

Deposition of platinum monolayers on gold

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Abstract Deposition of small amount of Pt is reported onto polycrystalline Au from H_2PtCl_6 -containing solutions. Spontaneous deposition, yielding about 5% of a full-packed monolayer, has been found at the steady-state open circuit potential. Formation of a somewhat more dense, but still a partial monolayer could be observed at potentials between the steady-state open circuit potential and that of the onset of bulk deposition. A specific difference of monolayer and bulk deposition is that Pt surface area levels off with time and keeps increasing for the former and latter types of deposition, respectively. Pt monolayers with quite high coverages can be formed in a rather narrow, 20–30 mV potential region only. The surface areas of Pt and of the Pt-free Au have been simultaneously measured as cyclic voltammetry peak charges. From these measurements, the site requirement of the Pt atoms was determined to be around four; that is, each Pt atom blocks the oxidation of about four underlying/neighbouring Au atoms, implying their distant positions. Based on the results, Au surfaces coated with monoatomic Pt layers of quite high coverages can be prepared.

Keywords Spontaneous Pt deposition · Platinum · Gold · Monolayer · Adsorption · Underpotential deposition

Introduction

In recent years, considerable efforts have been made to understand initial stages of Pt deposition onto other noble metals and to elaborate methods for obtaining surfaces covered with very thin (preferably monoatomic) Pt layers [1–22]. In these studies, Pt was deposited

- electrochemically on Au [1–4] and on Ru [5];
- spontaneously onto various metal surfaces (on single crystalline [23–25] and polycrystalline Au [26], on carbon-supported Au nanoparticles [27] and on Ru [5, 9, 22, 28]);
- by redox replacement of underpotentially deposited (UPD) Cu monolayer on Au and Pd [6–20] as well as of overpotentially deposited Ni on Au [21].

Furthermore, the adsorption of $[\text{PtCl}_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$ complexes on Au(111) surface was studied by in situ scanning tunnelling microscopy [23, 29].

It was also recognised that on Au substrates, the Pt layers were formed electrochemically or by a spontaneous surface reaction or by a combination of these. The first method, direct electrochemical deposition of Pt on Au(111) yields incomplete monolayers and the deposit was found not to be perfectly two-dimensional [1]. Pt deposition, in general, needs a rather high overpotential [2]. The second method, i.e. spontaneous deposition: dipping Au into $[\text{PtCl}_6]^{2-}$ containing solutions, then taking it out, rinsing and reducing electrochemically in a platinum-free solution also yields partial monolayers of Pt on Au [24–27]. The third method, the redox replacement of UPD metal monolayers by Pt [6–21], involves two steps: an electro-

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chemical reduction step followed by a chemical reaction; by this procedure, coverages as high as of a monolayer can be attained.

As a continuation of our earlier works on deposition of noble metals onto foreign noble metal surfaces [30–33], the subject of the present study is the analysis of the conditions and characteristics of spontaneous and electrochemical deposition of a small amount of Pt onto Au. The main difference of our work and of the above ones is that we always measure both the Pt and Au fractional areas rather than Pt area alone. In this way, we demonstrate that in a fairly narrow potential range, near-monolayer Pt can be deposited on polycrystalline Au.

Experimental

Deposition of Pt was carried out onto Au wire of 99.99% purity and of 1 mm diameter (the electrode surface area, actually 0.4 cm², plays no role in the present context; therefore, the current is given without normalization to area). Prior to the experiments, the Au wire was etched by aqua regia, then thoroughly rinsed with triply distilled water.

The experiments were performed at room temperature, in two identical, three-compartment electrochemical cells. One of these was used for platinum deposition; the cyclic voltammograms (CVs) in 0.5 M H₂SO₄ solution were taken in the other. Solutions were deoxygenated by Ar of 99.9995% purity within the cells; exchange or mixing of solutions could be done with the exclusion of air. A hydrogen electrode was used as a reference; all the potentials are given on the reversible hydrogen electrode (RHE) scale. A platinum sheet was used as counter electrode.

