresponding to other electroodic materials [1–7], as the $j(\eta)$ dependence in steady state displays a discontinuity in the range $0.04 < \eta/V < 0.10$, which contains the potential of the transition α -Pd/H \rightarrow β -Pd/H (Fig. 3). Therefore, it can be considered that the first domain ($\eta < 0.04$ V) should correspond to β -Pd/H and the more anodic region ($\eta > 0.10$ V) to α -Pd/H. As the gold substrate is impermeable to hydrogen and the film thickness is about 300 nm, the hydrogen absorption/desorption process is confined to the electrode-solution interphase. This explains the high rate of the hydrogen charge/discharge process (Fig. 3), as well as the fastness whereupon is reached the steady state in the potentiostatic pulses (Fig. 4). This situation is clearly different from that of Pd membranes where a continuous hydrogen permeation is established.

To describe the relationship between the surface coverage of the reaction intermediate $H_{ad}(\theta)$ for the hor and the concentration of the absorbed hydrogen ($c_{H_{ab}}$), it is first analysed at the equilibrium condition. From the thermodynamic point of view the system consists in three phases, gaseous humidified hydrogen, liquid electrolyte solution saturated with molecular hydrogen and solid Pd film with absorbed hydrogen. When temperature, hydrogen pressure and proton concentration are fixed, all the intensive thermodynamic variables are determined. Among them, the well known pressure-composition diagram of the Pd–H system must be accomplished [19,20]. According to it, the hydrogen absorbed inside the film corresponds only to β -Pd/H. In these conditions, the concentration of absorbed hydrogen $c_{H_{ab}}^e$ and that in solution $c_{H_2(sol)}^e$ are fixed. When the overpotential is increased in the anodic direction, all hydrogen sources, $H_{2(sol)}$, H_{ab} and H_{ad} start to be oxidized to proton. Then, the system reaches a steady state characterized by a given current value. In these conditions, the unique source of hydrogen for the hor is that provided by the solution through the diffusion layer, which defines the superficial concentration of hydrogen in solution $c_{H_2(sol)}^s(\eta)$, being the surface coverage $\theta(\eta)$ and the concentration of absorbed hydrogen $c_{H_{ab}}(\eta)$ invariant upon time and less than those corresponding to the equilibrium condition. Therefore, the steady state for the hor implies the equilibrium between H_{ad} and H_{ab} , independently if this last one is α or β -Pd/H. This fact is extremely important, as it makes unnecessary to postulate a mechanism for the hydrogen absorption, simplifying the analysis of the experimental results. Furthermore, for the interval $0.04 < \eta/V < 0.10$, the dynamics of the processes involved is more complex and required other considerations (H_{ad} spillover, etc.), which are beyond the scope of the present work.

As at equilibrium the film consists of β -Pd/H, the hor would be verified on this phase in the range $0 < \eta/V < 0.04$. In the overpotential region where both phases coexist ($0.04 < \eta/V < 0.10$), the hor would take place on a kind of surface mosaic with different proportions of α and β depending on the applied overpotential. Furthermore, in the last region ($0.10 < \eta/V < 0.40$), the hor would occurred on α -Pd/H. Consequently, the strong decrease of the amount of absorbed hydrogen on going from the β to α phase should produce a marked decrease of the surface coverage and therefore the reaction rate on α -Pd/H should be significantly less than that observed on β -Pd/H, which is in agreement with the experimental $j(\eta)$ curve shown in Fig. 5 (dots).

To complete the analysis of the experimental results, the kinetic parameters corresponding to the Volmer–Heyrovsky–Tafel mechanism were evaluated through the application of kinetic expressions for $j(\eta, j_L)$ and $\theta(\eta, j_L)$ previously derived [21]. They involve the following kinetic parameters: the equilibrium reaction rate of the step i (i : V, H and T) v_i^e ; the symmetry factor of the step i (i : V and H) α_i ; the symmetry factor of adsorption λ ; the energy of adsorption interaction u (in RT units) and θ^e .

The experimental dependence $j(\eta)$ was correlated in the overpotential ranges corresponding to β -Pd/H and α -Pd/H, respectively. The values of the kinetic parameters for α -Pd/H were: $v_T^e = 5.61 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, $v_H^e = 6.70 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$, $v_V^e = 7.99 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, $\theta^e = 0.03$, $u/RT = 1.323$, $\alpha_V = 0.46$ and $\alpha_H = \lambda = 0.5$. The corresponding values for β -Pd/H were: $v_T^e = 2.26 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, $v_H^e = 5.71 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$, $v_V^e = 1.66 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, $\theta^e = 0.46$, $u/RT = 0.33$, $\alpha_V = 0.48$ and $\alpha_H = \lambda = 0.5$. It can be appreciated that θ^e of β -Pd/H is significantly greater than that of α -Pd/H, which is consistent with the analysis given above. The corresponding simulation curves are also illustrated in Fig. 5 (continuous lines). These results indicate that at low overpotentials the electrocatalytic activity of the β phase is greater. In this context, if a higher concentration of absorbed hydrogen implies an increase of θ^e , as it seems to be in the present case, then the kinetic expressions [5,17,18,21] predict that the current density is also increased. This hypothesis could orientate the search of electrocatalysts for the hydrogen oxidation reaction to materials with high capacity to absorb hydrogen, as well as an adequate resistance to acidic solutions.

5. Conclusion

In this study, the hydrogen oxidation reaction (hor) was carried out on a palladium thin film electrode supported on a gold rotating disc. The results obtained indicate that the reaction takes place on the β -Pd/H for $\eta < 0.04 \text{ V}$ and on the α -Pd/H when $\eta > 0.1 \text{ V}$. It was also demonstrated that at low overpotentials the electrocatalytic activity of the β phase is greater than that of the α phase.

Acknowledgements

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