

The third anodic hydrogen peak on platinum; subsurface H₂ adsorption.

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THE THIRD ANODIC HYDROGEN PEAK ON PLATINUM; SUBSURFACE H₂ ADSORPTION

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Abstract—The occurrence of the third anodic hydrogen peak was investigated on platinized platinum. Using DEMS in combination with Cyclic Voltammetry it is shown that adsorbed molecular hydrogen is the cause of this third peak. It is suggested that this hydrogen is presented in a subsurface state of Pt since disturbance of the Pt surface structure by oxide formation is necessary for the third peak to appear.

Key words: platinum, DEMS, third anodic hydrogen peak, subsurface hydrogen.

INTRODUCTION

The electrochemical adsorption of hydrogen on Pt in acid electrolytes has long been a major subject of investigations[1–3]. The early research on this subject has been excellently reviewed by Woods[4]. It is shown that on polycrystalline platinum and platinized platinum, multiple adsorption states are possible. These different adsorption states were ascribed by Will[5] to adsorption on different crystal planes ((100), (110) and (111)). This idea has been generally accepted since then, though the assignment of the peaks to the different crystal planes has been changing throughout the years. It seems to be well established now that strongly bonded hydrogen (H_s, $E_p = +0.28$ V vs. RHE) is due to adsorption on the Pt(100) plane. Weakly bonded hydrogen (H_w, $E_p = +0.12$ V vs. RHE) has been assigned to both the Pt(110) and the Pt(111) plane[6, 7]. Often also a so-called third anodic hydrogen peak (H_{3rd}), is observed at a potential between the strongly and weakly bonded hydrogen peaks. There has been much discussion on the origin of this peak because it only appears in the anodic part of the cyclic voltammogram and not in the cathodic part; furthermore at high sweep rates, it is not observed at all[8]. This peak was assigned by Will[5] to H adsorption on Pt(111) sites. From measurements at platinized platinum Kinoshita *et al.*[7] concluded that the amount of third anodic hydrogen depends on the amount of edge and vertex atoms. The fact that the third peak only appears when low sweep rates are used combined with the condition that the potential scan must be taken to potentials below +0.13 V, led Breiter and others to the conclusion that it is due to hydrogen absorption[9–11]. Kinoshita *et al.*[12], however, calculated that hydrogen absorption cannot be responsible for the third anodic hydrogen

peak because hydrogen only dissolves in Pt in very small amounts. Stonehart[13] found that the third peak grows with time when the potential is held at a value below +0.12 V and suggested that the peak might be due to surface diffusion and reorientation of adsorbed hydrogen thus forming a H₃⁺ species. Tegtmeier *et al.*[14] showed with DEMS that H₂ formation is indeed possible below +0.12 V. It was observed by Loo and Furtak[6] that the third peak disappears if the anodic sweep is reversed at potentials in the double layer region while the strongly and weakly bonded hydrogen peaks grow in intensity. If the reverse potential is then increased to the oxide formation region, the third peak reappears. It was suggested that certain active sites have to be formed capable of sorbing the hydrogen species of the third peak. Gomez and Clavilier[15] showed that Pt(110) behaves similarly to the polycrystalline Pt: the third peak is clearly present in the cyclic voltammogram of the single crystal after one oxidation-reduction cycle between 0 and +1.2 V vs. RHE. It is argued that Pt(110) sites are necessary for the third anodic hydrogen peak to appear. Recently Sumino and Shibata[16] confirmed the Stonehart results and concluded that it is very plausible that *upd* H₂ is responsible for the third peak. This hydrogen molecule is supposed to be occluded into the surface layer reconstructed during the anodic cycle. Upon conditioning at low potentials, not only the third peak increases with time, but also the amount of weakly adsorbed hydrogen decreases. It follows from the change in H_{3rd}/H_w that twice as many electrons must be involved in the process responsible for the third hydrogen peak, when compared to the weakly adsorbed hydrogen.

Until now most studies have been dealing with smooth Pt. To seek further evidence for the assignment of the third peak to ad- or absorbed H₂, and thus substantiate the results of Sumino and Shibata[16], we performed experiments with platinized Pt.

