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Pd deposition onto Au(111) electrodes from sulphuric acid solution

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Abstract

The initial stages of palladium deposition onto Au(111) from 0.1 M H₂SO₄ + 0.1 mM PdSO₄ have been studied by cyclic voltammetry and in situ scanning tunnelling microscopy. While Pd is commonly deposited from chloride solutions, the effect of sulphate adsorption is considered in this work. A Pd monolayer is formed at underpotentials before a second monolayer grows at overpotentials. There is strong evidence that these two Pd layers are pseudomorphic with the Au(111) substrate. Sulphate is adsorbed on the pseudomorphic Pd layers over a wide potential range in a ($\sqrt{3} \times \sqrt{7}$)*R*19.1° structure like in the case of massive Pd(111). The deposition process changes to three-dimensional growth with the third Pd layer, which has already bulk properties. This is indicated by the appearance of a voltammetric peak in the hydrogen adsorption region, which is characteristic for the behaviour of massive Pd(111). Differences to Pd deposition from chloride solutions are discussed. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Cyclic voltammetry; Scanning tunnelling microscopy; Surface structure; Pseudomorphism; Gold; Palladium

1. Introduction

Thin metal overlayers have gained considerable interest in various fields of physical chemistry, including electrocatalysis. Epitaxially grown thin Pd films on Au(111) have been used as model systems to study various electrochemical reactions, like adsorption and absorption of hydrogen [1], formic acid oxidation [2,3], oxygen reduction [4], formaldehyde oxidation [5] and CO adlayer oxidation [6]. Systematic changes in the activity of Pd on Au(111) with coverage have been observed for all of these reactions.

In order to understand such effects, geometric and electronic modifications of the thin Pd overlayers have been considered [2–7]. The combination of detailed structure data from surface X-ray diffraction [8] and scanning tunnelling microscopy (STM) [1,9–11] with theoretical studies like DFT calculations [12–14] made a substantial contribution to the interpretation of electrochemical data. Especially the first and the second Pd monolayer on Au(111), which have been shown to be pseudomorphic with the substrate [8], reveal an altered electrochemical behaviour as compared to massive Pd(111) [3].

Most electrochemical studies of the initial stages of Pd deposition onto Au(*hkl*), including those mentioned above, have been performed with chloride solutions [1,9–11,15,16], since noble metals are commonly deposited from their stable chlorine compounds. However, anion effects play an important role for Pd deposition and for the electrochemical behaviour of the Pd overlayers [3]. While Pd is alloying with Au(111) under ultrahigh vacuum conditions at room temperature [17], there has been no indication of alloy formation upon electrochemical Pd deposition in the presence of chloride [10]. It has been assumed that the adsorption of PdCl₄]^{2–} plays an important role for the monolayer growth of Pd [9].

In this publication, we show that the presence of $[PdCl_4]^{2-}$ is not mandatory for the two-dimensional growth of Pd on Au(111), i.e., Pd monolayers can also be obtained from

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halide-free sulphate solutions. The initial stages of Pd deposition onto Au(111) have been studied by cyclic voltammetry (CV) and in situ STM. Ordered anion structures, nucleation and growth of Pd and the morphology of the resulting deposit are discussed. The findings are compared with Pd deposition from chloride solution and the effect of anion adsorption is reassessed.

2. Experimental

The STM measurements were performed with a PicoSPM (Molecular Imaging Corporation), a Nanoscope E (Digital Instruments) and a Topometrix Discoverer 2010. All images were recorded in the feedback mode at constant currents of usually $I_T = 2 \text{ nA}$. Pt/Ir and W tips were prepared by electrochemical etching of 0.25 mm wires in a lamella of 3.4 M NaCN and 2 M NaOH, respectively. The tips were coated with electrophoretic paint in order to minimize the Faraday current at the tip electrode. Pt wires were used as counter and quasi-reference electrodes ($E_{Pt} = +0.55 \pm 0.05 \text{ V}$ versus SCE) for the STM. A saturated calomel electrode (SCE) served as reference for *CV* experiments in a standard electrochemical cell, and in the following, all potentials are quoted with respect to SCE.

