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ORIGINAL PAPER

Hydrogen evolution and Cu UPD at stepped gold single crystals modified with Pd

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Abstract The evolution of hydrogen on Au(332) and Au (665) surfaces modified with Pd was studied by cyclic voltammetry in hydrogen-saturated sulfuric acid. A strong catalytic activity of Pd decorating the steps, and even monoatomic rows, reflected in the exchange current density for the hydrogen evolution reaction, was found. In comparison, the activity of Pd at terrace sites is negligible. This is explained by the previously observed weak adsorption of hydrogen at monoatomic Pd rows according to the Sabatier principle. For Au(665)/Pd electrodes where the Pd steps have been blocked with Cu, the catalytic activity decreases to values in the same order of magnitude of those for Au(665) surfaces modified with more than a full monolayer of Pd. No direct evidence of hydrogen spillover from Pd-covered areas to the Au substrate was found. Cu underpotential deposition measurements also suggest that no alloy formation takes place between the Cu atoms and the underlying Pd film, nor between Pd and the gold substrate.

Keywords Hydrogen evolution reaction · Cu UPD · Gold · Palladium · Stepped single crystals

Introduction

The modification of a substrate electrode by a second metal has recently attained much interest because, in many cases, the resulting catalytic activity exceeds that of either component. This is not only true for surfaces where both elements are exposed to the electrolyte but also in those cases where the substrate is completely covered. The first case is the typical bimetallic surface, for which the increased activity may originate from a bifunctional effect (as for CO oxidation at PtRu [1–3]), a geometric, ensemble effect (typically leading to a decreased activity as for methanol adsorption on PtRu [1]), or an electronic, ligand effect (as for CO oxidation at Sn-modified Pt [2, 4]). In the second case, only an electronic effect is active, either due to a direct modification of the electronic structure of the adlayer or indirectly, due to a shift of the d-band center caused by the lattice mismatch between substrate and adlayer and the resulting stress or strain [5–7]. An example is CO oxidation on Pt-modified Ru(0001) in ultra high vacuum (UHV) [8] and hydrogen adsorption at the same surface in an electrochemical environment [9]. The effect of the metal-hydrogen adsorption strength on the hydrogen evolution reaction (HER) and the corresponding volcano plot has recently been discussed in the context of calculated adsorption enthalpies [10–12]. A further, very interesting model system for the latter case is the catalytic activity of Pd on a variety of substrates for hydrogen adsorption and evolution, which has been systematically studied by Kibler [13–15]. There, an enhancement of the rate of hydrogen evolution of two orders of magnitude was found for Pd monolayers on Au compared to the bare substrates. A large enhancement of the HER was also observed for single Pd nanoparticles on Au electrodes, as determined using the tip of a scanning tunneling microscopy (STM) as a detector electrode for the generated H_2 [16–18]. It was found that the activity increased with decreasing size of the Pd particle [17]. In this context, it was suggested that surface diffusion of adsorbed hydrogen from the Pd particle onto Au (spillover)

Dedicated to Professor Dr. Algirdas Vaskelis on the occasion of his 70th birthday.

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may take place. Another proposed explanation is that the Pd clusters interact less strongly with adsorbates than the corresponding pseudomorphic Pd monolayers on Au [19].

Our interest in the Au/Pd system is twofold: First, the possibility of producing adsorbed hydrogen is intriguing; such adsorbed hydrogen, the existence of which is usually not taken into account, is also formed as an intermediate when hydrogen is formed during oxidation of formaldehyde in alkaline solution on Ib metals [20, 21]. It was also postulated as an intermediate in the course of hydrogen evolution from H^+ using hot electrons [22]. Second, in our continuing approach to model bimetallic surfaces by step decoration of regularly stepped single crystal surfaces, the Au/Pd system offers the advantage that single rows of a d metal on a catalytically less active Ib metal can be generated. It is the opposite of stepped Pt surfaces with steps being decorated by Cu or Ag, which we also examined recently with regard to the adsorption behavior of ethene and benzene [23, 24]. A detailed electrochemical characterization of stepped Au[n(111)×(111)] surfaces modified with Pd is the subject of another paper [25]. The possibility of step decoration with Pd on the Au(332) surface was already demonstrated in [26]. There, we showed that the hydrogen evolution rate is independent of the Pd coverage as long as it is below one monolayer but exceeds the value necessary for complete step decoration. Step decoration was further confirmed in studies on the adsorption of CO, ethene, and benzene at Au(332)/Pd and Au(331)/Pd [26, 27].

In this paper, we present a series of experiments with the aim of studying the catalytic properties of stepped gold surfaces modified with Pd towards hydrogen evolution in acidic media. Underpotential deposition (UPD) of copper, a method that has been used in the past to characterize the structure of thin palladium films deposited on several substrates like Pt(111) [28] and Au(111) [29, 30], was employed to gain information regarding the stability of the Pd layers and the structure-reactivity relationships for the Au [n(111)×(111)]/Pd system. Deactivation of Pd at the steps via Cu deposition is used to demonstrate the influence of these sites on the rate of hydrogen evolution.

