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Electrochemical study of hydrogen absorption in polycrystalline palladium

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Abstract

The hydrogen reactions on polycrystalline Pd in 0.1 M NaOH at 25°C have been studied by using transients at constant potential, and by impedance spectroscopy and X-ray diffraction techniques. At potentials, E_s , more positive than the reversible potential, E_r , for the H₂ evolution reaction, the current–time response and the impedance data indicate H atom diffusion into the bulk Pd. The X-ray diffraction pattern of electrodes cathodized during 20 min at these potentials are similar to those obtained for Pd. At $E_s < E_r$, the current transients exhibit a current maximum which increases as E_s moves in the negative direction. The Nyquist plot for the rising part of the transients indicates the H atom diffusion into the bulk metal and H₂ evolution on the Pd surface at high frequencies. The X-ray diffraction pattern of the electrodes cathodized at $E_s < E_r$ shows the presence of the β PdH phase and Pd. The experimental results indicate that different reactions take place simultaneously in this potential range: (i) H₂ evolution, (ii) H diffusion into the bulk Pd, (iii) nucleation and diffusion-controlled growth of the β PdH phase. Taking into account the contribution of these reactions, a model, which is able to reproduce the experimental current transients, is presented.

INTRODUCTION

The cold fusion debate makes the electrochemistry of palladium and palladium–hydrogen systems attractive for further basic investigations, particularly those concerning the rate of hydrogen atom charging and the influence of inhibiting layers at the palladium surface.

The kinetics of hydrogen evolution and hydrogen adsorption on palladium have been studied for a few decades [1–5]. The discharge of hydrogen atoms yielding adsorbed hydrogen atoms is rather slow and it can be enhanced by increasing the

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applied cathodic overpotential. On the other hand, the absorption of hydrogen involves a transport process into the bulk of the metal, the rate of which can be increased by providing a greater concentration of hydrogen atoms at the metal surface. This can be done also by increasing the applied cathodic overpotential to reach the saturation of the hydrogen surface concentration. For a certain electrolysis time the H-adsorption process is coupled to the parallel evolution of molecular hydrogen until the limiting uptake of hydrogen is reached [6]. Afterwards, the hydrogen evolution reaction proceeds under steady conditions on an electrode composed of the β PdH phase.

The purpose of the present work was to study of the early stages of cathodization of a palladium electrode in a base electrolyte. A kinetic analysis of the various processes occurring during the formation of the α PdH and β PdH phases is presented. The results from potentiostatic current–time transients, impedance measurements and X-ray diffractometry show that nucleation and growth models seem to be applicable to the phase changes involved in these reactions.

EXPERIMENTAL

Polycrystalline Pd (99.99%) wires (dia. 0.05 cm, ca 0.1 cm² area), polished with alumina (1 μ m dia.) and cleaned by immersion in HNO₃ + H₂SO₄ mixture (1 : 1) at 70 °C were used as working electrodes. The latter, a large Pt (3 × 3 cm²) counter electrode and a Hg/Hg₂SO₄ reference electrode were placed in a conventional electrochemical glass cell thermostated at 25 °C. The electrolyte solution was 0.1 M LiOH prepared from p.a. chemicals and bi-distilled water. Oxygen was removed from the cell solution by passing N₂ through it. Prior to the electrochemical measurements, the working electrode was cycled between 0.05 V and –1.1 V at 0.05 V/s in order to obtain stabilized voltammograms.

Voltammetric measurements combined with potentiostatic current–time transients and cell impedance measurements were made. The latter were obtained using a frequency response analyzer (Solartron 1250), coupled with a potentiostat. In this case, a large cylindrical Pt grid was used as the counter electrode. The amplitude of the ac signal was 8 mV peak-to-peak and the frequency range between 1 Hz and 10 kHz. Six points per decade were measured. The completion of a frequency spectrum required about 30 s. The analyzer was used in the two channel mode, one channel for the alternating current output of the potentiostat and the other for the corresponding alternating voltage output.

