



# Electrochemical behaviour of pseudomorphic overlayers: Pd on Au(1 1 1)

L.A. Kibler, A.M. El-Aziz<sup>1</sup>, D.M. Kolb\*

*Department of Electrochemistry, University of Ulm, 89069 Ulm, Germany*

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## Abstract

The electrochemical properties of palladium adlayers on Au(1 1 1) are compared with those of massive Pd(1 1 1). Electrodeposited Pd forms a pseudomorphic overlayer on the unreconstructed Au(1 1 1) surface following the stacking sequence of the substrate. The altered electrochemical behaviour of the overlayer can be ascribed to changes in the electronic structure due to lateral strain. A gradual change to bulk properties is observed with increasing Pd coverage. Besides hydrogen adsorption, sulphate adsorption and surface oxidation, formic acid oxidation was chosen as a test reaction. The influence of lateral strain on the reaction kinetics of formic acid oxidation is discussed.

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## 1. Introduction

Foreign metal overlayers on well-ordered substrates have been the subject of numerous studies in surface science [1] and electrochemistry [2]. Such systems are of interest for catalytic and electrocatalytic reactions because their physical and chemical properties do not necessarily resemble those of the pure components. A recent theoretical study using density functional calculations presented trends in the electronic structure of pseudomorphic monolayers on various substrates in correlation with their reactivity [3]. A pseudomorphic overlayer adapts to the interatomic distance of the substrate, and thus, the adatoms have a “wrong” lattice constant compared to the bulk material (Fig. 1).

As a consequence, the d-band position which is a crucial parameter for the adsorption behaviour may be changed [3]. Ruban et al. for example, have reported a d-band upward shift of approximately 0.35 eV for a pseudomorphic Pd monolayer on Au(1 1 1) [3]. Such laterally strained surfaces are believed to allow for a fine-tuning of catalytic properties. The idea of studying the role of pseudomorphy of overlayers in the electrochemical behaviour has been raised before [4].

The electrochemical deposition of palladium onto gold single crystals has been studied in detail by various groups [5–9]. Pd, the lattice constant of which is about 4.8% smaller than that of Au, grows epitaxially on Au surfaces and forms flat, well-ordered overlayers. While alloy formation takes place for Pd deposition on Au(1 0 0) and Au(1 1 0) [7,8], pure overlayers with very large terraces can be obtained for electrochemically deposited Pd on Au(1 1 1). It has been concluded from scanning tunnelling microscopy (STM) measurements that Pd grows pseudomorphically on

\* Corresponding author. Fax: +49-731-50-25409.

E-mail address: [dieter.kolb@chemie.uni-ulm.de](mailto:dieter.kolb@chemie.uni-ulm.de) (D.M. Kolb).

<sup>1</sup> Present address: National Research Center, Dokki, Cairo, Egypt.

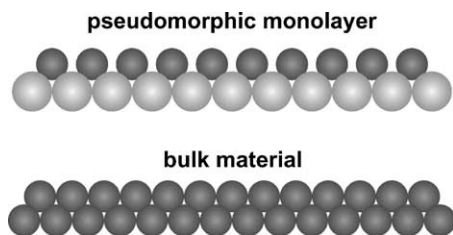


Fig. 1. Models of a pseudomorphic monolayer on a foreign metal substrate of larger lattice constant and of the corresponding bulk metal surface.

Au(1 1 1) up to about four monolayers (ML) [6]. For higher coverages, the electrochemical behaviour approaches that of massive Pd(1 1 1) [4,5]. However, the average terrace width of such films is clearly diminished as compared with 1 or 2 ML thick films [6].

Differences in the reactivity of thin Pd overlayers and that of bulk Pd towards formic acid oxidation have been explained by pseudomorphic growth [4]. Later on, it was shown by surface X-ray scattering that Pd on Au(1 1 1) has indeed the geometric structure of the substrate for at least two monolayers [10,11].

Recently, the electrocatalytic properties of thin Pd overlayers on Au(*hkl*) have been investigated for oxygen reduction [12] as well as the oxidation of formic acid [4], methanol [13], formaldehyde [14] and adsorbed CO [15]. A marked dependence of these reactions on the crystallographic orientation of the substrate and on the Pd film thickness was found. The main question still concerns the origin of this dependence.

