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Charge transfer reactions at nanostructured Au(111) surfaces: influence of the substrate material on electrocatalytic activity

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Abstract

Nanostructured electrodes can be used as model catalysts in order to gain a basic understanding of electrocatalytic properties. In particular, the influence of particle size and particle dispersion of noble metal catalysts and a possible influence of the support material can be studied in detail. Electrocatalytic reactions such as the hydrogen oxidation reaction (HOR), the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR) are important for technical applications. Hence, palladium and platinum as typical catalysts were investigated on Au(111) substrates regarding the HOR, HER and ORR. A significant increase in catalytic activity was found for Pd and Pt deposited on Au(111) where, with a decreasing amount of deposited metal, an increase of specific activity is observed which is contrary to expectations. A different behaviour was found for the ORR, where, according to expectations, the reactivity increases with increasing amounts of Pt. Parameters influencing the electrocatalytic activity of nanostructured surfaces, such as strain of the overlayers induced by the support and a possible direct involvement of the Au(111) surface in the mechanism of HER, are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The properties of nanoparticles and nanostructures (e.g. nanoislands on well-defined electrode surfaces) are the subject of scientific research with a wide range of potential applications in electronics, medical science and catalysis. This scientific interest is due to the size-dependent properties of the nanoparticles and nanostructures, which can result in behaviour different from that of the bulk material. Physical properties and a different chemical behaviour can be observed in catalysis in nanoscale dimensions because of low coordinated surface atoms, strain effects in particles due to interaction with the substrate material and other effects.

(i) Results reported by Meier and Goodman [1] show that the binding energy of carbon monoxide (CO) and oxygen

on small gold nanoparticles supported on TiO₂ is higher compared to larger gold particles.

- (ii) Using density functional theory (DFT) calculations Janssens *et al* [2] investigated gold particles which show increased catalytic activity with decreasing particle size, which was ascribed to low coordinated Au atoms. Typically, CO and oxygen do not adsorb on Au surfaces.
- (iii) Local reactivity measurements and combined DFT calculations of Pd nanoparticles on Au electrode surfaces were performed by Meier *et al* [3, 4]. By investigating for the first time electrocatalytic properties of single nanoparticles an increase of activity for HER by more than two orders of magnitude was found for a decrease of particle size from 200 to 6 nm. This result was explained by a strain effect in the Pd particles induced by the Au(111) substrate which has a larger lattice constant.

(iv) Recent investigations by Kibler [5] and Pandelov and Stimming [6] on monolayers and submonolayers of Pd on Au(111) electrode surfaces show an enhanced catalytic activity for HER with decreasing amount of palladium complementary to the results with Pd single particles [3, 4].

The results reported in this work describe the electrocatalytic activity of Pd or Pt multilayers, monolayers and submonolayers on Au(111) surfaces, also in comparison to the bulk material. These surfaces were investigated with respect to their electrocatalytic properties towards the HER, HOR and ORR.

It was shown by the groups of Kolb [7–10], Kibler [5] and Uosaki [11, 12] that the physical and chemical properties of thin Pd overlayers change with respect to the Pd bulk material. Baldauf and Kolb [8], as well as Kibler *et al* [9], investigated the catalytic behaviour regarding formic acid oxidation. The reactivity is obviously dependent on the thickness of the Pd layer, the crystallographic orientation and on the chemical identity of the substrate. The ORR was investigated by Naohara *et al* [11, 12] who found a dependence on the thickness of the Pd overlayer. Kibler *et al* [5, 9, 10] reported on the parameters influencing the HER; most of the observed experimental results can be explained by a lateral strain of thin Pd films on Au(111) electrodes according to the Nørskov model [13]. Pandelov and Stimming [6] recently reported an increased specific reactivity of Pd submonolayers on Au(111) which is two orders of magnitude higher compared to bulk Pd. This result may indicate a significant involvement of the gold substrate in the activity of Pd/Au(111). A spillover mechanism of the adsorbed hydrogen during the HER from the Pd sites to the Au substrate was able to explain the results for submonolayer coverage [14].