In order to detect the electroformation of the β PdH, Pd electrodes cathodized at various potentials were removed from the electrochemical cell and analyzed immediately by X-ray diffraction in the Debye chamber of a Philips diffractometer with Cu-K α radiation. In this case, Pd plates (1.5 cm²) were used as working electrodes.

RESULTS

The voltammogram of a polycrystalline Pd electrode in 0.1 M LiOH run between –1.25 V and 0.05 V at 0.05 V/s (Fig. 1) exhibits a current peak at –0.7 V in the

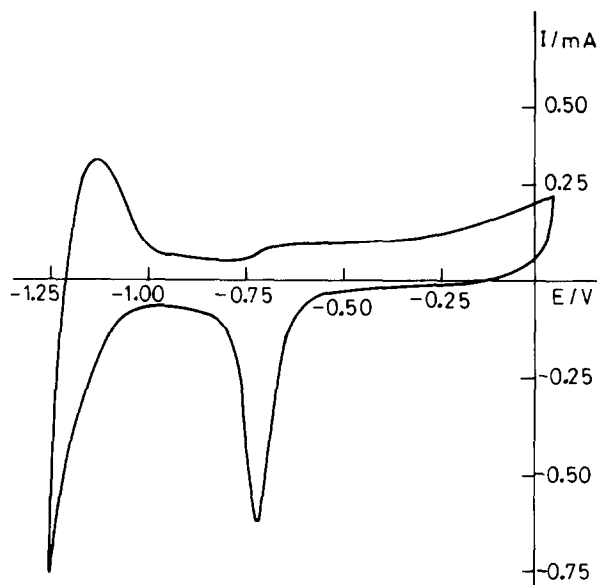


Fig. 1. Voltammetric current-potential curve obtained at 0.05 V s^{-1} for hydrogen deposition on palladium in 0.1 M LiOH .

scan to negative potentials corresponding to the PdO electroreduction [5]. At potentials lying between -1.0 V and E_r , the reversible potential of the hydrogen electrode ($E_r = -1.37 \text{ V}$), H atom electroadsorption and the simultaneous formation of the αPdH alloy takes place. Finally, at potentials more negative than E_r the large cathodic current is related to hydrogen evolution and βPdH alloy formation. The scan to positive potentials shows a broad current peak at -1.1 V corresponding to H_2 and H atom electrooxidation, the latter reaction extending over the double layer potential region. Finally for potentials more positive than -0.7 V a broad current region associated with the PdO formation is observed.

The current transients, run under a constant potential (E_s), were recorded by stepping the electrode from a potential of -1.1 V to E_s ($-1.20 \text{ V} > E_s > -1.9 \text{ V}$). For $E_s > -1.37 \text{ V}$ and time covered in the present work, the current transient decays continuously (Fig. 2a), yielding linear j vs. $t^{-1/2}$ plots. For $E_s < -1.37 \text{ V}$, the current decreases initially to a minimum value, j_m , at time t_m , and subsequently it increases to a maximum value, j_M , at time t_M (Fig. 2b). Finally, the current decreases slowly with time. In addition, t_M decreases and j_M increases as E_s is shifted negatively. Peaked current transients were also observed during H_2 evolution and hydride layer formation on Ti [8]. These transients were related to the time-dependent electroreduction of the oxidized species, i.e. O_2 , transported from the counter electrode to the Ti working electrode. However, in our case, the voltammograms run immediately after cathodization in the -1.25 V to -1.90 range