Experimental part

The gold single crystals (Metal Crystals and Oxides) used in this work are small disks of 10 mm in diameter and 3- to 4-mm thickness. Before each experiment, the crystals were annealed in the flame of a propane–butane burner for 2 min. Afterwards, they were immediately transferred to the electrochemical cell and cooled for at least 4 min over 0.1 M H_2SO_4 (Merck supra pur) in a reductive atmosphere of Ar/H_2 (2:1 v/v, Air Products) to minimize facetting [26]. After cooling, the quality of the surface was checked by cyclic voltammetry in 0.1 M H_2SO_4, see Fig. 1. The cyclic voltammograms were identical to those obtained after cooling over deaerated Millipore water. Whether these surfaces reconstruct is not clear from literature [31–34]. STM results revealed that facetting could be avoided for Au (332) indeed [25], but often not for Au(665) for which step bunching also was observed [35].

All solutions were prepared using Millipore water (resistivity>18 MΩ cm, total organic carbon (TOC)<3 ppb) from a Millipore-Q system. A reversible hydrogen electrode (RHE) in 0.1 M H_2SO_4 was used as reference for all the voltammetric experiments; the RHE was separated from the cell body by means of a stopcock. The cyclic voltammograms were recorded in a glass cell in the hanging meniscus arrangement using homemade software based on LabVIEW 5.1 (National Instruments). Solutions were deaerated with ultrapure argon (Air Products).

A 0.1-mM solution of $PdSO_4{\cdot}2H_2O$ (Merck) in 0.1 M H_2SO_4 was used for the Pd deposition. The gold electrode was immersed at a potential of 1.16 V, where no Pd deposition takes place, and the potential was cycled slowly (v=1 mV/s) in the cathodic direction until the UPD peak appeared. The charge under the UPD curve was used as a measure of the amount of Pd deposited. Taking a transfer of two electrons per Pd adatom, the equivalent charges for the deposition of a full Pd monolayer are q=492 μC cm^{-2} and q=470 μC cm^{-2} for the Au(332) and Au(665) surfaces, respectively [25]. As correctly noted by a referee, in principle, the change of anionic charge on the electrode surface due to Pd adsorption should be taken into account. However, at the comparatively positive potential of Pd deposition, (bi)sulfate is adsorbed on both metals. Moreover, our experiments in which we determined the Pd coverage by CO adsorption lead to surface coverages of Pd

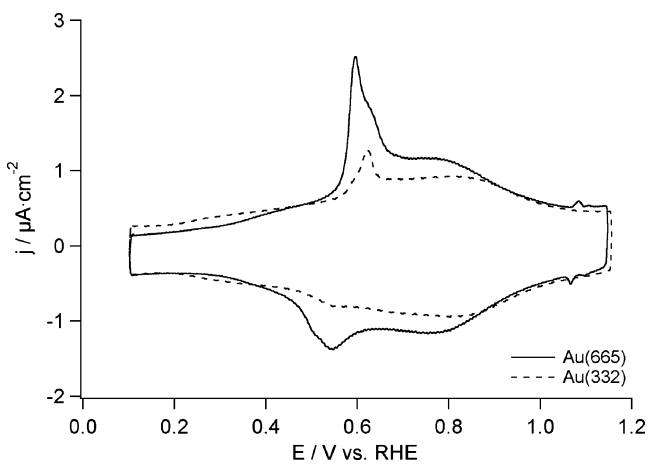

Fig. 1 First voltammetric cycles for clean Au(665) and Au(332) surfaces in 0.1 M H_2SO_4. Scan rate v=10 mV/s, starting potential 0.1 V

completely in agreement with those calculated from the Pd deposition charge. To attain fractional coverages, the potential was stopped at a given value before the UPD peak was complete, breaking immediately the contact with the electrolyte and rinsing the electrode with water. Integration of the peaks was performed with the trapezoidal rule using homemade subroutines written in LabVIEW.

Copper was deposited either in the underpotential or in the bulk deposition regime from solutions of $CuSO_4 \cdot 2H_2O$ (Fluka) with sulfuric acid as supporting electrolyte.

Measurement of the exchange current density for the HER was performed by cycling voltammetry of the electrode in 0.1 M H_2SO_4 saturated with H_2 (Air Products) in a potential range from −50 to +50 mV; by varying the sweep rate, it was checked that diffusion limitation was negligible. First, a controlled amount of Pd was deposited on the gold substrate. The electrode was then quickly rinsed with Millipore water and transferred to another electrochemical cell containing 0.1 M H_2SO_4 saturated with argon. Immersion of the electrode was performed under potential control at 0.5 V. Because the HER proved to be very sensitive to the structure and history of the surface, the voltammograms in the hydrogen adsorption region were used as an internal check before the hydrogen evolution measurements to make sure that the results between different experimental runs were comparable and reproducible. This internal check consisted in cycling the electrode five times between 0.1 and 0.5 V at a scan rate of 5 mV/s in the argon-saturated sulfuric acid solution. The experiment was aborted if the electrodes did not show steady-state voltammograms before five cycles or if the charge, shape, or position of the voltammetric peaks corresponding to hydrogen adsorption was not in agreement with previous measurements [25].

After this step, the potential was stopped at 0.5 V, and the electrolyte was carefully exchanged (keeping potential control) with a 0.1 M H_2SO_4 solution saturated with hydrogen. The potential was then scanned slowly (5 mV/s) in the cathodic direction until the equilibrium potential was reached; afterwards, current-potential curves were recorded at small overpotentials. A stream of hydrogen over the solution kept the electrolyte saturated with this gas and free from atmospheric oxygen.

After every experiment involving Pd deposition, the gold electrode was cleaned by cycling continuously in a solution containing 0.1 M H_2SO_4+0.6 mM HCl at 50 mV/s between 0 and 1.7 V until a steady response was attained, changing the electrolyte several times if necessary. In the presence of chloride, the deposited Pd dissolves completely, leaving a clean gold surface that was annealed before using it again. Between experiments, the gold single crystals are stored in 0.1 M H_2SO_4 to keep them free from contamination. All measurements were made at room temperature.

