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Occlusion of hydrogen in electrodeposited platinum layers

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Abstract Occlusion of hydrogen in platinized platinum electrodes has been studied in 1 mol/dm³ H₂SO₄ electrolyte. It has been found that the amount of hydrogen dissolved in the platinum layer depends on the structure of the Pt deposit, which is determined by the parameters of electrodeposition. Composition of the platinizing solution as well as the potential of Pt deposition are decisive parameters. On the basis of experimental results it is assumed that occlusion of hydrogen takes place in special structural elements of the platinum layer which are formed in the course of Pt deposition. Hydrogen dissolution versus H-deposition potential, H-deposition time and Pt layer thickness relationships are also presented.

Key words Platinum electrodes · Hydrogen · Platinized platinum

Introduction

In the field of aqueous phase electrochemistry, one of the most frequently studied systems is the platinum/hydrogen couple; however, there are still some uncertainties in our knowledge concerning the hydrogen sorption phenomena. Absorption of hydrogen in platinum is usually regarded as negligible by most electrochemists. Nevertheless, the existence of some kind of “occluded” hydrogen was suggested by a number of authors to aid explaining some voltammetric features of platinum electrodes. For example, the “unusual” adsorption states of Pt(111) surfaces were attributed to incorporation of hydrogen into the platinum [1]. The “unusual”

peaks were reported firstly in 1980, as a result of the revolutionary new technique developed by Clavilier and co-workers [2, 3] for the preparation and pretreatment of clean Pt single crystal surfaces. Since then the allocation of the peaks has been the subject of intense research and scientific discussion, and at present it seems well understood that these characteristic peaks are due to anion adsorption-desorption [4, 5].

Many different explanations have been presented for the so called “third peak” on the voltammetric curve of polycrystalline platinum [6–15] (the small characteristic peak between the peaks of weakly and strongly bound hydrogen in the anodic branch of voltammograms). Some authors proposed that it should be assigned to the oxidation of occluded hydrogen [7, 13, 14]. This view was also represented quite recently by Martins et al. [15].

In the 1960s, from measurements of the potential of a platinum electrode at low partial pressures of hydrogen, Schuldiner and co-workers [16, 17] assumed that Pt electrodes can absorb considerable amounts of hydrogen just under their surface. Gileadi et al. [18] measured the permeation and absorption of electrolytically generated hydrogen in thin platinum foils. They found that most of the absorbed hydrogen is concentrated in regions of local strains in the crystal and take much longer to diffuse out than in. Hydrogen permeation became detectable only when the cathodic surface of the membrane was poisoned. According to their results, the concentration of absorbed hydrogen just below the cathodic surface was 2.7×10^{-5} g-atom/cm³ (at 70 °C), which is higher by orders of magnitude than the value calculated from gas phase measurements [19].

Investigation of the structural properties of platinized platinum electrodes has been the subject of several studies performed by Podlovchenko and co-workers [20–23]. They have found that:

1. The amount of hydrogen ionized between 0 and 400 mV during anodic polarization of Pt/Pt electrodes depended on the current density of the charging curve. This observation could be explained

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by assuming the slow oxidation of some amount of hydrogen absorbed in the platinum deposit.

- Absorption could be observed in the case of electrodes platinized at negative potentials (on RHE scale). It was presumed that differences in the properties of the deposits were caused by the particularities of the porous structure.
- Both the absorption and oxidative elimination of absorbed hydrogen were slow processes.
- Absorption of hydrogen took place only in thick deposits ($\sim 10 \text{ mg/cm}^2$). Electrodes with an amount of deposit equal to $1\text{--}2 \text{ mg/cm}^2$ behaved basically the same as electrodes obtained at positive potential.

In our previous publications [24–27] we have presented results about the hydrogen-adsorption and electrocatalytic properties of different types of platinized platinum electrodes. As a continuation of these works, the present paper is devoted to the phenomenology associated with occlusion of hydrogen in electrodeposited platinum layers.