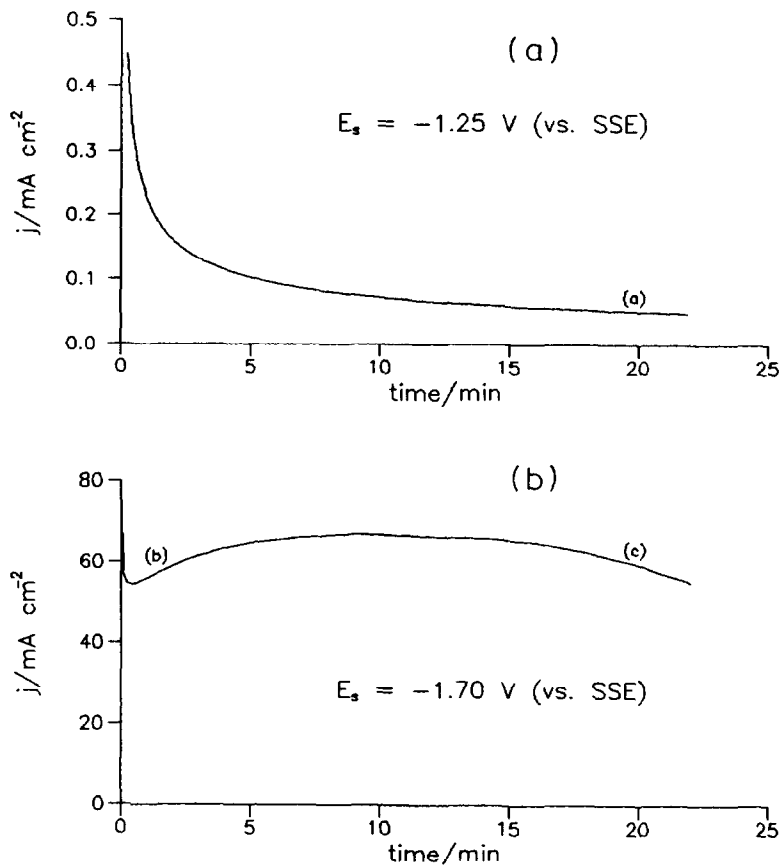


Fig. 2. Potentiostatic current transients of the hydrogen reaction on Pd.

reveal no significant traces of O_2 which would cause a distortion in the shape of the voltammogram.

Impedance measurements were also made in the $-1.25 \text{ V} > E_s > -1.90 \text{ V}$ range. For $E_s = -1.25 \text{ V}$, the Nyquist plot shows, at high frequencies (ω), the characteristic circular plot corresponding to a charge transfer controlled process. On the other hand, at low ω values, a straight line with slope close to unity, representing the Warburg impedance was found (Fig. 3a). For $E_s = -1.70 \text{ V}$, the Nyquist plot (Fig. 3b) recorded in the rising part of the transient, at high ω values, shows the semicircle expected for a charge transfer controlled process, although it is perturbed by H_2 bubble formation at the electrode. It should be noted that at sufficiently low values of ω there is a diffusional process. The latter is no longer observed for $t > t_M$ but in this case an increase of the charge transfer resistance is observed (Fig. 3c).