The platinizing solution contained 0.2 mM H₂PtCl₆ + 1 mM HCl in 0.5 M H₂SO₄. It was freshly prepared before depositions by the addition of H₂PtCl₆ to the 0.5 M H₂SO₄ supporting electrolyte from a stock solution (H₂PtCl₆ × 6 H₂O in HCl).

The acids were Merck p.a. grade chemicals; the H₂PtCl₆ × 6 H₂O was an Aldrich ACS reagent. For preparing solutions, triply distilled water was used.

Spontaneous deposition of platinum

Experiments

In preliminary experiments, the steady-state open circuit potential (OCP) of the Au in the platinizing solution was found to be 950 mV: if the potential of the Au in deoxygenated 0.5 M H₂SO₄ was set to any value in the 50

to 700 mV range, followed by the disconnecting of the potentiostat and adding the Pt compound in the cell to yield the platinizing solution of composition specified in the **Experimental** section, then, the potential of the Au electrode rose to and stabilized at ≈950 mV in 10–15 min.

In order to start the spontaneous deposition experiments with a reproducible state of the surface, instead of directly dipping Au in the platinizing solution, it was immersed in deoxygenated 0.5 M H₂SO₄ thereafter its potential set to 950 mV. After a while, the same procedure was performed as above: the potentiostat was disconnected, and H₂PtCl₆ was added yielding the platinizing solution within the cell. This procedure ensured that no additional Pt⁴⁺ ions were reduced due to the initially not-defined charge state of the Au electrode (its consequences are discussed later). After the initial potential excursions, the OCP value was resumed and stabilized (Fig. 1, inset).

The electrode was removed after a certain platinization time from the platinizing solution, rinsed with water and entered in the other cell, and CVs were taken in 0.5 M H₂SO₄. (In these experiments, despite of the thorough rinsing, some chloride might always have remained on the surface, somewhat altering the first cycles of the voltammograms; therefore, in this report, always the third cycle is presented.) The CV of Au before and after the 90-min platinization is shown in Fig. 1. Due to platinization, the CV changes in two ways: (1) the peaks characteristic to Au decrease, the reduction peak at 1,200 mV shrinks by about 20% indicating a 20% decrease of apparent Au surface area; (2) the humps appear wherever on Pt voltammograms used to do

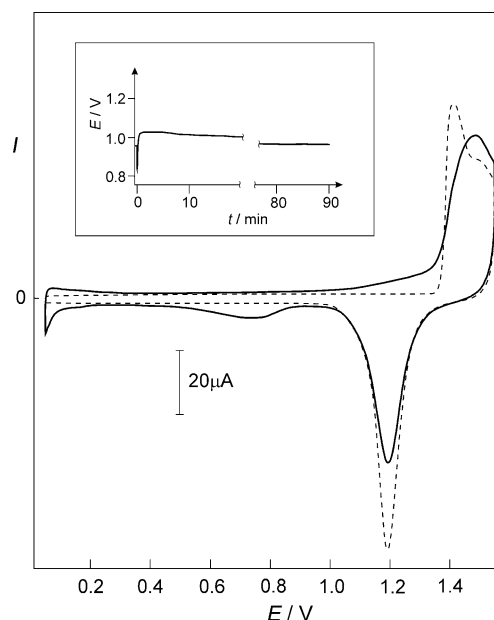


Fig. 1 CVs (50 mV/s in 0.5 M H₂SO₄) of the Au (*dashed line*) and the platinized Au electrode after spontaneous Pt deposition (*solid line*). Inset, open circuit potential during deposition

so (in the regions of hydrogen adsorption/desorption and oxide formation/reduction). The platinum CV features are, however, much less pronounced; the Pt area calculated from the H desorption charge is about one quarter of the covered Au area.