The electrolyte was prepared from H_2SO_4 (Merck suprapur), PdSO₄·2H₂O (99.95% Alfa Aesar), and high-quality Milli-Q water (18.2 M Ω cm and <2 ppb total organic carbon).

The Au single crystal electrodes (MaTecK Jülich, Germany) had surfaces oriented to better than 1° and were polished down to 0.03 μ m. Disks with a diameter of 12 mm were used for STM, while the crystals used for *CV* were 4 mm in diameter. However, for some experiments, the 4 mm crystals were transferred to the STM cell after Pd deposition and *CV* characterisation in a conventional electrochemical glass cell. The electrodes were flame-annealed prior to each measurement either in a hydrogen flame (STM) or with a Bunsen burner (*CV*), in order to obtain clean and structurally welldefined surfaces. After each measurement, the electrodes were anodically polarised in 0.1 M H₂SO₄ for 20 s and then immersed in 1 M HCl to remove residues of palladium.

3. Results and discussion

3.1. Electrochemical measurements

Fig. 1 shows a current–potential curve (solid line) for Au(111) in 0.1 M $H_2SO_4 + 0.1$ mM PdSO₄ and the well-known cyclic voltammogram (dashed line) for the same electrode in Pd²⁺-free 0.1 M H_2SO_4 for comparison, both at 10 mV/s. After immersing the electrode into the deposition solution at 0.7 V, where the surface reconstruction is known to be lifted [18], the potential was scanned in positive direction until 0.8 V. Obviously, in this potential region, the electrochemical behaviour of Au(111) is not influenced by the



Fig. 1. Current–potential curves for Au(111) in 0.1 M H_2SO_4 with (solid line) and without (dashed line) 0.1 mM PdSO₄. Scan rate: 10 mV/s. The measured equilibrium potential for Pd/Pd²⁺ in that solution is indicated as vertical line at 0.53 V.

presence of Pd^{2+} ions. This is indicated by the characteristic current spike, which originates from a phase transition within the sulphate adlayer [19]. At potentials positive of the spike, the well-known ($\sqrt{3} \times \sqrt{7}$)*R*19.1° structure of adsorbed sulphate can be clearly seen by STM (see below, Fig. 5a) like in Pd^{2+} -free solution [20,21]. It should be noted that the absence of chloride in solution is verified by the stability of this ordered sulphate adlayer. Otherwise, the current spike in the voltammogram would be decreased, because sulphate would be replaced by the more strongly adsorbing chloride [22].

In the negative-going sweep, Pd deposition commences below 0.7 V, where the ordered sulphate structure on Au(111) is no longer stable (Fig. 1). The deposition current decreases after having reached a maximum at 0.54 V. In order to obtain certain Pd coverage, the potential scan was stopped at 0.31 V, until the charge had reached the desired value. Other reactions like hydrogen adsorption and absorption are avoided this way.

The equilibrium potential for Pd/Pd^{2+} in 0.1 M H₂SO₄ + 0.1 mM PdSO₄ was measured with a flame-annealed Pd wire to be 0.53 V (indicated by the vertical line in Fig. 1). Since Pd deposition on Au(111) starts at potentials more positive than 0.53 V, lowering the scan rate should yield separate peaks for underpotential deposition (upd) and bulk deposition. It is known already that Pd deposition on Au(111) from chloride solutions starts in the underpotential region [10].