Results

Cu UPD on Au(665)/Pd and Au(332)/Pd

To get a better understanding of the structure-reactivity relationships for the Au[n(111)×(111)]/Pd system, UPD of copper was performed on Au(665) and Au(332) electrodes modified with different amounts of Pd. Figure 2 shows cyclic voltammograms for the Cu UPD on these electrodes before and after deposition of different amounts of Pd. On the bare Au substrates, Cu UPD is characterized by three cathodic voltammetric peaks A, B, and C at 0.55, 0.51, and 0.35 V, respectively, as already reported for other high-index n(111)×(111) planes of gold with n larger than six atoms [36]. On the other hand, the Pd-modified surfaces show an additional peak D at about 0.48 V. This peak is strongly dependent on the amount of Pd present.

Because Pd can be oxidized and the resulting PdO dissolves slowly in acidic media [25, 37], we decided to

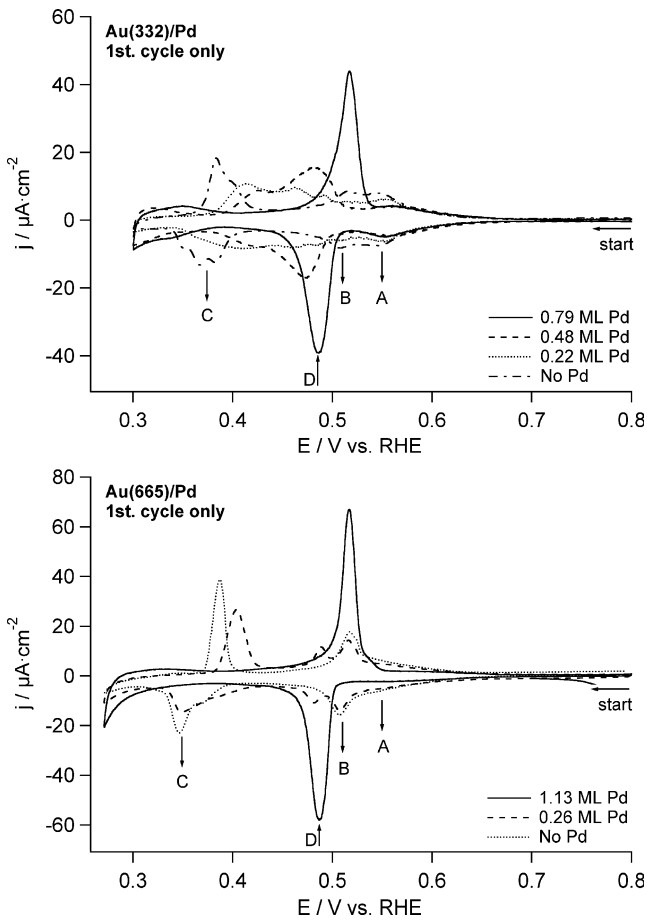

Fig. 2 Voltammograms for Cu UPD on two stepped gold electrodes modified with Pd. Electrolyte, 0.1 M H_2SO_4+1 mM $CuSO_4$. Scan rate, v=5 mV/s. The *arrows* indicate the changes in the peaks with decreasing Pd coverage

study the dissolution behavior of mono- and submonolayers of Pd deposited on stepped Au single crystals in the presence of Cu^{2+} ions. Consecutive cycling of the electrode leads to the changes in the voltammetric profiles shown in Fig. 3. In the first cycle, the electrode is fully covered with Pd, and only the signal for peak D is significant in the Cu UPD region. Incursion to potentials more positive than 0.8 V results into oxygen adsorption and partial dissolution of the Pd layer; in consequence, peaks A, B, and C increase, whereas peak D decreases. Notice that, in the oxide formation region, the contribution from Pd terraces diminishes at a faster pace than the corresponding peak for Pd at the steps, which remains constant for the first two voltammetric cycles. Further cycling of the electrode results in complete dissolution of the Pd adlayer. The cyclic voltammogram after full dissolution of the Pd layer strongly resembles the Cu UPD on an intact, bare gold monocrystalline substrate, as can be seen in Fig. 4 for a Au (665) electrode.