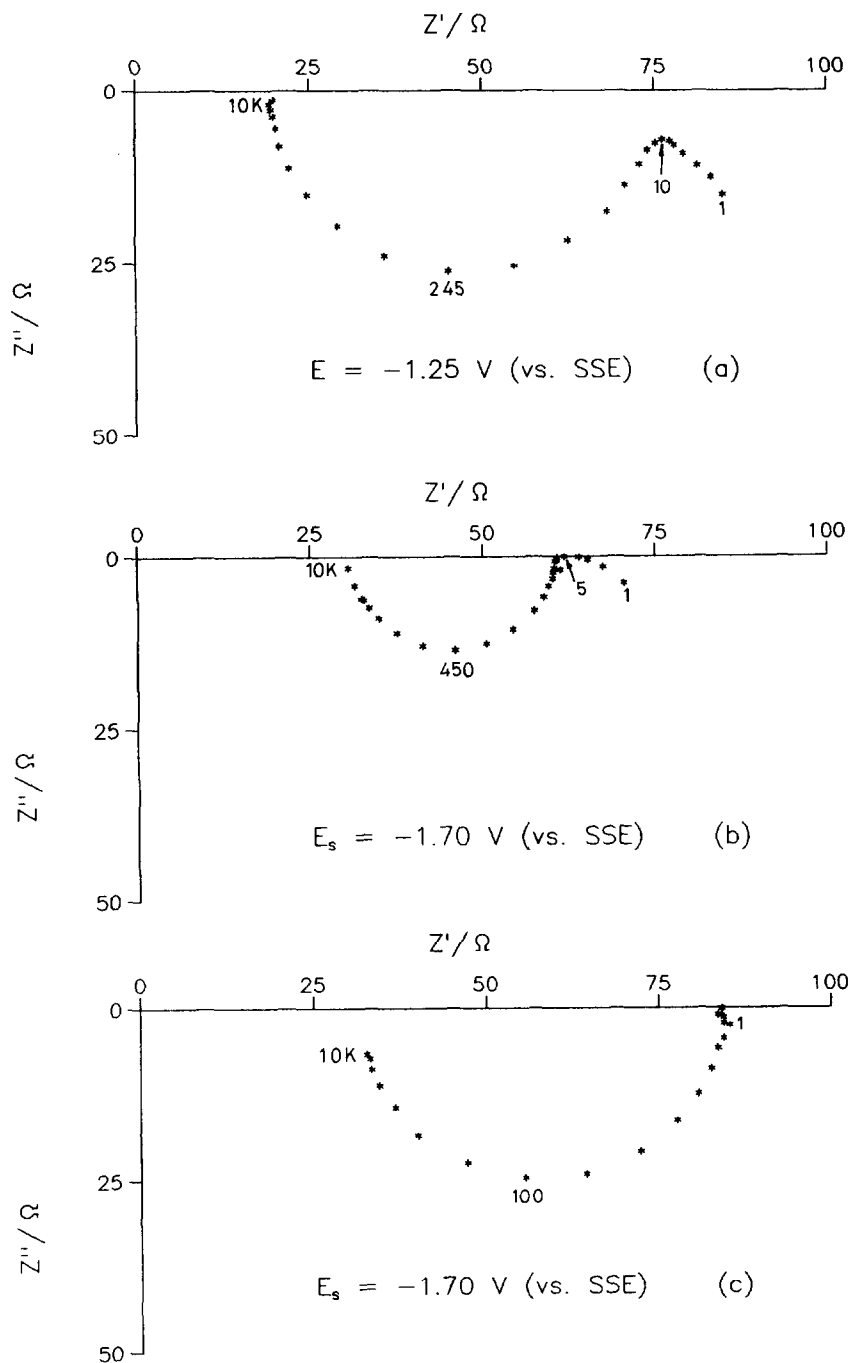


Fig. 3. Complex impedance plots for the hydrogen reaction on Pd at the potential indicated and times corresponding to points (a), (b) and (c) of Figs. 2a and 2b respectively.