Fig. 2 shows a current–potential curve (dotted line) for Au(111) in 0.1 M H₂SO₄ + 0.1 mM PdSO₄ at 0.1 mV/s. At this very low scan rate, two well-defined deposition peaks are observed, one being in the upd regime. The charge density for the latter amounts to 410 μ C cm⁻², corresponding almost perfectly to the deposition charge of a full pseudo-morphic Pd monolayer on Au(111) (1 ML = 445 μ C cm⁻²). The change of the pzc in the course of deposition (from 0.24 V for bare Au(111) [23] to -0.09 V for the complete Pd monolayer [7]) and further adsorption of sulphate may contribute about 10 μ C cm⁻² to the small deviation from the theoretical charge density for net deposition. In addition, the Pd monolayer may not be complete at 0.53 V due to the very slow deposition kinetics. As will be shown below with in situ



Fig. 2. Current–potential curves, starting at +0.7 V, for a high-quality Au(111) electrode (dotted line) and a Au(111) with a 3° miscut (solid line) in 0.1 M H₂SO₄ + 0.1 mM PdSO₄. Scan rate: 0.1 mV/s.

STM, Pd deposition on top of the Au islands covering about 5% of the surface, only occurs in the overpotential region.

The formation of a second Pd monolayer equivalent takes place in the overpotential deposition region at 0.45 V, overlapping with further bulk deposition (Fig. 2). This peak has only been observed for Au(111) crystals of high-quality, i.e., it could not be resolved for surfaces with high defect density (Fig. 2, solid line, for Au(111) with 3° miscut). However, the deposition of Pd on stepped Au(111) surfaces yielded an additional upd peak located at 0.58 V (Fig. 2, solid line), which for the high-quality electrode surface is already discernable as small shoulder. This peak can be attributed to Pd deposition at surface defects like monoatomic high steps; whereas the upd peak at 0.56 V corresponds to Pd deposition onto flat terraces. Such a behaviour is often found for upd of metals, e.g., for Pd upd on Au(111) from chloride solutions [10] or Cu upd on Au(111) [10,24]. Thus it is concluded that Pd preferentially nucleates at step sites and that two Pd monolayers on Au(111) have a remarkable stability, resulting in two pronounced deposition peaks as seen in Fig. 2. These findings are confirmed by the STM measurements described in the following.

3.2. In situ STM measurements

3.2.1. Pd deposition

A series of 10 STM images for Pd deposition onto Au(111) from 0.1 M $H_2SO_4 + 0.1$ mM PdSO₄ is shown in Fig. 3. The freshly prepared, reconstructed Au(111) surface was brought in contact with the solution at 0.6 V. The spontaneous lifting of the thermally induced reconstruction leaves a surface with monatomic high gold islands [18,25]. The small holes seen in Fig. 3a, probably originating from partial surface oxidation during cell assembly, do not significantly influence the Pd deposition process.

After lowering the potential, electrodeposition of Pd is seen to start at the monoatomic high steps including the rims of the relatively round Au islands (Fig. 3b). Starting from these surface imperfections, Pd progressively grows in equilateral triangular islands reflecting the symmetry of the substrate, and gradually covers the whole Au surface with a uniform monolayer, except for the Au islands (Fig. 3c–e).

The Pd monolayer appears slightly higher than the monoatomic high Au islands, which was also observed in STM experiments for Pd deposition from chloride solution, where $[PdCl_4]^{2-}$ is adsorbed on Au(111) [10]. As will be shown below, Pd is covered by an ordered sulphate adlayer at this potential, whereas the Pd-free Au(111) is not. This may contribute to the height variation seen in the STM images.

The small Au islands in Fig. 3a are not covered with Pd at 0.52 V (Fig. 3e). Only after stepping the potential to 0.45 V, Pd is deposited onto these islands and the first monolayer is going to be complete (Fig. 3f). The resulting surface reproduces nicely the topography of the Au(111) substrate, including the small Au islands. This behaviour is similar to Pd deposition in the presence of chloride [10] and it clearly demonstrates that the overpotential for Pd nucleation is markedly higher on terraces than at steps.

After waiting some minutes at 0.45 V, a second Pd monolayer starts to grow, but in a different way (Fig. 3g). Small Pd islands are formed, the shape of which is relatively round. These islands gradually merge and form an almost complete second Pd monolayer (Fig. 3h), which still reproduces the substrate morphology like the first layer. A threedimensional growth is observed after a potential step to 0.4 V (Fig. 3i and j).