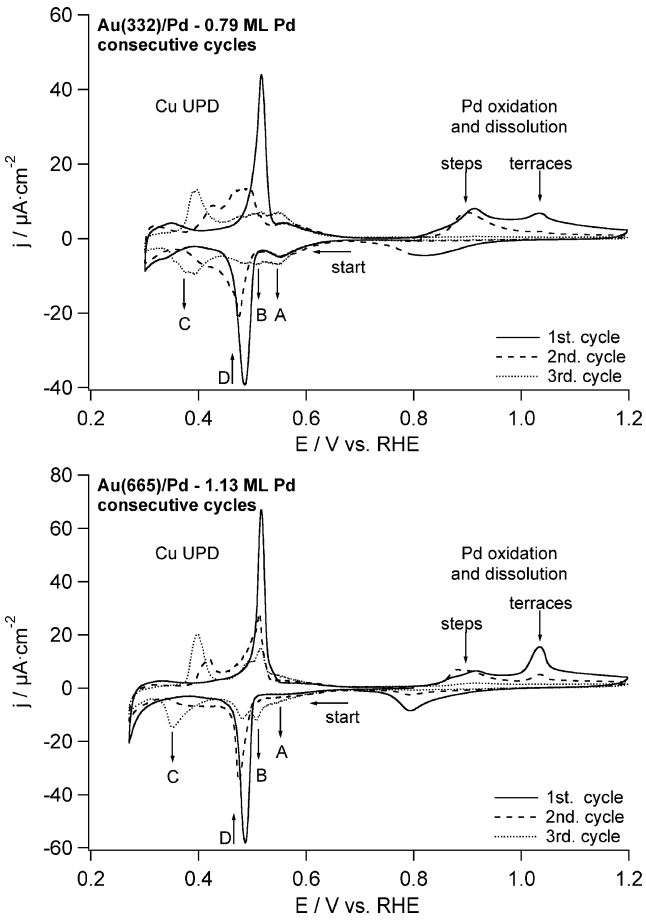

Fig. 3 Consecutive voltammetric cycles (v=5 mV/s) in 0.1 M H_2SO_4 +1 mM $CuSO_4$ for stepped gold electrodes modified with Pd. The *arrows* indicate the evolution of the voltammetric peaks upon cycling. Initial Pd coverage as given in the graphs

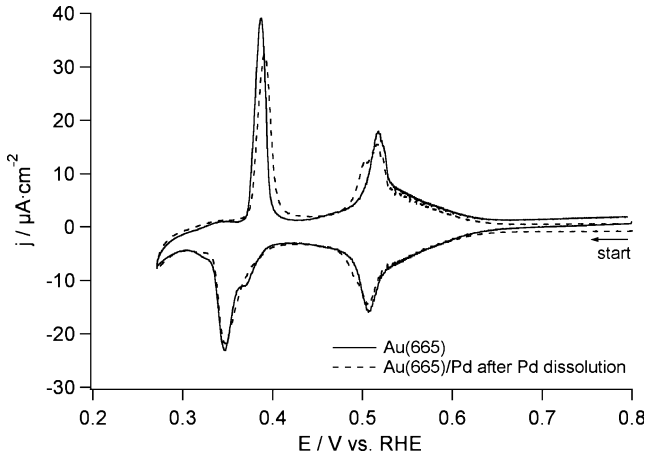

Fig. 4 Comparison of Cu UPD voltammetric cycles on a clean Au (665) surface and on the same electrode after deposition and subsequent dissolution of 1.13 ML of Pd. Electrolyte, 0.1 M H_2SO_4+1 mM $CuSO_4$, scan rate v=5 mV/s

H_2 evolution on Au(332)/Pd

The rate of hydrogen evolution on regularly stepped surfaces of gold modified with Pd was determined by cycling voltammetry using the Au(332) substrate as model surface. Figure 5 shows current-potential curves for the hydrogen evolution on Au(332) for different Pd coverages.

The influence of Pd on the kinetics of hydrogen evolution is evident when comparing the voltammetric curves of the Pd-modified surfaces and the corresponding for the bare substrate. The cyclic voltammograms for those surfaces modified with submonolayers of Pd are essentially independent of the Pd coverage, as indicated by the overlapping of the six voltammetric curves corresponding to Pd amounts between 0.29 and 0.80 ML. Deposition of more than one monolayer of Pd leads to a dramatic decrease in the catalytic activity of the electrode.

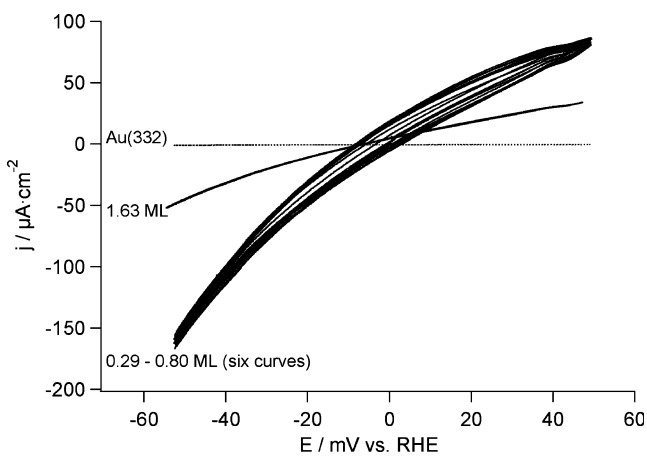

Fig. 5 Current-potential curves for the HER on Au(332)/Pd in 0.1 M H_2SO_4 saturated with H_2 as a function of Pd coverage. Scan rate v=1 mV/s

The trends mentioned above are visualized in a quantitative way in Fig. 6, which shows the exchange current density values for the HER on Au(332)/Pd calculated from the slope of the voltammetric curves near to the equilibrium potential. For the bare substrate, the exchange current density is extremely low (0.12 μA cm^{-2}). Between 0.29 and 0.80 ML of Pd, the exchange current density (referred to the geometric area of the electrode) is nearly constant and around 55 μA cm^{-2}. It decreases then until reaching a value of about 20 μA cm^{-2} for Pd coverages larger than a monolayer. Experiments recorded at different scan rates (v= 1, 5, 25, and 50 mV/s) lead to similar qualitative and quantitative conclusions (cf. [26]).

Also shown in Fig. 6 are data (open symbols) obtained after frequently using the single crystal electrode in a differential electrochemical mass spectrometry cell, where the gold electrode was unintentionally exposed to some mechanical stress. After such a—albeit slight—mechanical damage, the current density values for the HER increase dramatically, especially for small Pd coverages. No change was visible in cyclic voltammetry though, neither in the supporting electrolyte nor in Cu^{2+}-containing solution, signifying that the overall change in surface structure was small, at least the average number of steps did not change.