A set of experiments with varied deposition time revealed that for an observable amount of Pt, at least 1–2 min is needed; the maximum change ($\approx 20\%$ covered Au area, $\approx 5\%$ Pt area) is attained in about half an hour. These values could be exceeded neither by prolonged, 1-day deposition time, nor by repeating the procedure.

An additional experiment demonstrated the stability of the layer formed in the platinizing solution: the experiment yielding Fig. 1 was repeated with the sole difference that before rinsing by water, the electrode was held in deoxygenated 0.1 M HCl for 30 min. The resulting CV was practically indistinguishable from that of Fig. 1, indicating that the platinum layer formed spontaneously could not be, even partially, washed off by hydrochloric acid.

Interpretation

The following terms will be used to characterize the extent of the Pt and Au areas:

The uncovered (free) part of the Au substrate is $A(\text{Au})/A_0$, where $A(\text{Au})$ area is calculated from the charge of oxide reduction [34], A_0 is the original electrode surface area (i.e. $A(\text{Au})$ prior to platinization). Au coverage is defined as the fraction of the covered area, i.e. as $1-A(\text{Au})/A_0$. The area fraction of Pt, $A(\text{Pt})$ is calculated from the hydrogen and/or OH desorption charge of Pt with all corrections suggested in [34] and given as $A(\text{Pt})/A_0$. This way, the area fraction of 1 corresponds to a monoatomic densely packed Pt layer having the same atom density as of a polycrystalline Pt. Note that whereas the area determination includes uncertainties related to the scan limits, the $A(\text{Au})/A_0$ ratios—calculated from measurements made with the one and the same scan limits—are much more accurate; the same applies for the $A(\text{Pt})/A_0$ values.

Usually the terms ‘spontaneous’, ‘under open circuit conditions’ or ‘electroless’ in context of metal deposition have the same meaning: metal ions get attached to the surface, with their charge change compensated by an oppositely equal charge change of some other species—the reducing agent—present locally. The reducing agent can be a species in the solution, or one adsorbed on the surface, or the substrate itself can act as a reducing agent. A special case is when reduction yields adsorbed species with intermediate (non-zero) oxidation state, the example is spontaneous deposition of Pt from Pt(IV) solution on Ru, when stable Pt(II)-chloride and Pt(II)-oxide/hydroxide are deposited [28] on the expense of the equivalent oxidation of the Ru substrate.

The conditions of the experiments determine the presence/absence of the reducing agent, which in turn, caused the difference of our results and of those ones reported in Refs. [25–28]:

Spontaneous deposition of platinum from $[\text{PtCl}_6]^{2-}$ -containing solutions onto Au(111) [24, 25], onto Au(poly) [26] and onto carbon-supported Au nanoparticles [27] were observed by dipping the Au in platinizing solution, then rinsing by water [24–26] or by 0.5 M H_2SO_4 [27] and finally reducing cathodically in a platinum-free solution. Platinum of coverages between 0.2 and 0.3 monolayer [24, 25, 27] or even more (up to one monolayer, after repetitive depositions) [26] have been found (these values are Pt area fractions in our terms). In contrast, we never obtained Pt area fractions larger than 0.05 and the corresponding 0.2 Au coverage. The reason of the difference presumably can be traced back to the uncontrolled and unknown potential of the Au substrate in the experiments of Refs. [24–27] at that moment when the electrode got into contact with the platinizing solution.