Compared to deposition from chloride solution [10], the shape of the Pd islands is different during growth of the first two monolayers from sulphate solution. While in the former case a round shape is observed for submonolayers of Pd [10], a triangular shape is seen here (Fig. 3c and d). The situation is opposite for the formation of the second Pd monolayer. Hence, it is concluded that the adsorbed anions, either $[PdCl_4]^{2-}$ or sulphate, have an opposite influence on the diffusion of Pd atoms on a Au and on a Pd surface. For example, the mobility of Pd atoms seems higher for Pd on Au with adsorbed sulphate, but higher for Pd on Pd with adsorbed $[PdCl_4]^{2-}$.

Experiments have been performed, where Pd was deposited in a conventional electrochemical cell from 0.1 M $H_2SO_4 + 0.1 \text{ mM PdSO}_4$, and the electrode was subsequently transferred to the STM cell, filled with Pd²⁺-free sulphuric acid solution. The observed morphology of the first and second monolayer is very much the same as that in Fig. 3. However, there is evidence that Pd forms tremendously huge deposits at stepped sites for higher coverage. This is seen in Fig. 4, where an equivalent of four Pd monolayers had been deposited at 0.4 V from 0.1 M H₂SO₄+0.1 mM PdSO₄. While the second monolayer is widely uncovered, large Pd particles are formed at step bunching sites with a maximum height of 4 nm corresponding to almost 20 Pd layers. This means that the electrochemical behaviour of the second (pseudomorphic) monolayer might still be predominant for high Pd coverages, where bulk properties are expected.

250 nm x 250 nm



E_{SCE} = 0.38 V

Fig. 3. Sequence of STM images, showing the initial stages of Pd deposition onto Au(111) in 0.1 M H₂SO₄ + 0.1 mM PdSO₄, 250 nm × 250 nm. Deposition potential and deposition time are given in the images. Tip potential $E_{tip} = 0.35$ V.

3.2.2. Sulphate adsorption on Pd overlayers on Au(111)

For Pd deposition from chloride-containing electrolytes, the $[PdCl_4]^{2-}$ anion is adsorbed in ordered structures over a



Fig. 4. STM image (570 nm × 570 nm) of Au(111), obtained at 0.25 V in 0.1 M H₂SO₄, after deposition of four monolayer equivalents of Pd at 0.4 V from $0.1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ mM PdSO}_4$.

wide potential range, both on the Au(111) surface and on the Pd layers [9,10]. It is known that sulphate forms an ordered structure on Au(111) only at potentials positive of the current spike (Fig. 1) at 0.8 V. Since this $(\sqrt{3} \times \sqrt{7})R19.1^{\circ}$ structure is also formed on a Pd(111) surface [26], we searched for this structure on the pseudomorphic Pd monolayers on Au(111) as well. Fig. 5 shows the STM images of sulphate on the bare Au(111) surface, the first (b and c) and the second (d) Pd layer at 0.85, 0.45 and 0.38 V, respectively. The noticeable different appearance of the structure in the images (a) and (b), for example, arises from the fact that the bias voltage was changed because the tip potential was kept constant at 0.35 V. The unit cells for the structures shown in Fig. 5 are rotated by 60° , since the position of the substrate was not changed. Only rather small domains of the $(\sqrt{3} \times \sqrt{7})R19.1^{\circ}$ structure could be found on the Pd layers by STM.

High-resolution STM images of the Pd overlayers, which would allow a direct determination of the Pd-Pd distances



Fig. 5. High-resolution STM images of the $(\sqrt{3} \times \sqrt{7})R19.1^{\circ}$ structure of adsorbed sulphate on Au(111) (a), and on the first (b and c) and the second (d) Pd monolayer on Au(111) in 0.1 M H₂SO₄ + 0.1 mM PdSO₄. Tip potential $E_{tip} = 0.35$ V.

in the monolayers, and hence, provide direct support for the pseudomorphism with the Au(111) substrate, were possible only at negative potentials – where sulphate is desorbed – for measurements with Pd^{2+} -free electrolytes (Fig. 6). In this case, atomic resolution of the second monolayer was obtained after Pd deposition in a separate electrochemical cell and transfer to the STM cell filled with 0.1 M H₂SO₄. Albeit some drift, the atomic distances in the STM image of Fig. 6 are in agreement with a pseudomorphic overlayer.