Influence of Cu on the kinetics of H_2 evolution

In an attempt to elucidate the mechanism of hydrogen evolution on Pd-modified stepped gold surfaces, we decided to block (deactivate) the Pd step sites with Cu, which itself has a low catalytic activity towards hydrogen evolution. The Au(665)/Pd electrode was prepared in the usual way, and current-potential curves were measured in

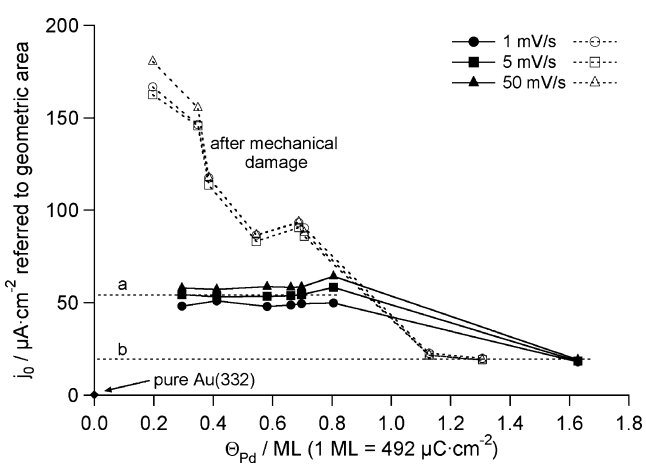

Fig. 6 Exchange current density for the HER on Au(332)/Pd as a function of Pd coverage. The *dashed straight lines* represent the limiting cases observed when a submonolayer (**a**) and more than one monolayer (**b**) of Pd is deposited. *Open symbols* are data points obtained after accidental mechanical damage to the crystal (*all lines* serve as a guide to the eye only)

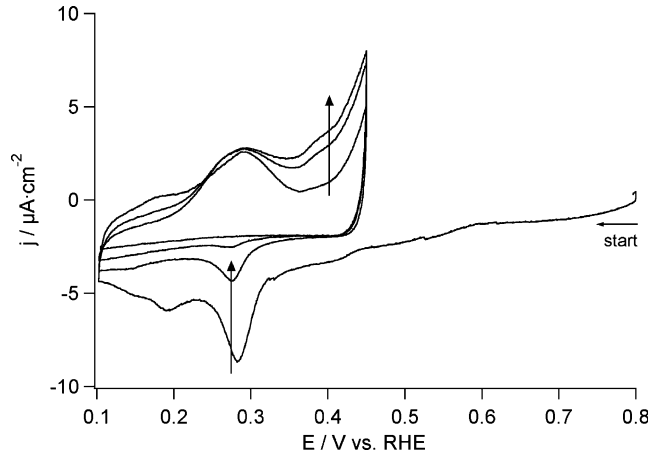

Fig. 7 Deposition of Cu from 10^{-5} M $CuSO_4$+0.1 M H_2SO_4 on Au (665) modified with 1.03 ML of Pd. The *arrows* indicate the changes in the voltammogram. Scan rate v=5 mV/s

0.1 M H_2SO_4 saturated with H_2; afterwards, the electrode was transferred to another cell, and Cu was deposited from a solution containing 10^{-5} M $CuSO_4$+0.1 M H_2SO_4 as shown in Fig. 7. The starting potential of 0.8 V is positive enough to avoid Cu deposition at immersion, but negative enough to preserve the integrity of the Pd layer.

At this low concentration, it is possible to deposit very small amounts of Cu on the electrode in a controlled way. Due to diffusion limitations, no Cu deposition peaks are evident in the UPD region (compare with Fig. 2). Therefore, suppression of the hydrogen adsorption peak at about 0.28 V was used to monitor the deposition of Cu on the electrode. After four cathodic runs, suppression of the hydrogen adsorption peak was complete. The potential was then stopped at 0.1 V, and the electrolyte was exhaustively exchanged under potential control with a solution of 0.1 M H_2SO_4 to avoid further deposition of Cu. Before the measurement of the new current-potential curves for the HER, the potential was scanned slowly (5 mV/s) to 0 V, stopped there, and H_2 was bubbled through the solution for 6 min to reach saturation; the current-voltage curves were measured right afterwards. Finally, to study the effect of Cu coverage on the electrode, partial dissolution of pre-deposited Cu was achieved by increasing the potential from the equilibrium value (in the H_2-saturated solution) up to 0.45 V and back, changing the electrolyte immediately afterwards, bubbling with H_2, and measuring the current-potential curves again as described before.