Experimental

Platinizations were carried out by a potentiostatic method. A smooth polycrystalline platinum sheet of 2 cm^2 was used as a support for the preparation of Pt/Pt electrodes. Before platinization it was treated in aqua regia, then rinsed with triply distilled water. The mass of the electrode was measured before and after the platinization to obtain the mass degree of platinization (mass of the deposit/geometric area of the substrate). The real surface area was determined from the hydrogen adsorption capacity [28].

Polarization measurements were performed in conventional three-compartment electrochemical cells. The potential of the working electrode was recorded (and is reported) with respect to a hydrogen electrode (RHE scale). During the experiments, argon gas (99.9995%) was bubbled through the main compartment of the cells to deoxygenate the solution.

In the course of studying the hydrogen occlusion the Pt/Pt electrodes were treated according to the potential program depicted in Fig. 1. Two identical electrochemical cells of the same form were used. Deposition of hydrogen (in cell “2”) and oxidation of the occluded hydrogen (in cell “1”) were carried out in $1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ solution.

Electrolytes were prepared from Merck p.a. grade concentrated acid using triply distilled water. (Preparation of the triply distilled water is described in Ref. [29].) All experiments were carried out at room temperature.

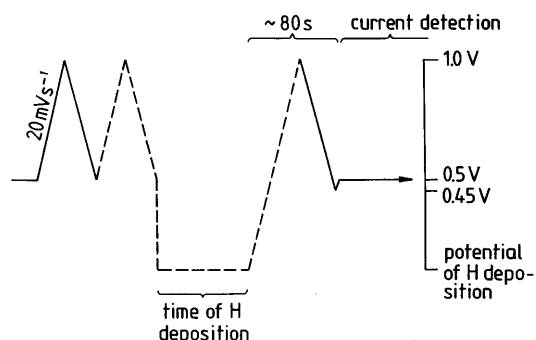


Fig. 1 Potential program for determination of occluded hydrogen. Dashed line: polarization in cell “2”. Solid line: polarization in cell “1”

Results and discussion

Hydrogen or impurities?

A typical voltammetric response of a Pt/Pt electrode can be seen in Fig. 2a. The peculiarity of these curves is that on decreasing the cathodic potential limit of the cycles, broadening of the double layer region can be observed (enlargement of the double layer region also can be seen in Fig. 2b). This behavior is easily reproducible at certain kinds of Pt/Pt electrodes, while in other cases it is less pronounced or is not observable at all.

When the potential program was stopped and the potential of the Pt/Pt electrode was held at 500 mV after obtaining curve 3 of Fig. 2, a small anodic current could be detected for a relatively longer period of time ($\sim 10\text{--}15 \text{ min}$). The amount of this oxidation charge which could be measured at 500 mV after polarizing the Pt/Pt electrode into the hydrogen region depended on the value of the negative potential limit of the cycle. Moreover, increasing the time of H-deposition (stopping the potential program in the hydrogen region for a certain time) resulted in a significant increase in the oxidation charge. On the basis of the above-mentioned results of Podlovchenko et al. [20–23], these findings can be related to the occlusion of hydrogen in the Pt layer and to the oxidation of this hydrogen, although we have