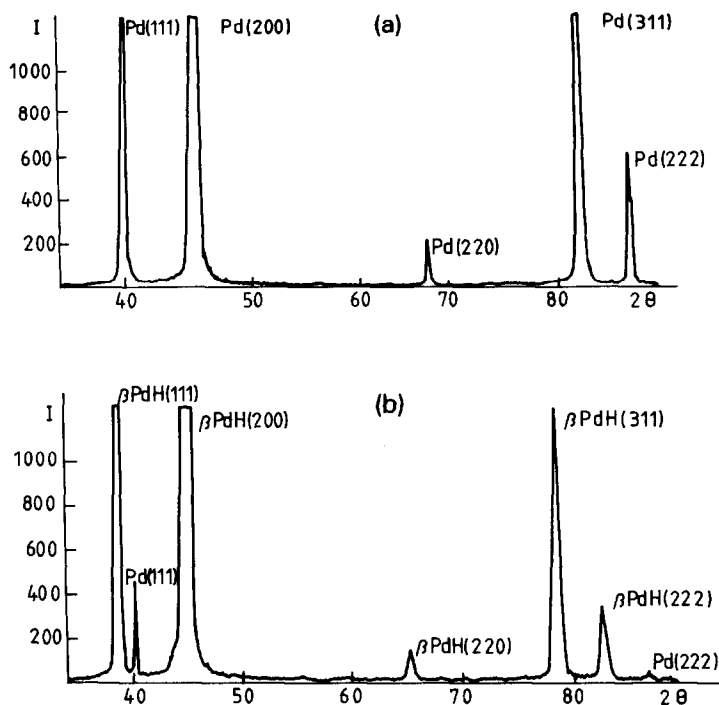


Fig. 4. X-ray diffraction patterns corresponding to (a) Pd cathodized at -1.25 V during 20 min. (b) Pd cathodized at -1.70 V (β PdH).

In order to verify that peaks in the current transients are related to the growth of the β PdH phase, X-ray diffractograms of the electrodes cathodized at various potentials (20 min) were made. For $E_s = -1.25$ V, that is for decreasing current transients, the diffractograms coincide, as can be seen from Fig. 4a, with those obtained for untreated Pd. Conversely, for $E_s = -1.70$ V, where peaks in the current transients are observed, the diffractograms are closely related to those of β PdH alloy with only a small signal from Pd (Fig. 4b).

DISCUSSION

The results obtained from the potentiostatic current transients combined with those from ac impedance measurements, indicate that several electrochemical processes are taking place in the potential range of the hydrogen electrode reactions. These processes can be considered separately by operating under certain defined potential and time windows. Thus, for $E_s > -1.37$ V the main reaction can be represented formally as the following successive steps [9]:



TABLE 1

Parameter values of the proposed model at various potentials.

E_s/V	$P_1/\text{mA cm}^{-2} \text{ s}^{-1/2}$	$10^3 P_2/\text{s}^{-1/2}$	$P_3/\text{mA cm}^{-2}$	$10^4 P_4/\text{s}^{-1}$
-1.25	1.74	-	-	-
-1.55	29.0	8.3	7.1	12
-1.65	32.9	1.0	29.6	2.0
-1.70	21.3	15	49.37	4.3
-1.80	36.7	37	67.2	15
-1.90	34.8	33	119.8	6.6

where (H) stands for an adsorbed H-atom on the Pd_x surface and $\alpha(\text{HPd})_x$ refers to the αPdH phase. Steps (1a) correspond to the H-atom electroadsorption and step (2a) to the diffusion of H-atom into the bulk Pd. The total current related to the αPdH phase formation is

$$j_t = j_{1\alpha} = j_{2\alpha} \quad (3)$$

where $j_{1\alpha}$ and $j_{2\alpha}$ are the current of steps (1a) and (2a), respectively. Voltammetric results in this potential range suggest that step (2a) is the rate determining step [9]. Furthermore, the linear j vs. $t^{-1/2}$ relationship indicates that the hydrogen penetration into Pd can be described as a linear diffusion process. Thus, one can write [10]

$$j_t = P_1/t^{1/2} \quad (4)$$

with

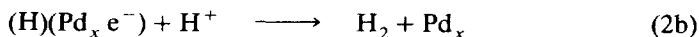
$$P_1 = zFD^{1/2}c_H^s/\pi^{1/2} \quad (5)$$