Figure 8 shows the corresponding current-voltage curves. After Cu deposition, the activity of the Au(665)/Pd surface towards hydrogen evolution decreases dramatically. The exchange current density for hydrogen evolution on the Cu-covered electrode (between 1 and 5 μA cm^{-2}) is only slightly higher than that for the bare Au(665) substrate (0.12 μA cm^{-2}). This trend can be partially reverted after dissolution of some of the Cu; however, even after four

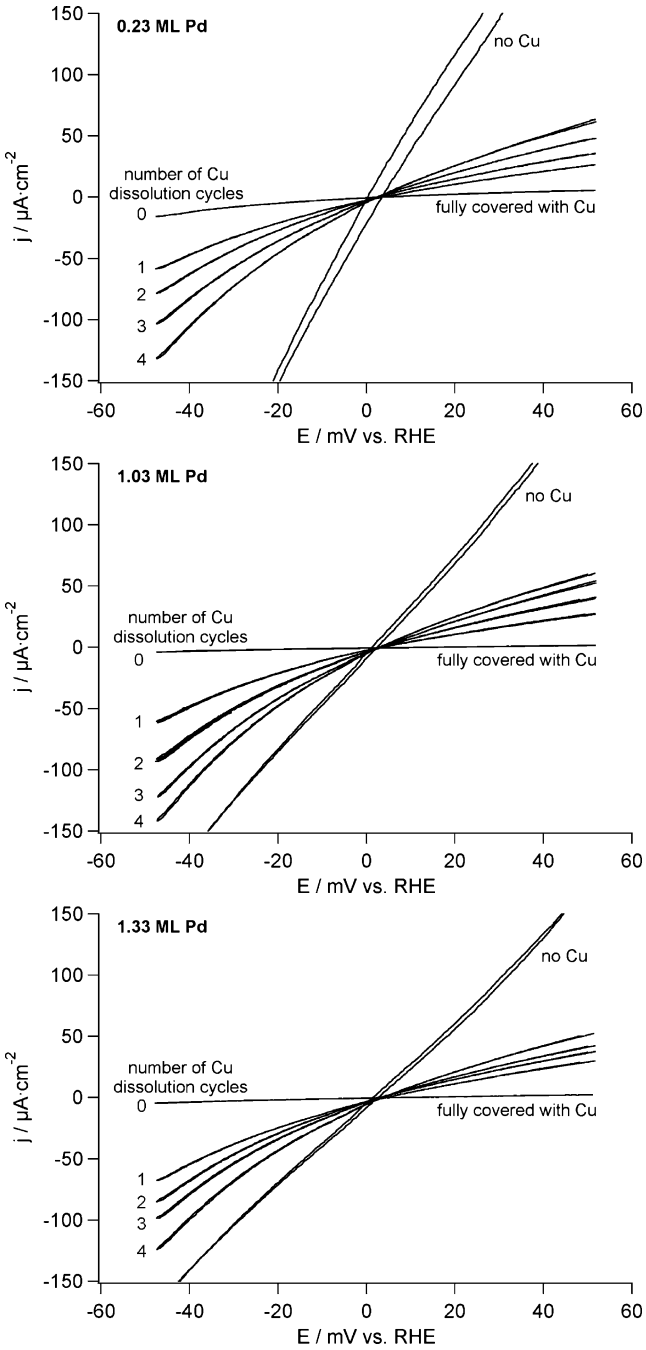

Fig. 8 Effect of the presence of Cu on the HER at Au(665) modified with different amounts of Pd. Electrolyte, 0.1 M H_2SO_4 saturated with H_2. Scan rate v=5 mV/s

dissolution cycles, the activity of the surface turns out to be much lower (j_0=45 μA cm^{-2}) than in the absence of Cu. The hydrogen evolution rate was larger than on Au(332)—between 80 μA cm^{-2} when more than 1 ML is deposited and 155 μA cm^{-2} when only the steps are decorated with Pd—probably because of irregularities like step bunching etc. No influence of the scan rate was observed when repeating the experiment at 1 and 50 mV/s.

Discussion

Cu UPD on stepped gold surfaces

Investigation of the voltammetric peaks for Cu UPD on the stepped surfaces and comparison with Au(111) reveal that the peak at 0.51 V is due to the formation of the so-called honeycomb $(\sqrt{3}\times\sqrt{3})R30°$ structure on the (111)-oriented terraces (with a Cu coverage at two thirds and bisulfate coverage at one third), whereas the voltammetric feature at about 0.35 V can be ascribed to a phase transition between this honeycomb structure and a (1×1) Cu adlayer [36, 38–41]. Both of these peaks are affected in shape and height even by such small amounts of Pd as 0.26 ML, suggesting that an energetic influence on the honeycomb structure on the terraces is relatively extended.

In contrast to the Cu UPD on Au(111) and Pt(111) from sulfate solutions, which show at least two distinctive voltammetric peaks, Cu UPD on Pd(111) is characterized by a single voltammetric feature [40, 42]. The voltammetric peak at 0.48 V appears only in the presence of Pd. Its shape and position are very similar to the Cu UPD peak observed on well-ordered Pd(111) electrodes [42–44] and on pseudomorphic Pd films deposited on Au(111) [29, 30]. For this reason, it is safe to assign this peak to the UPD of copper on (111)-oriented Pd terraces. For a Pd coverage of 0.26 ML on Au(665), corresponding to the deposition of practically three rows of Pd atoms at the steps, threefold hollow sites formed by adjacent Pd atoms with (111) geometry are responsible for the small voltammetric feature seen in Fig. 2 at 0.48 V. Although there are characteristic peaks for the Cu UPD on Pd terraces and on the gold substrate, it was not possible to clearly separate the voltammetric contribution corresponding to the deposition of Cu at the Pd decorating the steps, although for the lowest Pd coverage, the broad feature in the cathodic sweep may originate from Cu deposition at such sites. Similar conclusions can be drawn from the experiments with the Au(332) single crystal.