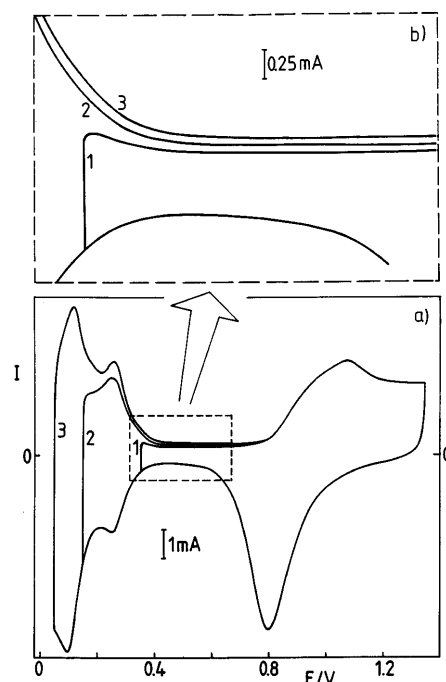


Fig. 2 Cyclic voltammetric curves of a Pt/Pt electrode **a** obtained in $1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ solution and enlargement of the double layer section. **b** Cathodic potential limit: 350 mV (1), 150 mV (2), 50 mV (3). Sweep rate: 20 mV/s . Parameters of platinization: from solution containing $0.07 \text{ mol/dm}^3 \text{ H}_2\text{PtCl}_6$ and $2 \text{ mol/dm}^3 \text{ HCl}$, at -35 mV potential, for 5 min. Mass degree of platinization: 2 mg/cm^2 . Roughness factor: ~ 120

to take into consideration that the presence of some kind of reducible (and reoxidizable) impurities could result in similar effects. The concept of the occurrence of hydrogen absorption is usually rejected on the basis that the experimental results ascribed to absorption can be interpreted in terms of electrochemical transformation of impurities present in the system studied. In order to exclude the role of any kind of impurities, two cells were used (see the potential program in Fig. 1). In the first cell, after a couple of potential cycles between 500 and 1000 mV the electrode was polarized to 500 mV to control that there was no oxidizable species on the electrode or in the solution (there was no measurable current). It was followed by another cycle and then the electrode was moved to the second cell. The hydrogen deposition took place in this cell: the potential of the platinized electrode was held at a given potential for a preselected period of time. (The "hydrogen deposition" term in this case is used for the polarization of the electrode at a potential which is sufficiently negative for the formation of occluded hydrogen. This potential, as will be demonstrated later, can either be in the underpotential or in the overpotential region.) After hydrogen deposition the electrode was polarized to 1000 mV, so adsorbed hydrogen (and the possible impurities) were oxidized. At 1000 mV the potential program was interrupted and the electrode was moved back to the first cell. Here polarization was continued in the negative direction to 450 mV, then it was reversed and finally at 500 mV the current was registered as a function of time. Applying this treatment, we failed to measure the amount of hydrogen oxidized in the first ~ 80 s after hydrogen deposition; however, we managed to remove the effect of hydrogen (and impurities) adsorbed on the surface or dissolved in the solution.

The curves presented in Fig. 3 were recorded after the above detailed procedure using the same electrode as in the experiment represented by Fig. 2. Hydrogen deposition was carried out at different potentials for 10 min. As can be seen from Fig. 3, oxidation of the dissolved hydrogen took longer time than 10 min in all experiments. In the case of the -50 mV deposition potential (curve 3), a positive current could be detected for more than 3 h. This confirms that the emergence of hydrogen from the platinum is a considerably slower process than its getting in. It is noteworthy that at a potential as positive as 200 mV, occlusion of hydrogen occurred as curve 1 of Fig. 3 demonstrates.

Dependence of hydrogen dissolution on the duration and potential of H-deposition

Similar measurements as represented by Fig. 3 were performed applying 100 mV as hydrogen deposition potential, and changing the time of hydrogen deposition. Charge passed through the cell at 500 mV, while the current decreased to zero, and was determined (Q_{H^*}) and is plotted in Fig. 4 as a function of time of

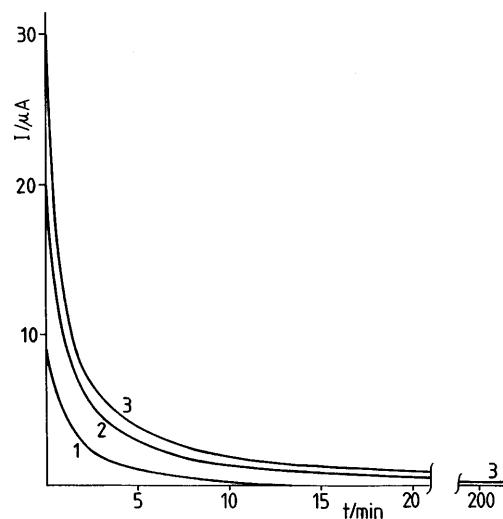


Fig. 3 Current vs. time curves measured at 500 mV on a Pt/Pt electrode after applying the potential program depicted in Fig. 1. Time of H-deposition was 10 min, potential of H-deposition: 200 mV (curve 1), 100 mV (curve 2) and -50 mV (curve 3). Electrode: as in the case of Fig. 2