In the experiments of Refs. [24–27], the Au electrode is in reduced state after quenching in H_2 saturated water, or after prolonged cathodic polarisation, its potential is indefinite, it can be even near to 0 V. With the following line-of-thoughts, the order of magnitude of the uncertainty of Pt coverage can be estimated: When such an electrode is dipped in the platinizing solution, its potential shifts almost 1 V causing a charge rearrangement within the double layer (in this case, the heavily charged double layer, as a whole, plays the role of the reducing agent). By taking the usual $20 \mu\text{F}/\text{cm}^2$ value for double layer capacitance, the corresponding charge change is around $20 \mu\text{C}/\text{cm}^2$, which charge is associated with the Pt species attached to the surface during the initial rise of the OCP from the initial low to its final ≈ 1 V value. The $20 \mu\text{C}/\text{cm}^2$ charge is equivalent to 2–3% Pt area fraction if it is formed by a four-electron reduction reaction or its double if a reduction with two electrons is assumed. If a loose structure of Pt ad-species is formed with the site requirement of four (see [Electrochemical deposition of platinum](#) section) then the Pt area fraction is $\approx 10\%$ or $\approx 20\%$ for the four and two electron reductions, respectively. In case of repeated depositions, uncertainties increase with the number of steps. Moreover, adsorbed hydrogen (on the Pt deposited in the previous cycles) can act as reducing agent in the next deposition step.

The present study demonstrates that even in the apparent absence of reducing agents, spontaneous deposition proceeds, although it results in a much smaller Pt area fractions than that was found in Refs. [24–27]. The question is whether this ‘apparent absence’ of reducing species is in fact an absence of any reducing species, implying that the spontaneous step at the OCP is the adsorption of some Pt

species, or there is a subtle reduction step. This question cannot be answered definitely from the experimental results, but the following speculation can be offered.

Obviously, after rinsing and transferring the electrode to the cell with 0.5 M H₂SO₄ and as the first cycle of the CV having completed, Pt exists on the Au surface as discharged Pt(0). However, at the moment of immobilization at the surface (that is, still within the platinizing solution) it can be (1) an adsorbed undischarged Pt^{IV} complex, or (2) discharged Pt(0), or (3) some intermediate as an adsorbed Pt^{II} chloro- or oxocomplex.

1. The layer formed at the OCP adheres to the surface so strongly that it cannot be removed either by rinsing or by a prolonged washing by 0.1 M HCl. In the case of single-crystal Au surfaces, it has been found that [PtCl₆]²⁻ (the Pt^{IV} complex) is adsorbed weakly [29], while [PtCl₄]²⁻ (the Pt^{II} complex) is adsorbed on Au (111) surface strongly, it could not be washed off by water or by 0.1 M HClO₄ [23]. Nevertheless, it is conceivable that on the polycrystalline Au surface, there exist active sites where Pt^{IV} species are irreversibly adsorbed. (Recently, it has been shown that asperities on polycrystalline Au surfaces can be very active [35, 36].)
2. Pt(0), per se, is bound also very strongly to the substrate. For Pt(0) as deposited species, the presence of some reducing agent has to be assumed. It might be some Pt^{II} complex being present in low concentration in the H₂PtCl₆ solution (then the reaction is the disproportionation of Pt^{II}: 2Pt²⁺ → Pt + Pt⁴⁺), or the Au substrate itself. The latter, the oxidation of Au at the OCP (950 mV) is improbable.
3. If we consider some Pt^{II} content in the H₂PtCl₆ solution, irreversible adsorption of Pt²⁺ species can also be an explanation of the observed experimental results.

According to our opinion, mostly on the basis of similar dipping experiments with Au single crystals [24, 29], the most probable version is the last one, i.e. the spontaneous step of the Pt deposition can be the adsorption of some Pt^{II} species being present in the solution. This adsorption step must be completely irreversible and exclusively characteristic to the gold surface: the latter statement is supported by that the 5% saturation Pt coverage cannot be exceeded by repeating the experiment.

Electrochemical deposition of platinum

As it was shown in the previous section, some kind of irreversibly adsorbed Pt species forms a layer at the OCP (≈950 mV) which can be reduced to Pt(0). Bulk phase of Pt can be deposited negative to the OCP by a few hundred millivolts. The subject of this section is to determine the

potential E_1 , at which bulk-phase deposition starts, and to clarify what happens at potentials between E_1 and the OCP.