In addition to the experimental results, the groups of Nørskov [13, 15–19] and Gross [20, 21] performed calculations concerning the electronic properties of such structures. Density functional theory (DFT) is an approach to calculate activation energies and adsorption energies of educt species and intermediates on surfaces [18]. The electrocatalytic properties of Pd islands on Au(111) are modified due to strain in the lattice of Pd by about 4.8%, resulting in a shift of the d-band centre of Pd to higher energies and thus a change in the interaction with reaction intermediates, e.g. with hydrogen [4]. Similar conclusions were reached by Roudgar and Gross [21] who investigated the adsorption energies of hydrogen and CO. Thus the d-band model, substrate interaction effects and effects of the second-nearest neighbour's interactions play an important role.

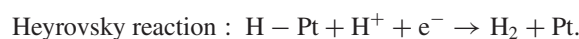
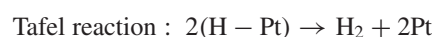
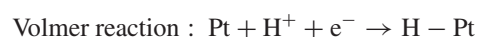
All the above-mentioned work contributes to a better understanding of the parameters influencing the electrocatalytic properties of catalysts, which is important for a rational design of catalysts. Parameters may be the interparticle distance, particle morphology, chemical composition and influence of the support. In an effort to better separate the various parameters, our studies follow the approach of depositing nanoislands of different reactive materials such as Pd and Pt onto nonreactive

model surfaces, for instance Au(111). Electrochemical methods (e.g. potentiostatic pulse techniques and cyclic voltammetry) are used in order to study the influence of these parameters on the HOR, HER and ORR. With *in situ* electrochemical STM (EC-STM) morphological and structural properties of the model catalysts were investigated in parallel to reactivity measurements. This combined approach helps us to obtain a more detailed picture of structural and morphological parameters influencing reactivity.

2. Investigated reactions and fundamentals

2.1. Fundamental aspects of hydrogen-related reactions

The hydrogen reaction kinetics is an important field of research in experimental and theoretical studies. For hydrogen evolution, there are three reaction steps, which can occur in different combinations:



Two different pathways for the reaction are known, the Tafel–Volmer [22, 23] and the Heyrovsky–Volmer [22, 24] pathway. In the first case, Tafel–Volmer, two protons are discharged and adsorbed as atomic hydrogen on the surface. Molecular hydrogen is formed by the recombination of two adsorbed hydrogen atoms. In the second case, Heyrovsky–Volmer, after the reduction of a proton a hydrogen atom is adsorbed on the surface. A second proton is discharged at the adsorbed hydrogen atom, forming molecular hydrogen. Adsorption sites are needed to bind the atomic hydrogen at the surface. These steps are also important for the reverse reaction, the hydrogen oxidation reaction (HOR).

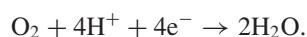
The electrocatalytic activity can be described by the exchange current density j_0 , which is dependent on the electrode material and the concentration of educts and products. A classical representation is the plot of $\log(j_0)$ versus the adsorption energy ΔG_{ad} of the hydrogen to the metal results in the so-called Volcano plot [25]. Both branches of the plot end in a vertex where $\Delta G_{\text{ad}} \approx 0$ [26]. Results from experimental and theoretical groups substantiate the relationship of $\log(j_0)$ and ΔG_{ad} in the Volcano plot [6, 27, 28]. Typically, noble metal catalysts such as Pd, Pt, etc. or alloys of these metals are located near the top of the Volcano plot. They exhibit a neither too strong nor too weak interaction of the respective metal with hydrogen ($\Delta G_{\text{ad}} \approx 0$).

Kibler [5] demonstrated a structure-sensitive activity of the HER on Au single crystals and thin Pd films on them, whereas the activity is based on the ability of free reaction sites to adsorb hydrogen; defect sites may be more effective than terrace sites. Experimental results from Hernandez and Baltruschat [29, 30] indicate the importance of step sites for the electrocatalytic reactivity of Pd layers on vicinally stepped gold electrode surfaces. The hydrogen adsorption and the HER were studied on Au single crystals of the

[1, $\bar{1}$, 0] zone of the crystallographic triangle with different step densities modified with Pd. For a good comparison of all mentioned results a direct access to reliable values of j_0 for hydrogen-related reactions seems to be a great challenge [5]. Although there are a number of experimental techniques and theoretical approaches values of j_0 differ considerably in the literature [31–34]. Furthermore, different explanations for an enhanced electrocatalytic activity are given [3, 5, 6, 9, 14, 19–21, 27, 29, 30, 35, 36].