Regarding the dissolution of the Pd adlayer, the anodic peaks located at potentials more positive than 0.8 V correspond to the oxygen adsorption on the Pd at the steps (0.9 V) and terraces (1.05 V), followed by slow dissolution of the PdO. This behavior is independent of the presence of copper in solution and has been reported by us in the past for the Au(332)/Pd system [25, 26]. The Pd deposited on the steps dissolves last, showing a higher stability in comparison to the Pd covering the terraces. The changes in the voltammetric peak at 0.51 V are in agreement with the picture that Pd is dissolving and diffusing slowly away from the surface, leaving bare gold terraces that can be covered by Cu in the UPD region. The fact that the voltammetric profile is not affected after complete dissolution of the Pd layer, as well as the evidence that it is

possible to cycle Au(665)/Pd and Au(332)/Pd electrodes several times in the Cu UPD region and obtain steady-state cyclic voltammetries (CV's), suggests that surface alloying (neither between Cu and Pd nor between Pd and Au) is not an important issue on the Au[n(111)×(111)]/Pd/Cu system. This behavior is similar as that reported for Cu on Pd(111), where up to 10 ML of bulk Cu can be deposited without affecting the structure of the underlying Pd(111) substrate [42]. In electrochemical environment, no alloy formation was observed after the deposition of Pd films on Au(111) from solutions containing chloride [45].

Hydrogen evolution

A higher catalytic activity of UPD Pd as compared to that of bulk Pd has already been found by Kibler et al. [14, 45] and has been explained by the shift of the d-band center. For Pd nanoparticles on Au(111), Stimming and coworkers [16, 17] have found that the exchange current for the HER is enhanced by several orders of magnitude as the diameter of the Pd particles decreases. This was interpreted by the spillover of hydrogen atoms from Pd to the uncovered Au surface, where formation of H_2 may take place more efficiently.

The independence of the reaction rate on the Pd amount for coverages below one monolayer may be explained by a particular activity of Pd step sites, the number of which is independent of the Pd coverage as long as the amount of Pd exceeds that necessary for complete step decoration. In this scenario, the Pd steps control the overall reaction rate, and the contribution from the Pd-covered terraces is negligible. On the other hand, an alternative explanation can be stated in terms of the importance of the boundary between the Pd layer and the uncovered Au terrace. In this model, hydrogen spillover from the Pd-covered areas to the Au substrate would limit the overall rate.

The decrease of the catalytic activity after completion of the first monolayer probably has to be explained by an electronic effect. However, a change of the morphology also has to be considered. STM images during deposition of Pd on Au(332) [26] show that the deposition of a second monolayer results in a facetted surface; terraces become broader, but they are not continuous in step direction. Although this seems to be in contrast to the overpotential deposition of Pd on Au(111), which occurs in a layer-by-layer growth mode for at least two Pd layers, this only results from the fact that 111 sites are more stable [29, 30, 45–48]. The decreased activity even at a Pd coverage of 1.1 renders this interpretation improbable. Rather, a direct contact between Pd and Au surface sites is a prerequisite for the high catalytic activity. In a recent paper, Kibler modeled his results on the hydrogen evolution at Au(111) covered by submonolayers of Pd by assuming a current density of about 100 μA cm^{-2} for the Pd atoms at the perimeter of the Pd islands [15]. If the current density at our (virgin) Pd-modified Au(332) is solely due to Pd at step sites, this corresponds to a current density of roughly 275 μA cm^{-2} (one fifth of the surface atoms are step atoms). If we assume that both 1D boundaries to either sides are important for the increased hydrogen evolution rate (e.g., because spillover of adsorbed H to either side, i.e., ‘step down’ and to the Au terrace at the same height is possible), we expect a value for the current density twice as large as that for the Pd atoms at the perimeter of the Au islands, which roughly is the case.

We have recently observed that, at potentials accessible in cyclic voltammetry, hydrogen adsorption at monoatomic rows does not occur [25]. Such a weak adsorption of hydrogen at the rows may also be the reason for the enhanced reactivity of such sites: According to the Sabatier principle, the intermediate must not be too strongly adsorbed at the surface—adsorption at terrace sites might be too strong (desorption of the product too slow), whereas at the rows, it is optimal. Of course, from sites where hydrogen is only very weakly adsorbed, it may also more easily spill over to Au sites, where adsorption is very weak as well.

Regarding the exchange current density values for the HER on Pd/Au(332) before and after unintentional introduction of defects to the substrate (Fig. 6), it is evident that, for Pd amounts larger than a full monolayer, a similar value for the current density is reached in both cases. However, the situation is different for lower Pd coverages, where the exchange current density values after some mechanical damage are much higher and show a larger dispersion than in the previous experiments. STM images of this gold single crystal surface showed that mechanical stress gave rise to the formation of numerous surface defects, especially kinks and dislocations, which are known to act as sites of high reactivity. Under these conditions, deposition of single Pd atoms at kinks or defects is likely to occur. This could contribute to the greatest deviations observed at low Pd coverages.

Our finding that hydrogen adsorption does not occur at monoatomic chains [25] means that the minimum size of an ensemble at Pd atoms for hydrogen adsorption is (at least) three atoms, i.e., hydrogen adsorbs in threefold hollow sites. In an earlier paper [49], it had been concluded that the smallest Pd ensemble, for which hydrogen adsorption on a Au/Pd(111) surface occurs, consists of two Pd atoms; we had explained this discrepancy to our result by an obvious underestimation of the anion contribution to the charge [25].

The increase in the exchange current density at low Pd coverages suggests that such a critical ensemble of Pd atoms does not exist for hydrogen evolution. If one

disregards the possibility of hydrogen adsorption on Au, this also means that hydrogen evolution has to follow the Volmer–Heyrovski mechanism (formation of adsorbed hydrogen out of protons, subsequent reaction of an adsorbed hydrogen with a proton to H_2), as the Tafel reaction (recombination of two adsorbed hydrogen) would not be possible.