D is the diffusion coefficient of H atoms into bulk Pd and C_H^s is the H atom concentration at the Pd surface. Using equation (4) the current transients recorded at $E_s > -1.37$ V can be reproduced with the set of parameters assembled in Table 1, the error being less than 1%. From the value of P_1 given by equation (5) and taking $z = 1$, and $D = 1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [7] one obtains $c_H^s = 1 \times 10^{-4} \text{ mol cm}^{-3}$. Our impedance measurements in this potential range show (Fig. 3a) the appearance of a straight line in the low frequency zone which is interpreted as a Warburg impedance. In principle, this frequency range seems rather narrow to be unambiguously assigned to a Warburg impedance. However, lower frequency measurements are not convenient under non-steady state conditions as they involve larger times than those corresponding to the processes under study. Nevertheless, our results are in good agreement with the detailed impedance study of Breiter [9] on the hydrogen adsorption and dissolution on Pd in acidic medium. In this case, the experimental data are in favor of case b (eqn. 14 of ref. 9) at sufficiently low frequencies, which corresponds to low values of an adsorption pseudocapacitance. Thus, it is possible to use a Warburg-like approach to describe the behaviour of the system. From the Warburg impedance, calculated from the low frequency region of Fig. 3a, and using the expression

$$\sigma = (4RT/z^2F^22^{1/2}cD) \cosh^2[(zF/2RT)] \eta \quad (6)$$

a value of $c_{\text{H}}^{\text{s}} = 0.9 \times 10^{-4} \text{ mol cm}^{-9}$ is obtained, which is in very good agreement with that obtained from P_1 data. It should be noted that C_{H}^{s} is lower than that required for βPdH formation [11]. This conclusion is supported by the X-ray diffractogram data showing no evidence for this phase in this potential range.

On the other hand, when $E_{\text{s}} < -1.37 \text{ V}$, the adsorbed H atom can react at least in three different ways to yield (i) H_2 molecules, (ii) αPdH phase, or (iii) βPdH phase. The entire process can be described by the following alternative reaction pathway:



As the reaction progresses, the electrode surface turns into a composite structure containing $\alpha(\text{Pd}_x\text{H})$ and $\beta(\text{Pd}_x\text{H})$ and Pd domains, the ratios of the domains depending on the extent of the corresponding reactions and applied potentials.

For the reaction scheme (2a–2c) the total instantaneous current j_{t} is

$$j_{\text{t}} = j_{2\alpha} + j_{2\text{b}} + j_{2\text{c}} \quad (7)$$

where $j_{2\alpha}$ is the current associated with the hydrogen evolution reaction, and $j_{2\text{b}}$ and $j_{2\text{c}}$ are the currents associated with the formation of the αPdH and βPdH phases respectively.

The X-ray diffractograms reveal that the current transients with peaks are related to the electroformation of the βPdH phase. The shape of these current transients resembles that observed for the nucleation and growth of a new phase. Thus, let us assume that the formation of the βPdH phase can be represented by an instantaneous nucleation in a thin region of the Pd surface supersaturated in H atoms, followed by diffusion controlled growth of N isolated 3D nuclei. It implies that the linear diffusion of the H atoms into the bulk Pd turns into hemispherical diffusion around the growing nuclei. Similar considerations are valid for hydrogen dissolved into the βPdH nuclei, which can also change from linear to hemispherical diffusion at the growing Pd/ βPdH interface [12]. Then the corresponding current transient run at a constant potential should obey the equation [13]

$$j_{2\text{c}} = P_2 t^{1/2} \quad (8)$$

where

$$P_2 = zF\pi(2Dc_{\text{H}}^{\text{s}})^{3/2} M^{1/2} N / \rho^{1/2} \quad (9)$$

In equation (9) M and ρ are the molar mass and density, and N is the number of growing nuclei of the βPdH phase.

On the other hand, the impedance data indicate that the H_2 evolution on a composite Pd/ βPdH / αPdH electrode becomes more difficult than on the Pd.