Electrochemical measurements with massive Pd single crystals had been rather scarce due to the lack of appropriate surface preparation methods that do not require an ultra-high-vacuum equipment. Some groups had used an electrochemical etching procedure [4,16], which certainly is not ideal because of the formation of etch pits and the strong adsorption of anions that might influence subsequent experiments. A few flame-annealing cycles may work for small Pd electrodes [17–19], but larger crystals inevitably are roughened. We have obtained our best results by inductive heating and cooling Pd single crystals in an inert gas atmosphere [15,20]. Thus, the electrochemical properties of Pd(1 1 1) can be measured and compared with those of thin Pd films deposited onto Au(1 1 1) or other substrates.

In this communication, hydrogen adsorption, oxide formation and formic acid oxidation for Pd overlayers on Au(1 1 1) are compared with the respective reactions on massive Pd(1 1 1) electrodes. This should yield information about the influence of different adlayer geometries on the reaction kinetics. A qualitative correlation of experimental data and theoretical predictions is attempted.

## 2. Experimental

The Au(1 1 1) and Pd(1 1 1) electrodes were single-crystal cylinders (MaTecK, Jülich), 4 mm in diameter and 4 mm long, with a wire of the same material attached to its rear for better handling. Before each experiment, the electrodes were annealed either by inductive heating in an argon atmosphere (Pd) or by flame-annealing (Au), cooled down to room temperature for 1 min in a stream of argon (Pd) or in air (Au), and protected against contamination from air with a water droplet. The electrode was then brought in contact with the electrolyte under potential control.

The Pd overlayers on Au(1 1 1) were obtained by electrodeposition from either 0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.1 mM PdCl<sub>2</sub> + 0.2 mM HCl or 0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.1 mM PdSO<sub>4</sub> at +0.4 V versus SCE, the film thickness being controlled by the charge flow through the interface (1 ML = ca. 440 μC/cm<sup>2</sup>). The Pd-covered Au(1 1 1) electrode was carefully rinsed with Milli-Q water and transferred to a second cell which contained 0.1 M H<sub>2</sub>SO<sub>4</sub> only. For studying the electrocatalytic activity of the Pd surfaces, formic acid was added to the latter solution.

The solutions were made of H<sub>2</sub>SO<sub>4</sub>, HCl (Merck, suprapur), PdCl<sub>2</sub> (Merck, for synthesis) and Milli-Q water (18.2 MΩ cm and <2 ppb TOC). All potentials were measured and are quoted with respect to the saturated calomel electrode (SCE).

## 3. Results and discussion

### 3.1. Pd(1 1 1)

A cyclic voltammogram for Pd(1 1 1) in 0.1 M H<sub>2</sub>SO<sub>4</sub> is shown in Fig. 2. The curve represents the electrochemical behaviour of a freshly-prepared

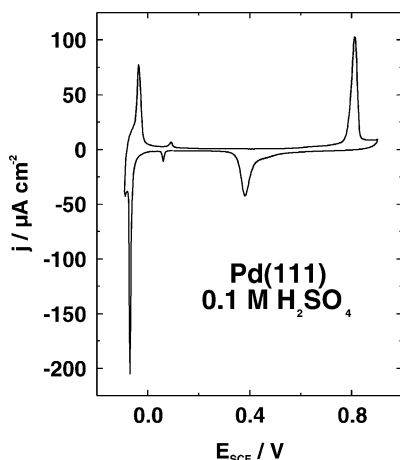


Fig. 2. Current–potential curve for a freshly-prepared well-ordered Pd(1 1 1) electrode in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Scan rate: 10 mV/s. First cycle after immersion at 0.1 V.

electrode after inductive heating in an argon atmosphere, immersion at 0.1 V and starting the potential scan in negative direction. While the voltammogram in Fig. 2 is in good agreement with voltammograms reported recently by other groups [17–19], we prefer heating our rather large electrodes in the absence of oxygen to the conventional flame-annealing and quenching method. The small peaks around 0.075 V arise from a phase transition within the adsorbed sulphate layer [17], which has been observed for many other surfaces with hexagonal structure. Sulphate is desorbed at  $-0.07$  V accompanied by hydrogen adsorption leading to a sharp spike that points towards large well-ordered terraces and that is absent in per-

chlorate solutions [18]. The peak for hydrogen desorption/sulphate adsorption at  $-0.03$  V is slightly broader than the corresponding cathodic peak. In contrast to the thin Pd overlayers on Au(1 1 1) (see further), hydrogen absorption into the bulk hampers the study of H adsorption due to the high Faraday current [5].