On the cathodic polarisation curve of Au in the platinizing solution, Fig. 2, two well-separated current plateaus are seen according to the Pt⁴⁺ → Pt²⁺ and Pt⁴⁺ → Pt²⁺ → Pt(0) reductions, respectively.

To characterize Pt deposition at various potentials, potentiostatic experiments were carried out in the following way: The Au electrode was held at E_d deposition potential in the platinizing solution for t_d deposition time; afterwards, it was taken out, rinsed and transferred into the other cell of 0.5 M H₂SO₄ where CVs were recorded. To determine the t_d dependencies, the whole procedure was performed repeatedly. The conclusions are drawn based on how the CVs depend on E_d and t_d .

Two potential regions can be distinguished:

1. For potentials $E_d \leq 720$ mV, the CVs reveal the formation of a bulk Pt layer, see Fig. 3. These CVs have been recorded for $t_d = 10$ min at potentials indicated by arrows in Fig. 2. At $E_d = 400$ mV, a large Pt surface developed, while apparently no Au surface remained free (Fig. 3a); at $E_d = 720$ mV, only a small part of the Au surface could be covered by Pt (Fig. 3c). In between, at $E_d = 600$ mV, the Pt surface is about the same as the original Au surface; the free Au surface is very small (Fig. 3b).

With increasing t_d , the Pt surface area increases at all three potential values; as an example, the set of CVs is shown in Fig. 4 for experiments performed at $E_d = 720$ mV. This potential is certainly within the region where bulk Pt deposition takes place: the Pt surface area increased steadily with t_d without any apparent limit, even after 200 min.

2. In contrast to the experiment of Fig. 4, the quantity of the deposited Pt levels off (along with the end of decrease of free Au surface) with time if deposition is made at $E_d \geq 750$ mV; the CVs recorded after $t_d = 100$ min or $t_d = 200$ min deposition time practically

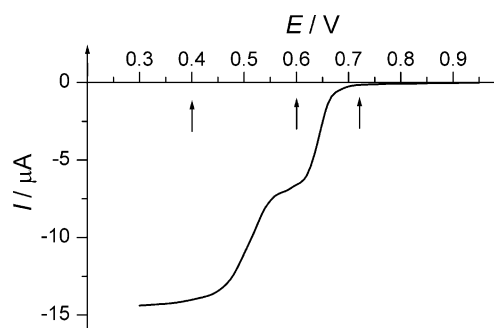


Fig. 2 Cathodic polarisation curve (taken with 1 mV/s scan rate) of Au electrode in 0.2 mM H₂PtCl₆ + 1 mM HCl + 0.5 M H₂SO₄ solution. The arrows indicate the potentials, at which the electrodes were platinized prior to taking the CVs of Fig. 3

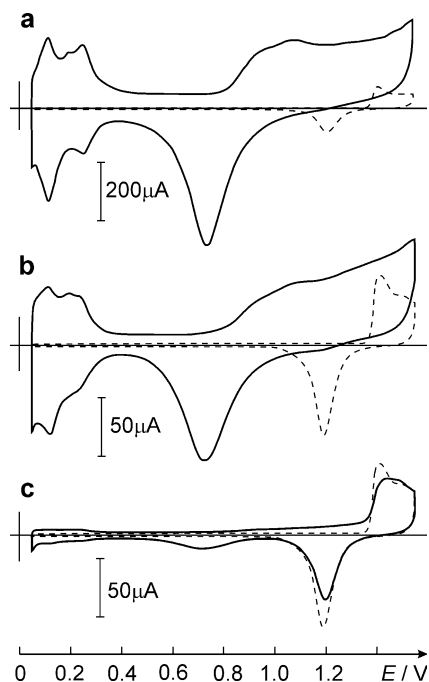


Fig. 3 CVs (50 mV/s in 0.5 MH_2SO_4) of the Au (dashed line) and the platinized Au electrode (solid line) prepared by a 10-min Pt deposition at potentials indicated by arrows in Fig. 2, that is at 400 (a), 600 (b) and 720 mV (c)

coincide (Fig. 5). Note that a similar effect: independence of free Au surface upon deposition time was found for spontaneous Pt deposition (i.e. deposition around $E_d=950$ mV), see previous section.