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EXPERIMENTAL

All measurements were performed in a conventional three electrode cell, with a Hg/Hg₂SO₄ (MSE $E = +0.65$ V vs. RHE) reference electrode and a platinum sheet as a counter electrode. All potentials are referred to the RHE. The working electrode was a Pt (area = 4 cm²) sheet which was platinized galvanostatically with a current density of 10 mA cm⁻² for 10 min. Roughness factors, calculated from hydrogen desorption in a cyclic voltammetric experiment and assuming that 1 cm² corresponds with 210 μ C, ranged from 200 to 300. For the Differential Electrochemical Mass Spectroscopy (DEMS) measurements a platinized Pt gauze was used. All currents in the cyclic voltammetric measurements are given with respect to the real surface areas of the electrodes, taking into account the roughness factor. Measurements were carried out in 0.5 M H₂SO₄ as a supporting electrolyte, which was prepared from ultrapure acid (Merck) and ultrapure (18.2 M Ω) water (Elgastat). The cyclic voltammetric measurements were performed with a computer controlled Autolab Potentiostat (Eco Chemie) or a Wenking POS 73 potentiostat. The setup of the DEMS is similar to those described before[7].

RESULTS AND DISCUSSION

The platinized electrode gives a cyclic voltammogram as is shown in Fig. 1, the potential limits are 0 and +1.3 V. When compared to the literature data on single crystal electrodes, the following results are obtained: The anodic peak at +0.10 V, due to weakly bonded hydrogen, is close to the potential which is given in literature for the hydrogen adsorption on a Pt(110) surface[18–20]. The peak at +0.23 V, due to the strongly bonded hydrogen, is close to the values given by Yamamoto[20] (scanrate, $v = 50$ mV/s) and Santos[21] ($v = 50$ mV/s) for Pt(100), but 100 mV lower than the values reported in [18] ($v = 50$ mV/s) and [19] (v not specified). Rodes *et al.*[22] showed that this difference is due to the presence of surface defects introduced during the pretreatment.

By varying the scan rate, slight changes in the peak potentials are noticed. In Fig. 2 the peak poten-

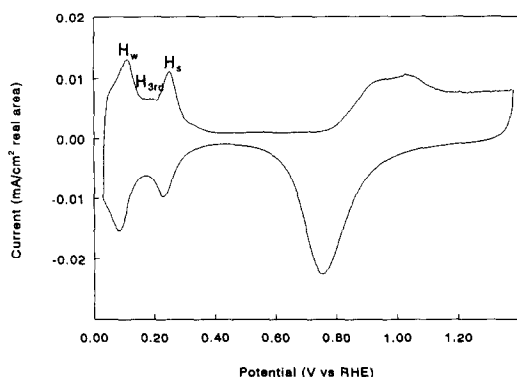


Fig. 1. Cyclic voltammogram of platinized platinum. 0.5 M H₂SO₄, $v = 10$ mV/s.

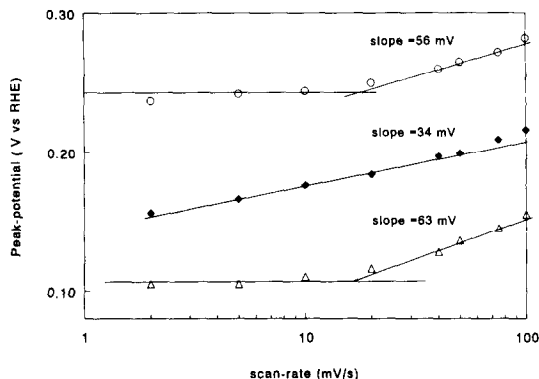


Fig. 2. Peak-potential as a function of the scan-rate for the three hydrogen desorption peaks on platinized platinum. (○): H_s; (◆): H_{3rd}; (△): H_w. 0.5 M H₂SO₄.