2.2. Fundamentals of the oxygen reduction reaction

The oxygen reduction reaction (ORR) is intensely studied due to the importance in, for example, fuel cell applications. The reaction equation of the four-electron process is



A number of publications [11, 12, 37–43] have dealt with the electrocatalytic properties of nanostructured and bimetallic surfaces, but a complete understanding is still missing. However, it is necessary to define design parameters for efficient ORR electrocatalysts. It is well known that there is a strong correlation between surface structure and catalytic activity; the crystallographic orientation, morphology and chemical composition are the main parameters. Grgur *et al* [37] reported an increased oxygen reduction activity from (111) < (100) < (110) orientation of Pt single crystals in aqueous sulfuric acid. Instead of pure platinum crystals, a possible approach for new and effective catalysts is to use 3d metals. For bimetallic systems such as Pt–Fe alloys, Toda *et al* [41] reported for the first time that the ORR is influenced by a so-called Pt skin effect. A significant increase of electrocatalytic activity was identified for Pt–Fe alloys, where the activity for the ORR was found to be 25 times higher than for pure Pt. It was shown that the surface of such alloys consists of pure Pt (Pt skin layer) and the reactivity decreases with increasing thickness of the skin layer. This effect is explained by a modified electronic structure of the skin layer compared to bulk Pt.

Stamenkovic *et al* [40, 44] suggested bimetallic systems such as Pt₃Ni Pt₃Ti, Pt₃Fe, Pt₃Co, etc. Due to a change in the electronic properties of Pt, the metal–oxygen binding energy to bimetallic surfaces can be advantageously modified. These results were explained by different states of adsorbed oxygen resulting in different activation energies. Paulus *et al* [38] reported experimental results which show an increase of the catalytic activity per Pt atom for different Pt alloys. Results at bimetallic Pt alloys such as Pt₃M (M = Ni, Co, Fe, Ti, V) reported by Stamenkovic *et al* [45] show enhanced ORR activities. Investigations by Schmidt *et al* [42] show an enhanced ORR electrocatalytic activity with Pd-modified Au and Pt single crystals. Naohara *et al* [11, 12] found a similar behaviour for the ORR for thin Pd overlayers on Au single crystals. Pd monolayers and alloy catalysts were also investigated by Shao *et al* [39, 46]. He found higher catalytic activity for alloys and Pd monolayers supported on Ru, Rh, Pt and Au. The origin of this effect is described by a d-band centre shift of the deposited overlayer [39, 46].

3. Experimental details

3.1. Technical equipment and chemical compounds

An EC-Tec BP 600 bipotentiostat/galvanostat in combination with a waveform generator (Agilent arbitrary 33220A) was used for the electrochemical deposition of Pd and Pt on Au(111). The electrochemical reactivity measurements with respect to the HER and HOR were performed using potentiostatic pulses and the ORR was investigated by cyclic voltammetry with a potentiostat/galvanostat (HEKA PG 310) with a standard three-electrode arrangement in a glass cell. A digital oscilloscope recorded the voltage and current transients.

Images were obtained by a Veeco Multimode EC-STM/AFM system and a homebuilt Veeco/MI EC-STM system under dry conditions for the determination of the amount of Pt and under electrochemical control for *in situ* Pd deposition. All STM images were taken in constant current mode using etched Au tips or cut Pt/Ir (atomic ratio 80:20) tips. The gold substrates used as working electrodes (Schroer GmbH) consisted of 0.7 mm borosilicate glass, 2.5 nm chromium and 250 nm gold layer with a square size of 11 × 11 mm². In addition, Pt(111) substrates (11 × 11 mm²) (Schroer GmbH) were used.

The solutions were prepared from HClO₄ (Merck, Suprapur), Pd(NO₃)₂ (MaTeck, *pro analysi* (p.a.)), K₂PtCl₄ (Aldrich, 99.995%) and K₂PtCl₆ (AlfaAesar, 99.9%) with deionized clean water obtained from a Millipore-Milli-Q (18.2 MΩ cm, 3 ppm total organic carbon). Caro's acid was prepared with H₂SO₄ (Merck, p.a.) and H₂O₂ (Merck, p.a.) at a ratio of 1:1. Mercury/mercury sulfate electrodes (Schott, B3610) in 0.1 M H₂SO₄ (660 mV versus NHE) were used in all experiments.