Consequently, the E_1 potential is between 720 and 750 mV. A somewhat more accurate value of E_1 can be

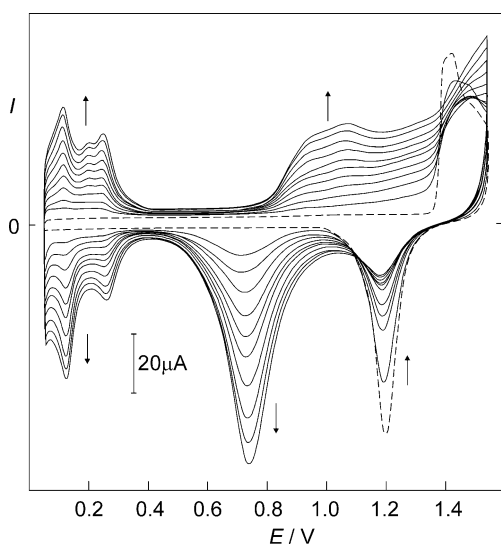


Fig. 4 CVs (50 mV/s in 0.5 MH_2SO_4) of the Au (dashed line) and the platinized Au electrode (solid line) prepared by Pt deposition at 720 mV potential for increasing times from 20 to 200 min in 20-min steps. Trends of CV features due to the increase of deposition time are indicated by the arrows

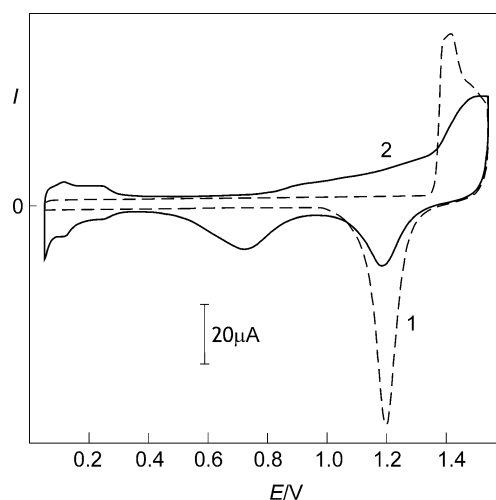


Fig. 5 CVs (50 mV/s in 0.5 MH_2SO_4) of the Au (1, dashed line) and platinized Au electrode (2, solid line) after Pt deposition at 750 mV for 140, 160, 180, 200 min—the latter four CVs completely coincide

obtained through calculating Au coverages and Pt area fractions. Pt area fraction is plotted in Fig. 6 as a function of t_d deposition time, for data sets of E_d s around E_1 . On the one hand, for the least positive E_d s, (700 and 720 mV), the Pt area fraction increases in an accelerating manner with t_d , i.e. with no apparent limit in the timeframe of the experiment; the values exceeding 100% imply rough surfaces. On the other hand, for the most positive E_d s, Pt area fraction reaches a limit value of about 8% (corresponding to 30–35% Au coverage, full symbols) after 40 min for $E_d=760$ mV, and about 17% (65–70% Au coverage, not shown) after 140 min deposition for $E_d=750$ mV.

The Pt area growth for the $E_d=740$ mV experiment exhibits no deceleration (albeit nor acceleration); thus, it is reasonable to conclude that E_1 is somewhat more