Kinetics of H_2 evolution in the presence of Cu

We used the suppression of the hydrogen adsorption peak at about 0.28 V to monitor the deposition of Cu on the electrode. The presence of this peak in the first cycle is indeed an internal check that the Pd layer has not suffered any significant contamination or damage from the previous transfers. During the Cu deposition procedure, an anodic shoulder emerges near to the upper potential limit (0.45 V; Fig. 7) due to the dissolution of some of the Cu deposited in the previous cathodic cycle.

As expected, deposition of Cu has a poisoning effect on the catalytic activity of the electrode for the HER. Even after four dissolution cycles, the exchange current density turns out to be much lower than in the absence of Cu. Interestingly, the amount of Pd deposited on the Au(665) electrode does not seem to influence this behavior, see Fig. 9.

For (at least) the first four Cu dissolution cycles, there is a linear relationship between the exchange current density and the cycle number. On the other side, no significant difference in the exchange current density was observed between the fully covered and the decorated surface. These facts suggest that (a) Cu is dissolving from the terraces first, leaving the Pd on terraces exposed but still blocking the Pd step edges, and (b) the HER is controlled mainly by the presence of these steps.

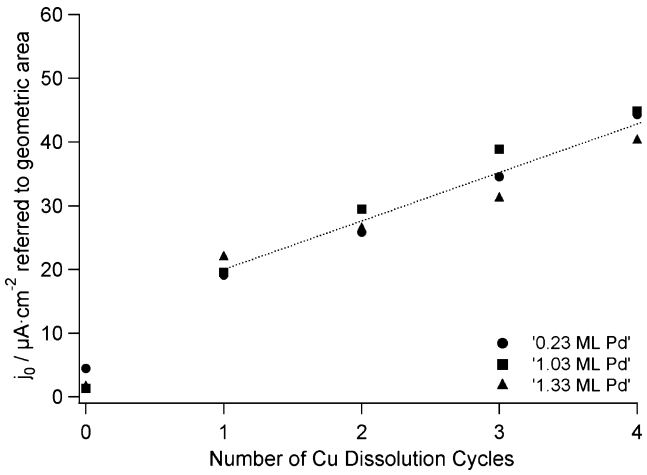

Fig. 9 Effect of copper depletion on the exchange current density for the HER at a Au(665)/Pd electrode modified with Cu

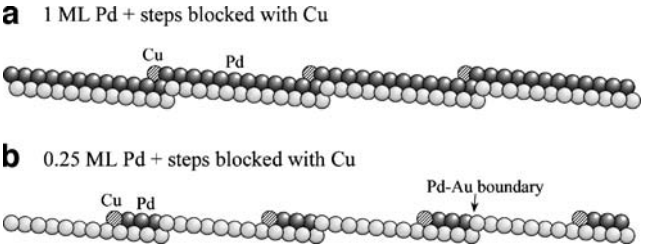

Fig. 10 Hard ball models of a Au(665)/Pd electrode where the Pd step sites have been blocked by Cu. **a** Modified with 1 ML of Pd. **b** Modified with 0.25 ML of Pd

Figure 10 shows hard ball models of the Au(665)/Pd surface after blocking the steps with Cu. If hydrogen spillover from the Pd-covered areas to the Au substrate was the rate-limiting step, the activity for hydrogen evolution at the surface (a) should be much lower than at the surface (b) because only in the latter case there is a free Pd–Au boundary where spillover could take place. On the other hand, if the overall reaction rate is controlled by the Pd step sites, the effect of the Pd-covered terraces is negligible, and both surfaces should exhibit similar reaction rates towards hydrogen evolution—before and after blocking the steps with copper. Our experimental results seem to support this hypothesis. It is also possible that—if hydrogen spillover takes place—such a spillover occurs onto the Cu surface. Such adsorbed hydrogen is formed as an intermediate during formaldehyde oxidation in alkaline solution on all Ib metals [20, 50, 51].

In the case of Au(665) surfaces modified with more than a monolayer of Pd, the exchange current densities for the HER before (80 μA cm^{-2}) and after blocking the steps with Cu (45 μA cm^{-2}) are similar but not identical. This fact also supports the hypothesis that the activity decrease of the surface after completion of the first Pd monolayer is not simply due to the loss of the Pd–Au boundary, but at the same time, it reveals that the picture is more complicated than assumed in our model. Thus, the influence of other effects not considered here cannot be excluded.

Conclusions

In the case of Pd decorating steps of a well-defined Au (332) surface, the rate of hydrogen evolution and oxidation is independent of the coverage with Pd as long as it is below one monolayer, suggesting (1) that the reaction mainly occurs at step sites and (2) that Au atoms in contact with Pd are necessary. Therefore, the kinetics of hydrogen evolution on stepped gold surfaces modified with Pd is controlled by the Pd at the steps; the influence of Pd on terraces is negligible. Cu UPD on Au(665) and Au(332) surfaces modified with Pd shows characteristic peaks due to the deposition of Cu on Pd terraces with (111) structure and

on the gold substrate. No separate voltammetric peak was observed for the Cu deposition at Pd decorating the steps. Hydrogen evolution on such surfaces is largely diminished. Regarding alloy formation, no evidence of alloying between Cu and Pd or between Pd and the substrate was found.

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