tial of the three different peaks are plotted against v . The figure shows that the kinetic behavior of the third desorption process is substantially different from that of the other two. The peaks due to strongly and weakly bonded hydrogen are reversible at low scan rates and start to show irreversible behavior at scan rates above 20 mV/s. This result is in agreement with earlier findings at polycrystalline Pt[3], but differs from the results of Sumino *et al.*[16] who found that both peaks are reversible up to 10 V/s. The third peak shows irreversible behavior even at low scan rates, and the slope of this line is approximately half of that for the other two peaks, and so these results might indicate that a different mechanism is responsible for the third peak. In order to check whether this is due to local pH changes caused by the roughness of the platinized Pt, we repeated the same experiments with smooth Pt. The change of the three hydrogen peaks with scan rate was similar to that for the platinized Pt. We can therefore conclude that the potential shift of the three hydrogen peaks as a function of the scan rate is not due to the roughness of the electrode.

In order to find out how the initial potential influences the third anodic peak, we fixed the potential between 0 and +0.12 V for different times before starting the anodic scan, these values are below the peak-potential of H_w. The results are given in Figs 3 and 4. In Fig. 3 it is shown that if the potential is fixed for 100 seconds at values below +0.08 V, the third anodic hydrogen peak increases, while if the fixed potential is at +0.08 V or higher, no increase in the third hydrogen peak is found.

Figure 4 shows the results for different conditioning times at +0.07 V vs. RHE (after which an anodic scan was started at +0.03 V) in H₂SO₄. An increase in the third-peak current is found with an increase in conditioning time up to 100 seconds; at values higher than 100 seconds no further increase was seen.

As mentioned in the introduction, these results can be explained by assuming that H₂ is already formed at these potentials. To verify whether this is indeed so, we performed DEMS experiments under the same conditions as well as under steady state conditions. The results are shown in Fig. 5. It is seen that during the cathodic scan H₂ is detected at potentials

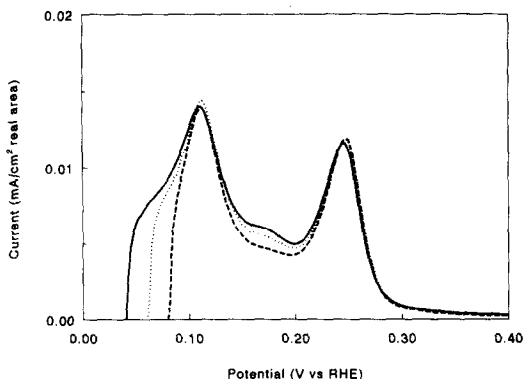


Fig. 3. Hydrogen desorption on platinumized Pt after holding the potential for $t = 100$ s, (—) $E_{\text{hold}} = +0.03$ V; (····) $E_{\text{hold}} = +0.06$ V; (---) $E_{\text{hold}} = +0.08$ V. $0.5 \text{ M H}_2\text{SO}_4$, $v = 10 \text{ mV/s}$.

of ca. +0.08 V and lower. The same holds for the anodic scan.

Further evidence for this was sought for by an experiment in which we adsorbed and oxidized

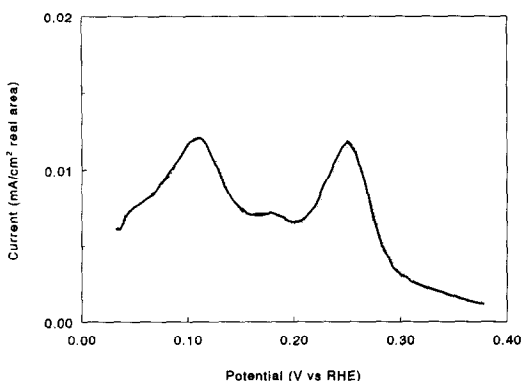


Fig. 4. Hydrogen desorption after holding the potential at $E = +0.03$ V for different times: (····) $t = 0$ s; (---) $t = 40$ s; (—) $t = 60$ s. $0.5 \text{ M H}_2\text{SO}_4$, $v = 10 \text{ mV/s}$.