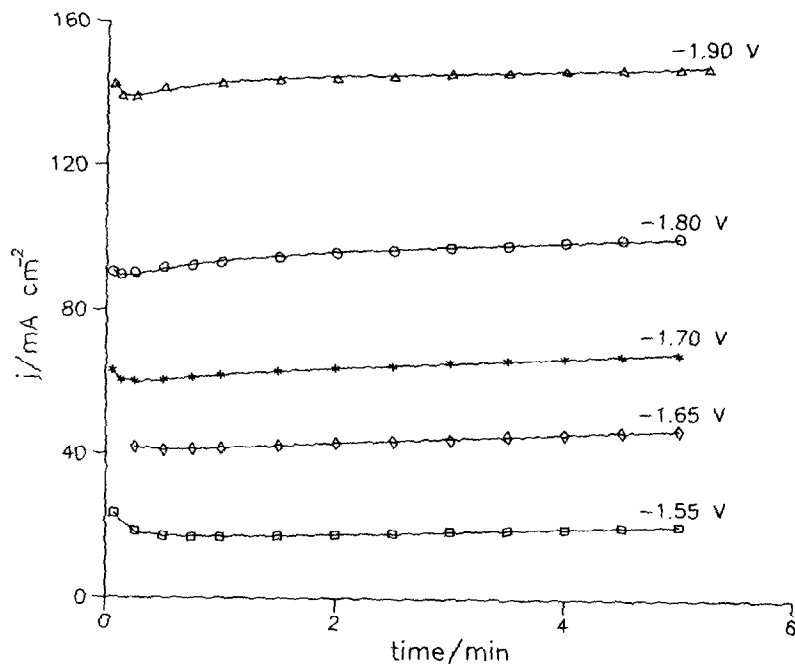


Fig. 5. Potentiostatic current transients at the indicated potentials. (Points) Experimental data. (Lines) Calculated with equation (5) and parameters of Table 1.

Therefore, one should expect that j_{2b} becomes a function of the fraction of Pd converted into the β PdH at the electrode surface. Accordingly, the rate of hydrogen evolution should gradually decrease as the Pd surface is replaced by the growth of the β PdH hemispherical nuclei. The intersection of the latter with the Pd surface generates circular growth centers. Thus, the fraction, S , of the Pd surface converted into the β PdH phase can be estimated from [14]

$$S = \pi KDN_s t \quad (10)$$

where N_s is the number of β PdH centers at the surface.

Thus, j_{2b} should be given by

$$j_{2b} = P_3[1 - P_4 t] + P_5(t) \quad (11)$$

where P_3 is the H_2 evolution current on an uncovered Pd ($t \rightarrow 0$), $P_4 = \pi KDN$ and $P_5(t)$ represents the hydrogen evolution on the β PdH phase. Assuming that $P_3[1 - P_4 t] \gg P_5(t)$, for $t < 300$ s, equation (11) becomes

$$j_{2b} = P_3[1 - P_4 t] \quad (12)$$

By using equations (7) and (4), (8) and (12), the initial part of the current transients recorded at $E_s < -1.4$ V can be reproduced (Fig. 5) with parameters assembled in Table 1.

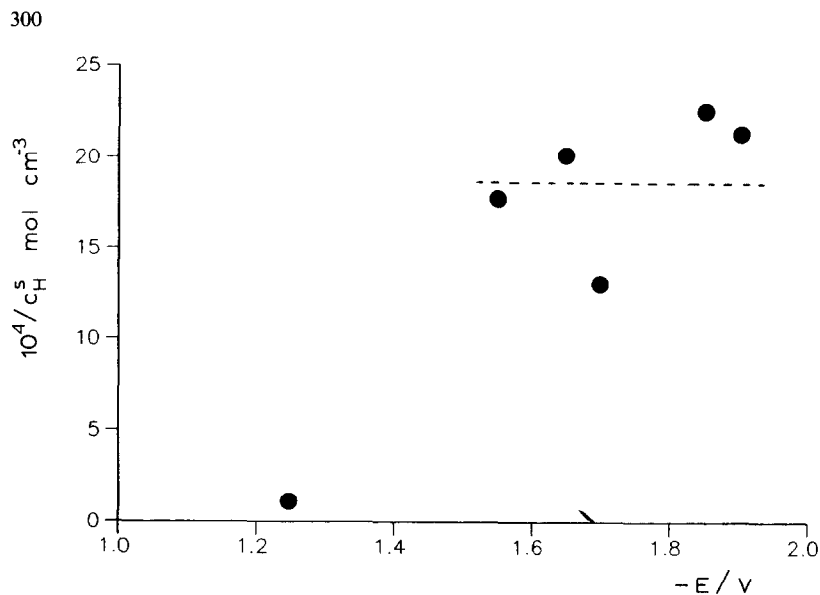


Fig. 6. Potential dependence of the H atoms concentration at the Pd surface.