A peak for oxide formation on Pd(1 1 1) is observed at 0.81 V, while oxide reduction occurs at 0.38 V. The charges for oxide formation and reduction, 450 and 360  $\mu\text{C cm}^{-2}$ , respectively, have a marked imbalance, pointing towards concomitant dissolution of Pd at positive potentials. These reactions bring about structural changes [21], which alter the subsequent current–potential curves. Therefore, surface oxidation is either completely avoided or restricted to a single cycle into the oxide region.

### 3.2. Pd/Au(1 1 1)

Cyclic voltammograms for Pd adlayers of 1, 2 and 3 ML thickness on Au(1 1 1) in 0.1 M H<sub>2</sub>SO<sub>4</sub>, deposited from chloride-containing solution are shown in Fig. 3, which reveal systematic changes with increasing coverage. For comparison, the voltammogram of Pd(1 1 1) in sulphuric acid is shown again as dotted line in each frame. With the first Pd monolayer, there are no more characteristic peaks of the Au(1 1 1) surface discernible in Fig. 3a. Thus, the complete covering of the substrate as seen by STM [5,6] is reflected also in the cyclic current–potential curves. The features in the hydrogen adsorption range have already been described elsewhere [5]. Briefly, the hydrogen absorption reaction, which proceeds at higher

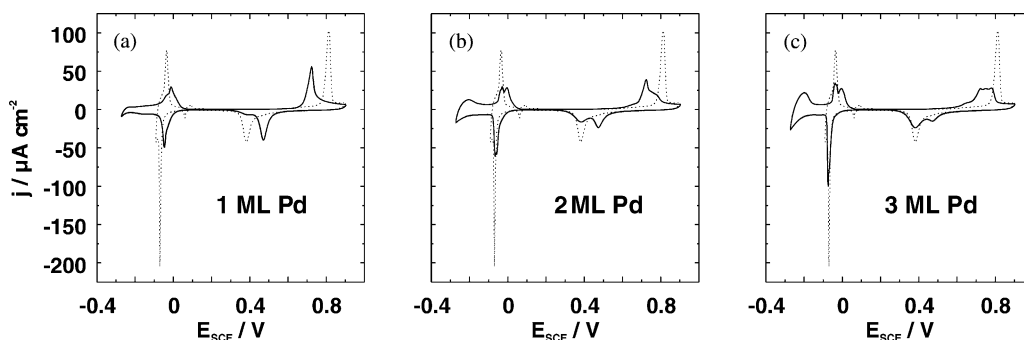


Fig. 3. Current–potential curves for (a) 1, (b) 2 and (c) 3 ML thick Pd overlayers on Au(1 1 1) in 0.1 M H<sub>2</sub>SO<sub>4</sub> after deposition from chloride-containing solution. Scan rate: 10 mV/s. The curve for massive Pd(1 1 1) is shown as dotted line for comparison.

overpotentials as compared to massive palladium, becomes more pronounced with increasing film thickness. The sulphate desorption/hydrogen adsorption peak for the pseudomorphic Pd monolayer is located at a potential slightly more positive than that of massive Pd(1 1 1). The corresponding anodic peak is also shifted positively by about 30 mV. The total voltammetric charge of this peak is composed of ca.  $145 \mu\text{C cm}^{-2}$  for adsorption of hydrogen and ca.  $72 \mu\text{C cm}^{-2}$  for adsorption of (bi)sulphate, as derived from CO charge displacement experiments at  $-0.2$  and  $+0.1$  V, respectively [15]. These charge values are somewhat higher for the thicker Pd films. Starting from 2 ML Pd on Au(1 1 1), there are two anodic peaks in the hydrogen adsorption range, one at  $-0.005$  V like for the first Pd monolayer, the other one at  $-0.035$  V corresponding to hydrogen desorption/(bi)sulphate adsorption on massive Pd(1 1 1). For even thicker Pd deposits, only the latter peak is left [5], reflecting the behaviour of bulk palladium. This systematic change in the hydrogen desorption peak goes along with the gradual structural transition from a pseudomorphic Pd monolayer with lateral strain to thicker Pd films with bulk properties (and higher surface defect density [6]) as also suggested by SXS measurements [10,11]. For intermediate Pd coverages, the two peaks point towards the presence of both bulk and laterally strained palladium. It is interesting to note, that a similar difference of 30 mV has been found for the potentials of zero charge (pzc) for massive Pd(1 1 1) ( $E_{\text{pzc}} = -0.12$  V) and the pseudomorphic Pd monolayer on Au(1 1 1) ( $E_{\text{pzc}} = -0.09$  V) in NaF solutions [22].