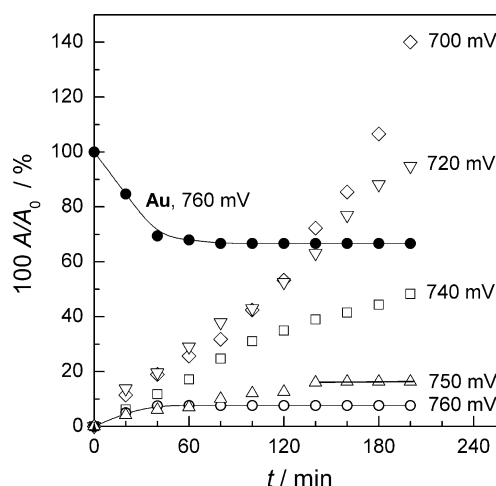


Fig. 6 Pt area fraction (open symbols) as a function of deposition time for various deposition potentials. Full symbols, Au coverage for $E_d=760$ mV

positive than 740 mV; determination of the exact value is beyond our present purpose.

Two additional findings are due here:

1. If Pt is deposited with $770 \text{ mV} \leq E_d \leq \text{OCP}$ ($\approx 950 \text{ mV}$), then, the Pt area fraction is independent of E_d ; it levels off at about 5% for a deposition time of about 20–30 min. However, some steady cathodic current flows even at long times when the Pt area has been levelled off, that is, when the Pt^{2+} adsorption has already been stopped. Thus, the current is due to the $\text{Pt}^{4+} \rightarrow \text{Pt}^{2+}$ reduction, and as such, it is a source of Pt^{2+} ions.
2. Practically, the same coverage/area fraction vs. deposition time curves were obtained if deposition was not interrupted by the CVs, but for all t_d s, the experiment started with freshly cleaned Au electrode and freshly prepared platinizing solution.

Discussion

1. Each atom of a monoatomic layer covers some part of the underlying metal. When a Pt atom is deposited onto Au atoms, Au surface decreases concomitantly with the increase of Pt surface. In contrast, when a Pt atom is deposited on the top of Pt atoms, the Pt surface increases without any decrease of the Au surface. Therefore, the layer is monoatomic if the Pt area increases on the expense of the decrease of the Au area. As a practical consequence, Pt surface area data can be transformed into coverages only if the monoatomic nature of the deposit is demonstrated; this is why both the Au and the Pt area must be measured simultaneously (through measuring the charges associated with H^+ and/or OH^- desorption for Pt and from OH^- desorption for Au, respectively).

The Pt surface increase is much smaller than the Au area decrease when deposition proceeds at potentials $E_1 \leq E_d \leq \text{OCP}$ (including the spontaneous deposition at the OCP); that is, one Pt atom blocks more than one Au atom. Quantitatively, this can be expressed by defining the site requirement [37] of a Pt atom as $S = (N_0^{\text{Au}} - N^{\text{Au}}) / N^{\text{Pt}}$ where N_0^{Au} and N^{Au} are the number of all and uncovered surface Au atoms, respectively and N^{Pt} is the number of Pt atoms; these values can be obtained from charges of oxide-reduction peak for Au and hydrogen desorption for Pt, respectively, according to the procedures described in Ref. 34. As it was obtained from the CVs following Pt deposition in the $E_1 \leq E_d \leq \text{OCP}$ potential range and also after spontaneous deposition, $S \approx 4$. One deposited Pt atom inhibits

approximately, and on an average, the oxidation of four underlying Au atoms. The $S \approx 4$ condition implies a fairly loose top layer structure involving distant Pt atoms.

2. The final Pt area fraction in the $E_1 \leq E_d \leq \text{OCP}$ range did not depend on whether or not the deposition was interrupted and a CV was taken, revealing that at this potential range, Pt can be deposited exclusively on Au surface.
3. The nature of the Pt deposit as a function of E_d is summarized in Fig. 7. In between the onset of bulk deposition $E_1 \approx 0.74 \text{ V}$ and the OCP ($\approx 0.95 \text{ V}$), Pt is deposited to form a partial monolayer. This range can be split up to two sections at $\approx 0.77 \text{ V}$:

Below $\approx 0.77 \text{ V}$ monolayers with $>5\%$ (e.g. $\approx 17\%$ for $E_d = 750 \text{ mV}$), area fractions are formed. Above $\approx 0.77 \text{ V}$, the Pt area fraction is around 5% in the full potential range, irrespective of whether or not current is flowing and Pt^{2+} ions are generated. The finding that the same amount of Pt^{2+} is adsorbed onto Au, independently on E_d and Pt^{2+} ion concentration implies, on the basis of exclusion, that the amount corresponds to that of the active sites of the Au.