Unfortunately, it was not possible to obtain atomic resolution of the Pd surface at more positive potentials due to the high stability of the ordered sulphate structure, which instead was easily imaged. For a safe assignment of any adlayer structure by STM, an internal standard for distance and angle calibration is mandatory. Such standards can be provided by the substrate or any known commensurate adlayer structure. Being aware that diffraction techniques are much better suited than STM to determine exact distances, we did evaluate the high-resolution images of the sulphate structures on Au(111) (like the one in Fig. 5a) and on the Pd monolayers for several experiments. Since the structures of sulphate on Au(111) and on the Pd monolayers were measured to be isomorphic within a precision of 3%, we have strong support that the second Pd monolayer on Au(111) is also pseudomorphic.

For a chloride-containing solution, it had been inferred from a Moiré pattern on the fifth Pd layer on Au(111) that up to four Pd layers can grow pseudomorphically [10]. Contrarily, the characteristic voltammetric peak for hydrogen adsorption on bulk Pd, which emerges after deposition of two or more Pd layers from sulphate solution, suggests that only two monolayers grow pseudomorphically on Au(111) [3]. However, the absence of a strict layer-by-layer growth for large Pd areas, hampers the electrochemical characterization of multilayers. Therefore, only the first and second Pd monolayer can serve as ideal model systems. It remains a challenge to

8.5 nm x 8.5 nm



E_{SCE} = -0.09 V

Fig. 6. High-resolution STM image ($8.5 \text{ nm} \times 8.5 \text{ nm}$) of the second Pd monolayer on Au(111) in 0.1 M H₂SO₄ at -0.09 V after deposition of an equivalent of about three Pd monolayers.

prepare a well-ordered Pd bulk phase on Au(111) with large terraces.

3.3. Electrochemical behaviour and stability of Pd overlayers on Au(111) in H_2SO_4

Fig. 7 shows typical voltammograms for various Pd monolayer equivalents (ML) deposited from a chloride-free solution onto Au(111) after transfer to 0.1 M H₂SO₄. The electrochemical behaviour of 1 ML Pd on Au(111) is essentially identical to that of a Pd monolayer deposited from chloridecontaining solution [3]. This supports the findings that the Pd monolayers formed in both cases have the same structure, i.e., Pd forms a pseudomorphic monolayer on Au(111). We would like to mention, however, that $[PdCl_4]^{2-}$ may still be adsorbed on the surface after deposition from chloride solution, even after thorough rinsing with water. When the electrode is subsequently immersed into 0.1 M H₂SO₄, a very small amount of Pd (ca. 0.1 ML) can be deposited and traces of chloride will be adsorbed on the surface. Fortunately, chloride can be desorbed completely at potentials negative of -0.2 V.

The various voltammetric peaks in Fig. 7 between +0.1 V and the onset of hydrogen evolution around -0.3 V can be attributed to sulphate adsorption, hydrogen adsorption and hydrogen absorption. The latter reaction starting around -0.2 V on the negative scan is only present for Pd overlayers with a thickness larger than two monolayers, as in the case of Pd deposition from chloride solution, and can be taken as measure of bulk Pd [1]. The peaks at more positive potentials are related to combined hydrogen adsorption/desorption and sulphate desorption/adsorption, as was demonstrated by the socalled CO displacement technique [6,27]. These adsorption peaks are less sharp for Pd on stepped Au(111) surfaces and much broader in perchloric acid solutions [28] and thus are related to sulphate adsorption on (111)-terraces with long range order. It is interesting to note that these adsorption peaks are very similar for two and three monolayer equivalents (ML) of Pd (Fig. 7). While the surface fraction of pseudomorphic Pd (second monolayer) is almost unchanged, there is a significant contribution of hydrogen absorption into bulk Pd for the 3 ML case. This is in good agreement with the STM observations, where a pronounced three-dimensional growth of Pd



Fig. 7. Cyclic voltammograms in the hydrogen adsorption/absorption region for various Pd monolayer equivalents (1-5 ML) on Au(111) in 0.1 M H₂SO₄. Scan rate: 5 mV/s.