The curves in Fig. 3 are stable up to 0.6 V during repetitive potential cycling. Surface oxidation (or OH

adsorption) of the pseudomorphic Pd monolayer is seen to occur at a potential which is about 100 mV more negative than that for the same process on massive Pd(1 1 1). This can be explained by the ability of the pseudomorphic surface to form stronger chemical bonds with adsorbed species, i.e. the adsorption energy of OH is increased for the strained surface [3]. The surface oxidation peak of the Pd adlayer decreases for 2 and 3 monolayers (Fig. 3b–c), while a shoulder at more positive potentials is developed. We know from our STM data [6] that the density of monoatomic high steps increases at the same time, the surface oxidation starting already at about 0.6 V. Hence, the voltammogram for a thick Pd deposit on Au(1 1 1) is no longer identical to the one for a well-prepared massive Pd(1 1 1).

Finally, also the potential for oxide reduction shows characteristic differences for a pseudomorphic monolayer and bulk palladium. In essence, surface oxidation and reduction appear to be less irreversible for the pseudomorphic layer than for the bulk.

Deposition of Pd onto Au(1 1 1) from 0.1 M  $\text{H}_2\text{SO}_4 + 0.1$  mM  $\text{PdSO}_4$  at 0.4 V and characterisation in 0.1 M  $\text{H}_2\text{SO}_4$  (Fig. 4) leads to similar, albeit not identical voltammograms as in Fig. 3. However, the following observations are noteworthy: (i) For the first Pd monolayer on Au(1 1 1) virtually identical current–potential curves are found. We assume that the Pd structure is pseudomorphic in both cases. (ii) Hydrogen absorption into the Pd film seems to be more suppressed after deposition from chloride-free solution. (iii) The sulphate desorption/hydrogen adsorption peak is sharper for the Pd multilayers in Fig. 4. (iv) Examination of the hydrogen desorption/

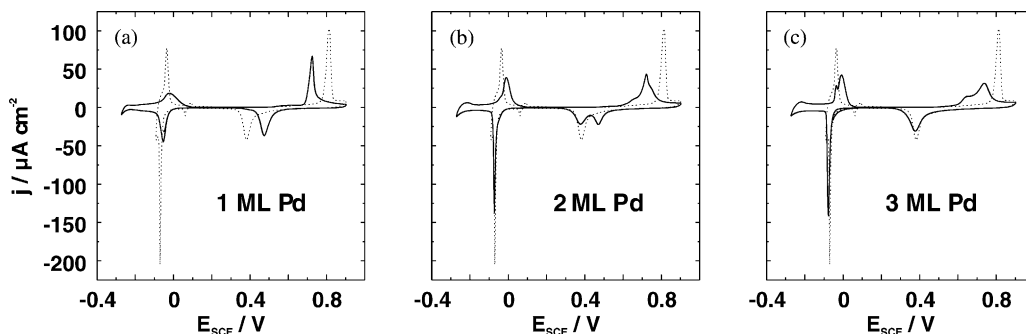


Fig. 4. Current–potential curves for (a) 1, (b) 2 and (c) 3 ML thick Pd overlayers on Au(1 1 1) in 0.1 M  $\text{H}_2\text{SO}_4$  after deposition from chloride-free solution. Scan rate: 10 mV/s. The curve for massive Pd(1 1 1) is shown as dotted line for comparison.