3.2. Preparation and nanostructuring of electrode surfaces

The gold and platinum substrates used as working electrodes were flame annealed and cooled down in Ar atmosphere before use in EC-STM and electrochemical experiments. This annealing procedure leads to a (111) orientation of the surface with atomically flat terraces. After annealing, the substrates were transferred to the electrochemical cell in order to avoid contamination. All glassware was cleaned in Caro's acid and rinsed many times with clean water. Counter electrodes made of gold or platinum, depending on the experiment, were also cleaned in an acid bath and flame annealed. Mercury/mercury sulfate references were used in all experiments in a separate compartment connected via a Luggin capillary to the working electrode. 0.1 M HClO₄ solution containing 0.5 mM Pd(NO₃)₂ was used for Pd deposition. Pd/Au(111) was characterized in an Ar-purged 0.1 M HClO₄ electrolyte. Reactivity measurements of the Pd/Au(111) system were carried out in H₂ purged 0.1 M HClO₄. The pulse deposition procedure starts at an initial potential of 860 mV versus NHE. The potential is then set to the deposition potential of 660 mV versus NHE for various times. The amount of deposited Pd on Au(111) was determined by integrating the current during the electrochemical deposition, by hydrogen adsorption experiments and by STM images of the substrates (see below),

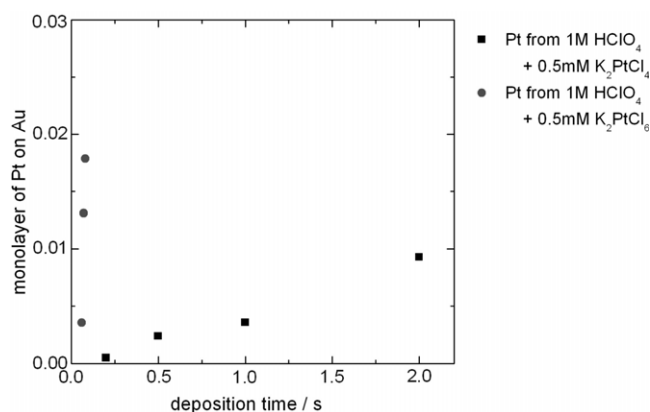


Figure 1. Amount of deposited Pt on Au(111) using different electrolytes. Pt was deposited from a Pt(II) complex (squares) and a Pt(IV) complex (circles) as a function of the deposition time t in seconds.

whereas a full monolayer of Pd, deposited from the Pd²⁺-containing solution, corresponds to a charge of 420 $\mu\text{C cm}^{-2}$.

Platinum deposition was performed in 1 M HClO₄ containing 0.5 mM K₂PtCl₄ or 0.5 mM K₂PtCl₆. Further measurements were performed in pure 1 M HClO₄. After the noble metal deposition, the substrate was rinsed several times with clean water to avoid spontaneous Pt deposition. Integrating the current transient during the deposition allowed calculating the charge of the deposited metal, taking into account the double layer charging. For determination of the surface of the deposited Pt hydrogen adsorption and CO stripping was used. The hydrogen adsorption method typically assumes a charge of about 210 $\mu\text{C cm}^{-2}$ for an underpotential deposition (upd) layer of hydrogen. The evaluation was done by integration of current transients in the hydrogen adsorption region. The same procedure was applied for CO stripping experiments with an estimated value of 280 $\mu\text{C cm}^{-2}$ for the oxidation of a monolayer of CO. STM images using the WSxM 4.0 image software (Nanotec Electronica S.L.) [47] showed the morphology of the particles, their size and distribution, and allowed a determination of the amount of the deposited metal. Under the given experimental conditions, the Pd and Pt deposits at submonolayer coverages consisted of monoatomically high nanoislands. All pictures with the EC-STM were taken in constant current mode with $I_{\text{tun}} = 1 \text{ nA}$ and $U_{\text{bias}} = 100 \text{ mV}$ as typical parameters. For low coverages $< 0.1 \text{ ML}$ the surface coverage of Pt was derived from STM images and the charge during the electrochemical deposition process. Figure 1 shows a comparison for the deposition of Pt from different Pt (Pt⁴⁺- and Pt²⁺-containing) electrolytes. The deposition process from the Pt⁴⁺-containing solution compared to the Pt²⁺-containing solution is more than two times faster, which is indicated by the different slopes for Pt⁴⁺ and Pt²⁺ deposition in figure 1.

