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 $2.7 \times 10^{-5}$ 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
by assuming the slow oxidation of some amount of hydrogen absorbed in the platinum deposit.

2. 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.

3. Both the absorption and oxidative elimination of absorbed hydrogen were slow processes.

4. Absorption of hydrogen took place only in thick deposits (≈10 mg/cm²). Electrodes with an amount of deposit equal to 1–2 mg/cm² 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 cm² 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 mol/dm³ H₂SO₄ 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.

**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 (≈10–15 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

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![Fig. 1](image1.png)

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

![Fig. 2](image2.png)

*Fig. 2* Cyclic voltammetric curves of a Pt/Pt electrode a obtained in 1 mol/dm³ H₂SO₄ solution and enlargement of the double layer section. b Cathodic potential limit: 350 mV (J), 150 mV (2), 50 mV (J). Sweep rate: 20 mV/s. Parameters of platinization: from solution containing 0.07 mol/dm³ H₂PtCl₆ and 2 mol/dm³ HCl, at ≈35 mV potential, for 5 min. Mass degree of platinization: 2 mg/cm². Roughness factor: ≈120