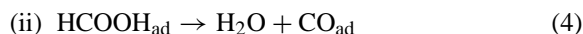
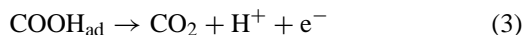
sulphate adsorption peaks suggests, according to the interpretation given above, that the pseudomorphic surface structure is still predominant for 3 ML Pd after deposition from chloride-free solution.

Because the cyclic voltammograms for the pseudomorphic Pd overlayers and for massive Pd(1 1 1) show characteristic differences, it seems obvious to use these for a more quantitative assessment of the surface structure. Characteristic features of the pseudomorphic surface are seen in the hydrogen desorption/(bi)sulphate adsorption region and in the oxide formation and reduction region. The latter, however, does not lend itself for a quantitative evaluation of the pseudomorphic surface fraction, because oxide formation causes irreversible changes, e.g. by Pd dissolution. Hence, the two oxide reduction peaks around 0.4 V are no longer reliable indicators for the composition of the surface structure. The features due to the hydrogen desorption on the other hand, are very reproducible and the area under the peak at  $-0.005$  V may be taken as direct measure of pseudomorphic Pd(1 1 1), whereas that under the  $-0.035$  V peak should be indicative of bulk Pd (Fig. 5). While up to 2 ML the growth is pseudomorphic, a quantitative evaluation yields about 90 and 50% pseudomorphic structure for 3 and 5 ML for deposition from sulphate solution. Earlier studies for a 10 ML film have revealed only the  $-0.035$  V peak corresponding

to bulk Pd [5]. For reasons not yet fully understood, the percentage of pseudomorphic structure is clearly smaller for overlayers deposited from chloride solution, although our STM studies revealed a very similar growth mode for both cases, the only marked difference being a higher deposition rate and a higher surface mobility for the chloride-containing electrolyte.

### 3.3. Formic acid oxidation

The effect of pseudomorphic growth is of special interest for electrocatalytic reactions, because changes in adsorbate binding energies could have significant consequences on the reaction kinetics. Formic acid oxidation has been studied in detail with platinum electrodes [23]. In essence, a dual-path mechanism first proposed by Capon and Parsons [24] is accepted for this reaction, involving (i) direct oxidation to carbon dioxide via a reactive intermediate (presumably  $\text{COOH}_{\text{ad}}$ ), and (ii) formation of strongly bound and thus poisonous carbon monoxide:



Palladium electrodes are rather selective in favour of the first pathway, the direct oxidation, because Pd surfaces highly resist poisoning by CO [4]. Thus, the curves in Fig. 6, showing cyclic voltammograms for HCOOH oxidation on Pd(1 1 1) and on the Pd films on Au(1 1 1) deposited from chloride solution, are very stable for many potential cycles. In contrast to earlier experiments [4], surface oxidation and subsequent structural perturbations were avoided in this study.

In general, the oxidation curves reveal a pronounced current maximum at potentials of apparent maximum activity. The current maxima for a pseudomorphic Pd monolayer on Au(1 1 1) and for the massive Pd(1 1 1) electrode are located at 0.15 and 0.04 V, respectively (Fig. 6). Like for hydrogen adsorption (see above), there is a systematic change towards the behaviour of the massive metal with increasing coverage of Pd on Au(1 1 1), the curve for 5 ML having two current peaks for oxidation on strained and unstrained parts of the Pd surface.

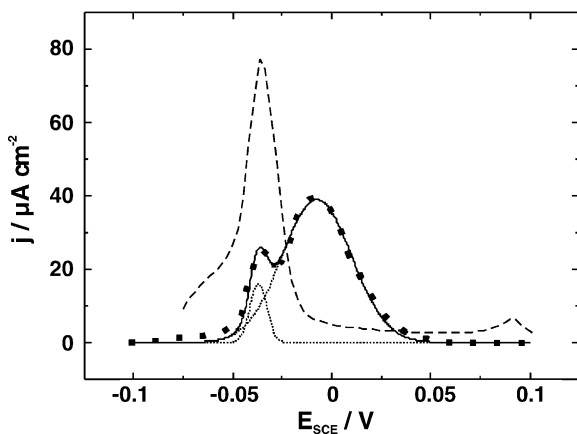


Fig. 5. Deconvolution of the hydrogen desorption/(bi)sulphate adsorption peak for 3 ML Pd on Au(1 1 1) (solid line, see Fig. 4c), that after baseline correction was fitted by two Gaussian curves, corresponding to the surface fractions of pseudomorphic and bulk structure. The peak for massive Pd(1 1 1) is shown as dashed line for comparison. Superposition of the two Gaussians, (■).