3.3. Investigation of the HER, HOR and ORR

Potential step experiments were performed with varying overpotentials. Such potentiostatic pulses and the related

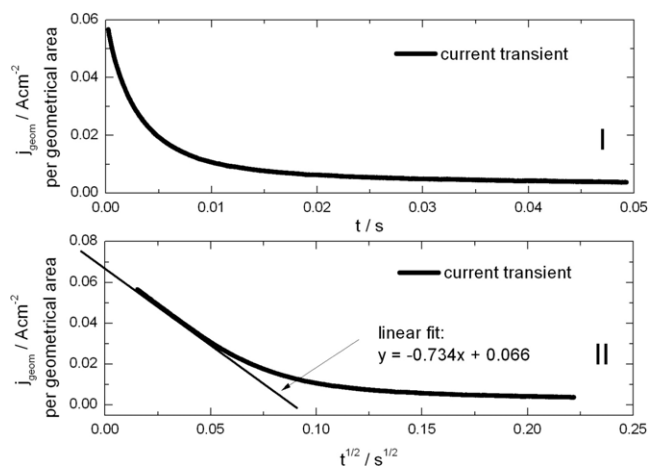


Figure 2. Example of a potential pulse and the evaluation method. The current transient shown in (I) is taken from the HOR experiments of a Pt(111) crystal with an applied overpotential of +130 mV versus RHE in H₂-saturated 1 M HClO₄. The lower figure (II) shows the plot of the current density versus the square root of time relative of the start of the pulse. This plot allows deriving the kinetic current density from a linear extrapolation of the first milliseconds of the current signal.

current transients were used in order to separate the kinetic from the mass-transport-controlled current. The sampling rate used of 1 kHz for the Pd/Au and up to 100 kHz for the Pt/Au system was chosen in order to have a sufficient resolution of the obtained current transients. A typical current transient for the kinetic investigation for the HOR is presented in figure 2(I). A potentiostatic pulse with a height of an overpotential of +130 mV was applied to a Pt(111) crystal in 1 M HClO₄. In order to extract the kinetic current the current transient is plotted versus the square root of the time [48] as shown in figure 2(II). Extrapolation from the first milliseconds after the potential step to $t = 0$ yields the kinetic current density, which is shown in figure 2(II). The kinetic currents obtained are referred to the geometric electrode surface but were also related to the surface of deposited Pd and Pt as specific current densities. A correction of the IR drop was performed for the Pt measurements because of the high current densities. The ORR was investigated by cyclic voltammetry (CV) in oxygen-saturated 1 M HClO₄. For small overpotentials the electrochemical process is not influenced by transport effects and can be taken as the kinetic current.

4. Experimental results

4.1. Characterization of the nanodeposits of Pd and Pt on Au(111)

The nanostructured Pd/Au(111) surfaces were prepared as described in the experimental section. In parallel, *in situ* EC-STM experiments were performed in order to image submonolayers of Pd. Figure 3a shows the STM image of a bare gold substrate at a potential of 860 mV versus NHE. Figure 3b shows the STM image with a scan direction from top to bottom starting at 860 mV versus NHE. At the indicated

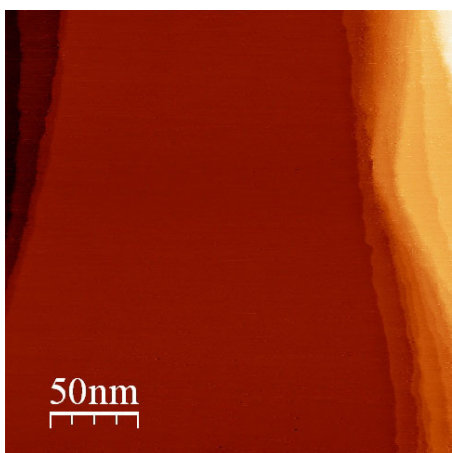


Figure 3a. Bare Au (111) imaged with EC-STM in 0.1 M HClO₄ + 0.5 mM Pd(NO₃)₂. $U_{we} = 860$ mV versus NHE for initial conditions.