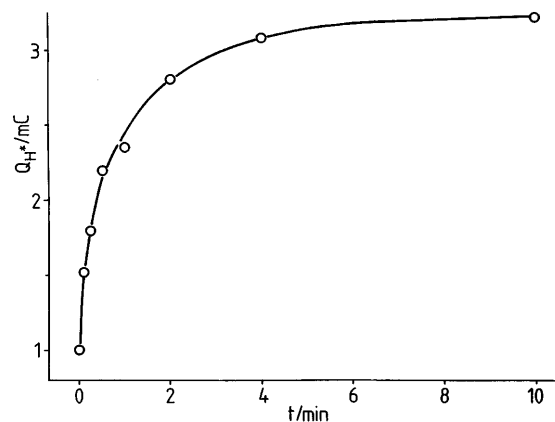


Fig. 4 Anodic charge (Q_{H^*} , see the text) measured at 500 mV as a function of time of H-deposition. Potential of H-deposition: 100 mV. Electrode: as in Fig. 2

H-deposition. It follows from the applied experimental procedure that Q_{H^*} should be slightly smaller (difference amounts to 5–10%) than the charge that would correspond to the total amount of occluded hydrogen. (Hydrogen oxidized in the first ~ 80 s, i.e. during the polarization to 1000 mV in the cell "2" and back to 500 mV in the cell "1" is left out of consideration; see the potential program in Fig. 1.) As can be seen from Fig. 4, the Pt/Pt electrode could be saturated by hydrogen in some minutes. There is only 4–5% increase in Q_{H^*} comparing depositions carried out for 4 and 10 min.

Results obtained at different hydrogen deposition potentials were similar to those depicted in Fig. 4. Q_{H^*} values measured after saturation of the electrode by

hydrogen (10 min depositing times) as a function of hydrogen deposition potential are presented in Fig. 5. It is evident from Fig. 5 that the slowly desorbing hydrogen under discussion can exist in the whole hydrogen adsorption region. The Pt/Pt electrode reaches a maximum hydrogen content at a potential slightly negative to the equilibrium hydrogen evolution potential.

The real state of the hydrogen in the Pt layer is questionable. Occlusion of hydrogen gas bubbles (generated during the H-deposition) in micro-voids of the porous Pt could be raised as well. However, as can be seen from Fig. 5, the Q_{H^*} value corresponding to hydrogen deposition at 0 mV is only about two times larger than Q_{H^*} at 100 mV. If we consider the equilibrium partial pressures of H_2 at these two potentials, the difference between the amounts of occluded H_2 should exceed three orders of magnitude according to relation:

$$E = \frac{RT}{F} \ln \frac{a_{H^*}}{\sqrt{p_{H_2}}}$$

Diffusion of the occluded hydrogen to the surface

The effect of oxidation potential on the rate of oxidative elimination of dissolved hydrogen was studied. In previous experiments, 500 mV oxidation potential was applied because there is certainly no hydrogen and oxygen (or OH) adsorption at this potential. This requirement is fulfilled over a relatively wide potential range, so oxidation of dissolved hydrogen was carried out at different potentials between 400 and 900 mV after applying the same H-deposition procedure and using the same electrode. The results of these measurements were identical within 5% error, and patterns of the current-time curves were similar. The fact that the oxidation potential has no