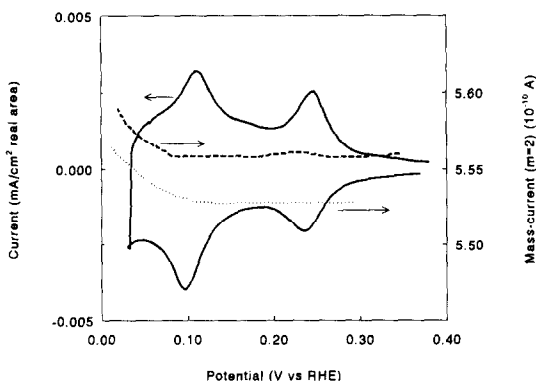


Fig. 5. Hydrogen adsorption-desorption area together with the change in the amount of hydrogen detected by the mass-spectrometer. The mass-signal is only shown for the cathodic scan; (····) change in H_2 signal during a steady state measurement; (---) change in H_2 signal during a cyclic voltammetric measurement ($v = 2 \text{ mV/s}$). $0.5 \text{ M H}_2\text{SO}_4$.

gaseous molecular hydrogen. This was done by bubbling a mixture of hydrogen/argon through the electrolyte for 40 seconds, followed by bubbling with pure argon to remove the hydrogen from the solution, while the potential was fixed at +0.08 V. In the following anodic scan a large increase in the third peak is observed, while almost no increase is found for the other two peaks (Fig. 6). It is thus evident that molecular hydrogen is responsible for the third peak. Because only the third hydrogen peak increases, oxidation of gaseous molecular hydrogen can be excluded.

Remains the question why the occurrence of the third peak is subject to potential cycling to potentials in the oxide region. To explore this further we carried out combined cyclic voltammetric and DEMS experiments in which we varied the upper potential limit. Figure 7a and b show that when the anodic reverse potential is lowered, the height of the third peak decreases. At potentials where no oxide formation takes place, the third anodic hydrogen peak can not be detected. This result is in agreement with that of Clavilier *et al.*[15] on Pt(110) and Loo[6]. In Fig. 8 a correlation is given between the peak current of $\text{H}_{3\text{rd}}$ and the percentage of the surface that is oxidized. The latter is calculated by taking the ratio between the oxide reduction charge and the oxide reduction charge of a full scan to +1.3 V. The linear relationship strongly suggests that the number of oxidized sites is directly related to the amount of $\text{H}_{3\text{rd}}$. It furthermore appears, *cf.* Fig. 7b, that the H_2 evolution commences at a lower potential on a non-oxidized surface. This is consistent with results[23] on hydrogen evolution which show that a different mechanism prevails when the Pt surface is oxidized before hydrogen is evolved.

The oxygen adsorption-desorption appears to be responsible for the formation of sites on which the species of the third anodic hydrogen peak may be formed. This may be related to the formation of (110) sites with surface structures, which sites were shown to be responsible for the appearance of the third peak[15] on the single crystal electrode. The process responsible for the formation of the third peak is a slow one (*vide infra*) and the species concerned in this process can therefore not be a hydrogen atom

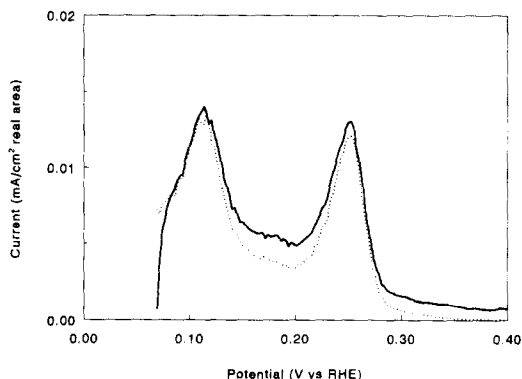


Fig. 6. Hydrogen desorption after adsorbing H_2 gas for $t = 40$ s at $E_{\text{ad}} = +0.08$ V. Before starting the anodic scan electrolyte was flushed with argon to remove the bulk hydrogen gas. $0.5 \text{ M H}_2\text{SO}_4$, $v = 10 \text{ mV/s}$.