The value of P_1 increases with with E_s to attain a limiting value which is close to $c_H^s = 2 \times 10^{-3} \text{ mol cm}^{-3}$ for $E_s < -1.37 \text{ V}$ (Fig. 6). This value is similar to that reported as the critical concentration of H atoms required to form the βPdH phase [11]. This means that in a thin Pd layer close to the surface the H supersaturation to form the nuclei of the βPdH is reached at more negative potentials than -1.37 V .

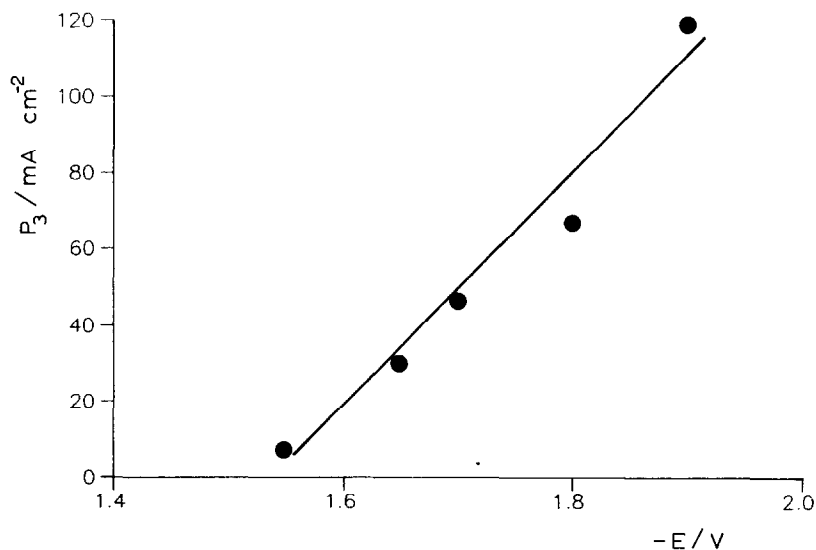


Fig. 7. Influence of the potential on the values of the parameter P_3 of equation (9).

On the other hand, despite the scatter, P_2 and P_4 show no marked dependence on E_s . This is consistent with the assumption of instantaneous nucleation with N being independent of the E_s value and a diffusion-controlled growth. From equation (9) one can estimate N close to 10^8 cm^{-2} . In addition, using equation (12) for $t = 300 \text{ s}$, values of S are in the range 0.1–0.3, that is, only a fraction of the Pd/ α PdH surface is covered by the β PdH phase. This figure justifies a posteriori the assumption that j_{2b} is related mainly to hydrogen evolution on the Pd surface.

The potential dependence of P_3 gives information on the H_2 evolution reaction on a Pd electrode at high negative potential. In this case, the P_3 vs. E_s plot (Fig. 7) corresponds to a straight line with a slope equal to 25Ω in good agreement with the impedance data ($20\text{--}30 \Omega$). These data are consistent with an ohmic controlled process.

Finally, it should be noted that the validity of the overall approach is supported by the physical meaning of the adjustable parameters yielding reasonable figures about the kinetics of the various processes in this potential range.

However, the kinetic model according to equation (7) accounts for the initial part of the current transients i.e. for $t < t_M$. Otherwise, for $t > t_M$ the overlap of growing nuclei and the depletion of the Pd phase leads to more complex current transient behaviour which is difficult to reproduce using simple models.

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