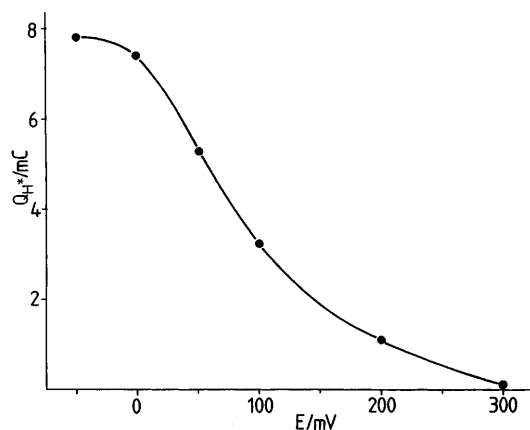


Fig. 5 Anodic charge (Q_{H^*}) measured at 500 mV as a function of the potential of H-deposition. Time of H-deposition: 10 min. Pt/Pt electrode: as in Fig. 2

influence on the rate of desorption supports that the rate determining step is the transport of hydrogen to the surface. All this can be clearly demonstrated by the next experiment.

The Pt/Pt electrode was saturated with hydrogen and the current-time curve at 500 mV was detected according to the previously applied procedure. A section of this curve is presented in Fig. 6 (curve 1). After oxidizing the occluded hydrogen, saturation was repeated but instead of oxidation at 500 mV the electrode was taken out of the cell, rinsed with distilled water, dried and held in air at room temperature for 20 min. After 20 min it was put into the cell 1, polarized to 500 mV and a current-time curve was registered (Fig. 6, curve 2). The curves of Fig. 6 demonstrate that during the first 20 min approximately the same amount of hydrogen was oxidized in both cases. It reveals that diffusion of the hydrogen from the inner part of the electrode to the surface is the rate determining process. It has no effect on the rate of oxidation of occluded hydrogen whether the cavities and micropores of Pt/Pt are filled with sulfuric acid or with air.

Relation between the parameters of Pt deposition and the hydrogen dissolving capacity of Pt/Pt electrodes

It was mentioned earlier that the solubility of hydrogen in the electrodeposited layers depends on the structure of the deposit. Podlovchenko and co-workers [20–23] considered that only those Pt layers which are deposited at negative potentials are able to absorb hydrogen. According to our findings, in addition to the potential, the chloride and platinum content of the platinizing solution have also decisive effects. The roles of these three parameters are discussed below.

Platinum layers were deposited potentiostatically at different potentials from different platinizing solutions whose composition is detailed in Table 1. The mass degree of the electrodeposited layers was between 1 and 1.5 g/cm^2 . (It means of course that different depositing

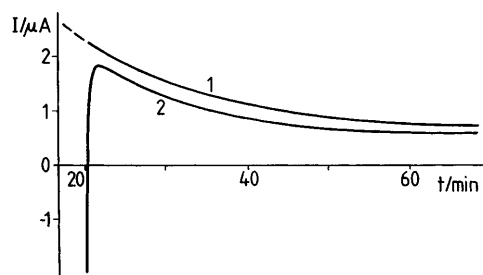


Fig. 6 Anodic current vs. time curves measured on the same Pt/Pt electrode saturated with hydrogen at 50 mV. Curve 1: oxidation of occluded hydrogen at 500 mV according to the program depicted in Fig. 1. Curve 2: after hydrogen deposition the electrode was kept in air for 20 min and the oxidation of occluded hydrogen was continued at 500 mV. Electrode: as in Fig. 2

Table 1 Composition of platinization solutions

No. of solution	[H ₂ PtCl ₆] (mol dm ⁻³)	[HCl] (mol dm ⁻³)
1	0.05	0.02
2	0.05	0.2
3	0.05	2
4	0.01	0.02
5	0.01	0.2
6	0.01	2

times were applied in the case of different solutions.) The platinized electrodes were saturated with hydrogen at 0 mV (for 10 min) and Q_{H^*} values were determined in the same way as in the previous experiments. The Q_{H^*}/m values are presented in Fig. 7 (m denotes the mass of the Pt deposit) as a function of the potential of Pt deposition, using different solutions. The curves in Fig. 7 marked with numbers refer to the numbered solutions of Table 1.