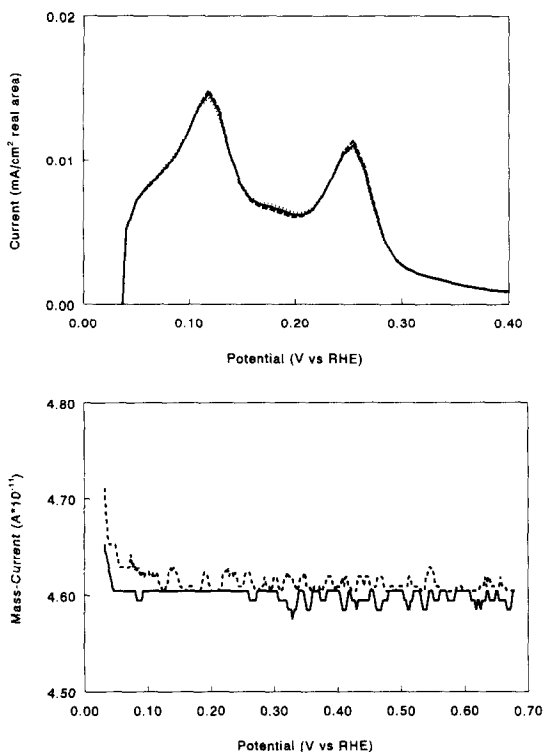


Fig. 7. Hydrogen desorption for cyclic voltammograms with different anodic scan limits. (a) Current-potential curve: (····) $E_{\text{anod}} = +1.28$ V; (—) $E_{\text{anod}} = +1.08$ V; (---) $E_{\text{anod}} = +0.78$ V. (b) Mass-potential curve: (—) $E_{\text{anod}} = +0.78$ V; (---) $E_{\text{anod}} = +1.28$ V. 0.5 M H_2SO_4 , $v = 10$ mV/s.

adsorbing on the surface. Furthermore, since the appearance of the third peak is closely related to the start of the hydrogen evolution, we suggest that adsorbed molecular hydrogen (which may well be the intermediate in the hydrogen evolution) is the species oxidized in the third anodic peak. To account for the slowness of the process, we suggest that the molecular hydrogen is sub-surface adsorbed and forms possibly on (110) sites with surface structures, generated by oxidation-reduction cycles. The fact

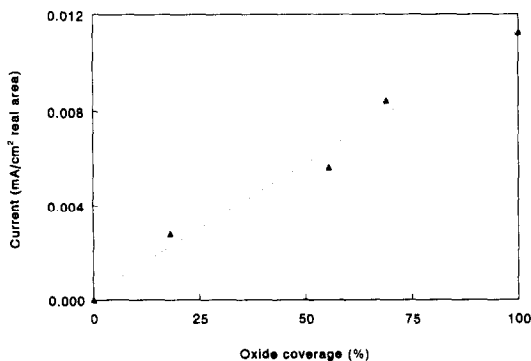


Fig. 8. Current of the third anodic hydrogen peak as a function of the amount of surface oxide coverage. The current is measured with respect to the value of the non-oxidized surface.

that the current for the third anodic hydrogen peak is limited, must then be due to the limited amount of Pt(110) sites with surface structures that can be formed on a platinized Pt surface.

CONCLUSIONS

In this work we confirmed the previous results of Sumino[16] and Loo[6] for Pt on the third anodic hydrogen peak on platinized Pt. By *in-situ* monitoring with DEMS we further gathered additional evidence for the hypothesis that H_2 is responsible for the third peak. These measurements showed that H_2 evolution occurs at potentials below +0.10 V and that this is retarded on those surfaces on which no third anodic hydrogen peak occurs. The fact that H_2 adsorbed from the gas phase, shows similar behavior as electrochemically generated H_2 , makes it very unlikely that the H_2 species is absorbed in the bulk of the electrode. The sites, where the H_2 species is formed, have to be created via oxidation of the surface and it is well known that this oxidation involves a place exchange. This probably involves formation of Pt(110) sites with surface structures. This in combination with the fact that the process responsible for the third peak is found to be slow, leads us to the conclusion that the third hydrogen species is sub-surface molecular hydrogen.

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