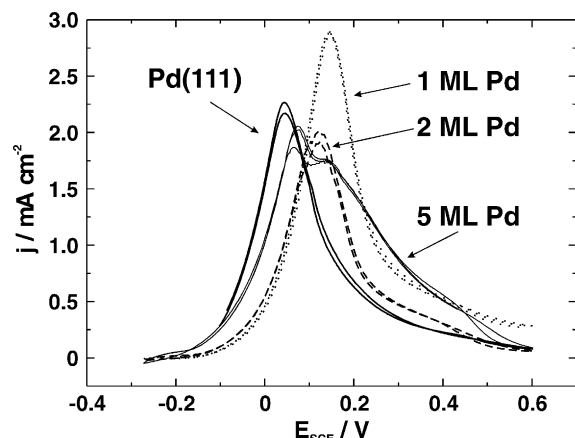


Fig. 6. Cyclic current–potential curves for thin Pd overlayers on Au(111) and for massive Pd(111) in 0.1 M  $\text{H}_2\text{SO}_4$  + 0.2 M  $\text{HCOOH}$ . Scan rate: 20 mV/s.

Since the upward shift of the d-band centre of Pd in the pseudomorphic monolayer on Au(111) [3] results in a higher bond strength for adsorbed species, this should have a direct influence on the rate-determining step. According to Smolin et al., the catalytic dehydrogenation of  $\text{HCOOH}_{\text{ad}}$  (reaction (2)) is the slow step of formic acid oxidation on Pd electrodeposits in sulphuric acid solutions under steady-state conditions [25]. Adsorption of formic acid (1) that involves no charge transfer is relatively fast. Since reaction step (2) is rate-determining, we can argue on the basis of interaction between the relevant adsorbed species,  $\text{HCOOH}_{\text{ad}}$  and  $\text{COOH}_{\text{ad}}$ , and the two types of Pd surface that there should be a clear difference in the electrocatalytic behaviour. In any case, both  $\text{HCOOH}$  and  $\text{COOH}$  will form stronger bonds to pseudomorphically grown Pd on Au(111) than to bulk Pd. Due to the relative change in activity of these two Pd surfaces, which is observed around 0.1 V, we assume the following: At  $E_{\text{SCE}} < 0.1$  V, i.e., around the potentials of zero charge [22], the adsorption energy of formic acid as a neutral molecule determines the rate of reaction (2). Therefore, bulk Pd is more active than pseudomorphic Pd on Au(111) in this potential regime. At  $E_{\text{SCE}} > 0.1$  V, the interaction of  $\text{COOH}_{\text{ad}}$  with the surface becomes more important. This facilitates formic acid oxidation on the laterally strained Pd surface due to a stabilisation of  $\text{COOH}_{\text{ad}}$  that accelerates the rate-determining step (2). The

latter argument could also explain, why the overall current density is decreasing at positive potentials. A strong adsorption of  $\text{COOH}$  on Pd will slow down the rate of reaction (3). Surface oxidation does not play a significant role at  $E_{\text{SCE}} < 0.6$  V. Furthermore, anion effects can be excluded, because electrooxidation of formic acid in perchloric acid shows also a current maximum of similar size in the voltammogram.

#### 4. Conclusions

The electrochemical characterisation of pseudomorphic Pd overlayers on Au(111) as compared with massive Pd(111) provides important information about basic relations between structure and reactivity. The impact of Pd film thickness on the adsorption behaviour and the reactivity can be explained by a change in lateral strain due to pseudomorphic growth that approaches bulk behaviour for thicker layers. Differences in the reaction kinetics for formic acid oxidation can be understood in terms of a modified interaction between the Pd surface and the adsorbed species relevant for the rate-determining step, due to changes in the electronic structure of the metal overlayer.

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