As can be seen, the influence of the platinum deposition potential on the hydrogen occlusion capacity of the deposited Pt layer is similar using different platinizing solutions. Upon decreasing E , Q_{H^*} starts to increase at about 50 mV, reaches a maximum between -30 and -50 mV and at more negative potentials decreases. It is probable that at these platinum deposition potentials the intensive H₂ evolution inhibits (at least to a certain extent) the formation of such kinds of deposits that are able to dissolve hydrogen. The curves of Fig. 7 clearly demonstrate that the earlier cited assumption [20-23], that only Pt layers deposited at negative potential are able to dissolve hydrogen, could be regarded as a first rough approximation. For example, curve 1 of Fig. 7

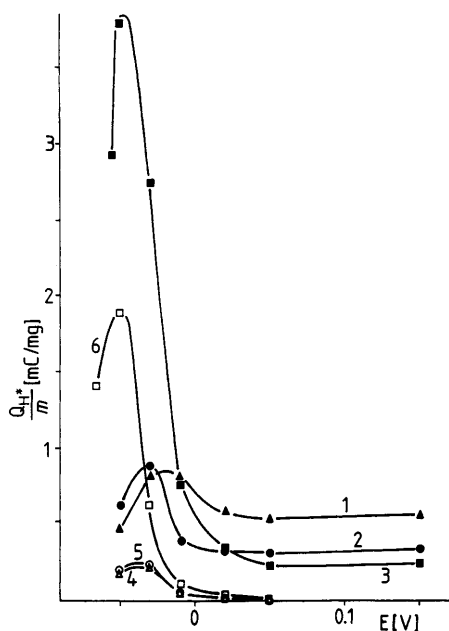


Fig. 7 Mass specific Q_{H^*} as a function of the platinum deposition potential using different platinization solutions. Composition of the solutions is shown in Table 1. Numbering (1-6) is the same as that in Table 1. Hydrogen deposition: 10 min, 0 mV

indicates that it was possible to deposit such a layer at 150 mV from solution 1 (actually its mass specific capacity for dissolving hydrogen was slightly higher compared to the coating deposited at -50 mV). Increasing the platinum content of the platinizing solution was favorable to the formation of the hydrogen occluding structure (in the studied concentration range). In addition to the solutions detailed in Table 1, solutions containing 0.005 mol/dm³ H₂PtCl₆ (chloride concentration: 0.02, 0.2 and 2 mol/dm³) were also studied, but from these a stable adherent deposit could not be obtained.

Chloride ion concentration has also a crucial effect, as can be seen from Fig. 7. Upon increasing the chloride content of the platinizing solution from 0.2 to 2 mol/dm³, the hydrogen occlusion capacity of the platinum layers deposited between -30 and -50 mV potential increased by a factor of 5-7. The considerable influence of chloride ion concentration of the platinizing solution on the structure of Pt deposit may be the consequence of the strong adsorbability of chloride on Pt surfaces.

Effect of the mass of Pt deposition on the hydrogen dissolution in the Pt/Pt electrode

The hydrogen occlusion capacity of platinized platinum electrodes is determined by the parameters of platinum deposition, as was demonstrated in the previous section. At given values of these parameters (solution 3 of Table 1, $E = -50$ mV), platinum layers were deposited by applying different deposition times. The Q_{H^*} values measured on three electrodes (having platinum deposits of different thicknesses) as a function of hydrogen deposition time are shown in Fig. 8. According to these curves, the quantity of dissolved hydrogen (corresponding to the saturation) is proportional to the mass of the platinum deposit. It can be also established that saturation of the platinum layers with hydrogen took place approximately in the same time. On the other