Fig. 8. Cyclic voltammograms for Au(111) with one monolayer Pd in 0.1 M H_2SO_4 . Scan rate: 5 mV/s. The changes from first (thick solid line) to second (dotted line), third (dashed line) and fourth oxidation–reduction cycle (thin solid line) reflect the dissolution of Pd.

at stepped sites is observed with deposition of more than two layers. It seems that a huge amount of Pd has to be deposited in order to cover the second monolayer completely.

Compared with deposition from chloride solution, significant differences in the electrochemical behaviour of Pd on Au(111) occur for coverages higher than one monolayer [3]. From the adsorption peaks in the hydrogen region in sulphuric acid solution, the surface fraction of pseudomorphic (anodic peak at -0.005 V) and of bulk Pd (anodic peak at -0.035 mV) can be estimated [3]. Pd deposited from chloride-free solution shows a higher tendency for three-dimensional growth than deposited from chloride-containing solution. Therefore, at comparable coverages the properties of the pseudomorphic Pd layer are more pronounced for deposition from sulphate solutions.

The dissolution kinetics of Pd in chloride-free electrolytes is extremely slow, since Pd forms a rather stable oxide already around 0.7 V. However, repeated oxidation-reduction cycles in 0.1 M H₂SO₄ lead to a gradual dissolution of palladium. This behaviour is illustrated in Fig. 8. After deposition of a Pd monolayer at 0.53 V, the electrode was rinsed with ultrapure water and transferred to another electrochemical cell filled with 0.1 M H₂SO₄ only, in order to avoid further Pd deposition. At potentials negative of 0.5 V, where no surface oxidation takes place, the cyclic voltammograms are rather stable. A potential excursion up to 0.9 V and subsequent oxide reduction leads to a significant decrease of the voltammetric peaks, both in the hydrogen adsorption region and for the oxide formation peak at 0.73 V in the following cycle. The peaks in the hydrogen adsorption region can be taken as a measure for the Pd coverage. Accordingly, Pd is slowly dissolving in the course of oxidation-reduction cycles. An additional peak is emerging at 0.6 V, which is related to oxide formation at defects created by the cycling routine. Note that surface oxidation on massive Pd(111) is very sensitive to defects, the latter being preferentially oxidized [6]. After four oxidation-reduction cycles, the Pd coverage has dropped from 1 ML to about 0.2 ML. On the average about a third of the Pd deposit is dissolved per cycle. Characteristic peaks

for Au(111) emerge in the 4th cycle, such as the sulphate adsorption peak and the current spike around 0.2 and 0.8 V, respectively. There was no indication of alloying under the present experimental conditions.

4. Summary

It has been shown that Pd forms two pseudomorphic monolayers on Au(111) upon electrochemical deposition from $0.1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ mM PdSO}_4$. The first monolayer is formed in the underpotential region, whereby Pd nucleates preferentially at step sites. Dissolution of Pd is kinetically hindered in sulphuric acid solutions. A distinctly different electrochemical behaviour is observed for the first and second pseudomorphic monolayer on the one hand, and bulk deposit formed at higher coverage on the other hand. A pronounced three-dimensional growth of Pd is observed on top of the second monolayer. Therefore, the electrochemical behaviour of the second, pseudomorphic Pd monolayer is still visible up to relatively large bulk deposits. The deposition process is accompanied by the adsorption of sulphate which forms a stable $(\sqrt{3} \times \sqrt{7})R19.1^{\circ}$ structure on the pseudomorphic Pd terraces in the potential region between hydrogen adsorption and surface oxidation. Anion adsorption has a strong impact on Pd deposition kinetics as well as on exact island shape.

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