Thus, we attribute the constant $\approx 5\%$ area fraction at $>0.77 \text{ V}$ potentials to adsorption at the active sites on Au, whereas the more dense monolayers formed at $<0.77 \text{ V}$ are assumed to be formed also on the uniform regions.

4. Using potentials somewhat more positive to that of the onset of bulk deposition, actually close to $E_1 \approx 0.74 \text{ V}$ close-to-uniform, monoatomic Pt layers can be prepared, with an area fraction of about 20–25% of a close-packed monolayer.
5. All potential data refer to the actual concentrations of Pt and other constituents of the platinizing solution; thus, with altered circumstances, e.g. E_1 needs to be determined.
6. We emphasize that the experiments all have been made with polycrystalline Au electrodes whose surface is not

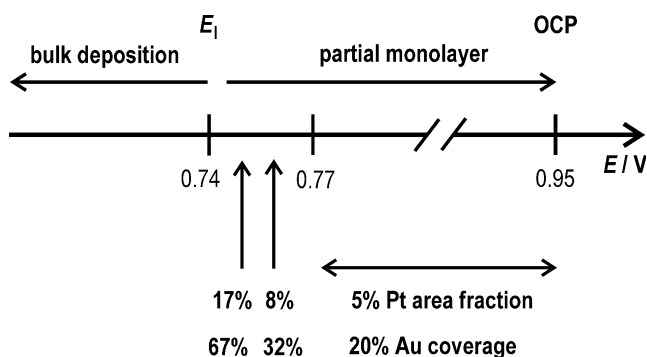


Fig. 7 The nature of the deposit and Pt area fraction as a function of deposition potential

as well defined as that of a single crystal. Polycrystalline surfaces may contain highly active sites resulting in different adsorption behaviour to that of single crystal surfaces. Site requirement and area fraction data refer to the polycrystalline Au surface. Obviously, the above numbers would be different if the experiments were made with various faces of single crystalline Au. We intentionally used polycrystalline Au electrodes rather than single crystals due to the need of simultaneous Au and Pt surface area measurement. This would have been impossible with single crystals, because their initially well-defined surfaces rapidly deteriorate if CVs including oxide formation and reduction are taken on them.

Summary and conclusions

It has been shown that Pt can be deposited on a polycrystalline Au surface from $[\text{PtCl}_6]^{2-}$ solution under OCP conditions; but only about 5% of a full-packed Pt monolayer.

In cathodic deposition experiments, three potential ranges were identified:

1. In the $770 \text{ mV} \leq E_d \leq \text{OCP}$ potential range 5% Pt area fraction can be attained which value is apparently independent of potential;
2. In a narrow, about 30 mV broad potential range ($740 \text{ mV} < E_d < 770 \text{ mV}$) Pt area fraction levels off with deposition time; the final steady-state coverage increases with decreasing potential (the observed maximum coverage was about 65–70%);
3. If the deposition potential is $< 740 \text{ mV}$, then the Pt surface increases with deposition time either with no apparent limit or attaining such a value which is much larger than that of the Au substrate. This is possible only if bulk deposition proceeds.

In the first two potential region, partial monolayers of Pt are formed; these are tentatively identified as adsorbed Pt^{II} species, which are readily reduced to $\text{Pt}(0)$, e.g. during the first cathodic scan in H_2SO_4 solution. In these potential ranges, site requirement of the platinum species was found to be around four. In other words, they block the oxidation of about four underlying Au atoms, which implies their distant positions. The present study opens a simple route to prepare monoatomic Pt layers on Au surfaces.

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