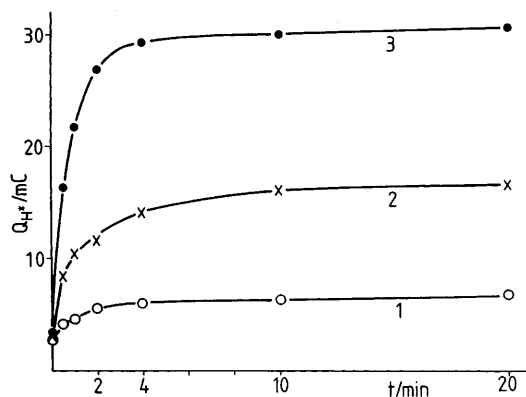


Fig. 8 Q_{H^*} as a function of time of hydrogen deposition measured on electrodes with different mass degrees of platinization: 0.9 mg/cm² (1), 2.1 mg/cm² (2), 4.2 mg/cm² (3). Potential of hydrogen deposition: -50 mV. Platinization: from solution "3" (see Table 1) at -50 mV for 5 min (1), 10 min (2), 20 min (3)

hand, there was a considerable difference in the desorption of hydrogen from the saturated layers. Oxidation of the larger amount of hydrogen occluded in the thicker layer took a longer time.

According to our results, alteration of the surface structure of Pt/Pt electrodes does not affect the hydrogen occlusion behaviour. After strong anodic polarization or potential cycling which resulted in significant modifications in cyclic voltammogram profiles of freshly platinized surfaces, indicating the transformation of the surface structure, the hydrogen occlusion characteristics of Pt/Pt electrodes did not change. Even in certain cases, the quantity of dissolved hydrogen as well as the rate of hydrogen occlusion and oxidation was unchanged, while a 30–50% decrease in the real surface area could be observed.

For the sake of comparison, some platinum layers deposited onto a gold support were also investigated and the results were identical to those deposited on platinum, proving that the hydrogen occlusion phenomenon under discussion can be attributed to the electrodeposited platinum layers.

Conclusions

1. Certain types of electrolytically deposited porous platinum layers are able to occlude significant amounts of hydrogen. The highest H-atom:Pt-atom ratio found in our experiments was 1:130 ($Q_{H^*}/m = 3.9 \text{ mC/mg}$). This value is higher by orders of magnitude than that reported by Gileadi et al. [18] for hydrogen just below the cathodic surface of smooth electrodes. On the basis of all these results, it seems convenient to consider that in the course of platinum deposition a special structure can form under appropriate circumstances which is able to dissolve hydrogen. This assumption is also supported by the fact that:
2. The occlusion capacity of platinum deposits is determined by the parameters of the platinization. According to our results, not only the potential of Pt deposition (as was published earlier [20–23]) but also the platinum and chloride concentration of the platinizing solution are of fundamental importance. Platinum layers having the same roughness factor and thickness with different hydrogen occlusion behaviour can be prepared by choosing appropriate platinizing parameters.
3. Upon increasing the mass degree of platinization (at constant platinization parameters) a proportional increase of occlusion capacity could be observed, indicating that hydrogen-dissolving structural elements are being formed uniformly at an approximately constant rate in the course of Pt deposition.
4. In the case of a given platinum deposit, a decrease of the real surface area did not influence the hydrogen dissolution, which confirms that this type of hydro-

gen cannot be on the surface or just under the surface.

5. However, similar to the behaviour of absorbed hydrogen in the case of smooth platinum as was reported by Gileadi et al. [18], getting through the platinum surface by the occluded hydrogen is a very slow process. Moreover, desorption is much slower than dissolution in both cases.
6. We could not find any difference between the occlusion behaviour of platinum layers deposited onto platinum and gold supports. This fact also reveals that the dissolution of a tremendous amount of hydrogen can be attributed to a certain platinum layer structure and not to the metal itself.
7. Occluded hydrogen appears in platinum layers (having the appropriate structure) at potentials as positive as +300 mV, and at +100 mV a considerable amount of hydrogen can be dissolved. So, according to our findings, underpotentially deposited hydrogen atoms in an adsorbed state are able to move further into the electrodeposited Pt layer. (It is noteworthy that in the case of smooth electrodes, Gileadi and his co-workers found [18] that hydrogen absorption took place only at poisoned platinum surfaces at high overpotentials.)

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