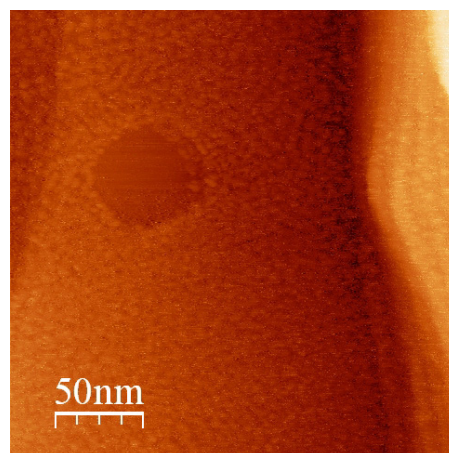


Figure 3c. Au(111) with deposited Pd in 0.1 M HClO₄ + 0.5 mM Pd(NO₃)₂. The image was recorded from bottom to top. The potential of the Au electrode was set to $U_{we} = 860$ mV versus NHE.

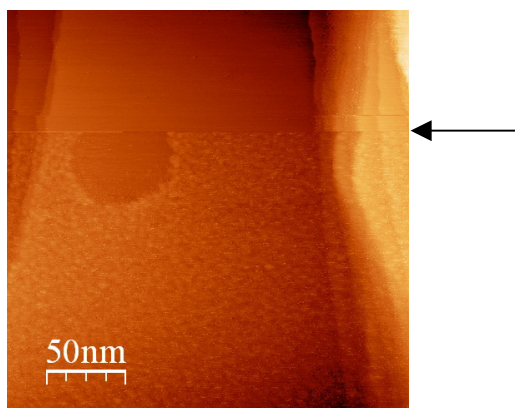


Figure 3b. Au(111) with *in situ* Pd deposition imaged with an EC-STM in 0.1 M HClO₄ + 0.5 mM Pd(NO₃)₂. The image was recorded from top to bottom of the picture. The potential of the Au electrode was switched from $U_{we} = 860$ mV versus NHE to $U_{we} = 460$ mV versus NHE marked with the arrow.

arrow, the scan was stopped and a potential of 400 mV versus NHE was applied for 2 s. Afterwards the scan was continued at 860 mV versus NHE. The area was scanned again from bottom to top and the Pd deposits are clearly visible (figure 3c). Close to the position where the deposition pulse was applied an uncovered surface can be detected which is probably due to an inhibition of the Pd deposition underneath the STM tip.

The Pt coverage was investigated by STM for determining the amount of deposited Pt, the particle morphology and the particle size distribution. Line scan analysis of the Pt nanoislands reveals that the deposited Pt particles are of monoatomic height. In figure 4, typical EC-STM images with different amounts of Pt are shown. The deposited amount of Pt was identified with the image software WSxM 4.0 [47]. The results were compared with electrochemical methods such as hydrogen underpotential deposition (H-upd), CO oxidation and Pt deposition charge. In figure 5, the results are plotted as a function of deposition time. For long deposition times, higher Pt coverage, the hydrogen adsorption charge, the CO stripping charge and the deposition charge are compared.

Below 0.1 ML (deposition times up to 0.08 s), STM pictures were taken in addition in order to evaluate the coverage of deposited Pt. For Pt coverage <0.1 ML the deposition charges are <84 $\mu\text{C cm}^{-2}$ for a deposition from a Pt⁴⁺-containing solution and <42 $\mu\text{C cm}^{-2}$ for deposition from a Pt²⁺-containing solution. The agreement of the obtained surface coverage from the various methods is reasonably good. Nevertheless, at low coverages and a given deposition time the hydrogen adsorption charge and the coverage determined by STM images is somewhat higher than the one determined by the Faradaic charge for Pt deposition. This may be due to a spontaneous deposition of Pt from residual Pt-containing solution before the substrate is rinsed with clean water after deposition in the electrochemical cell.

4.2. Hydrogen oxidation reaction (HOR) at Pd mono- and submonolayers on Au(111)

On Pd-modified Au(111) surfaces reactivity measurements were carried out in an H₂-saturated 0.1 M HClO₄ solution using potentiostatic pulses at various overpotentials. The current transients for the HOR were evaluated using a j versus $t^{1/2}$ plot in order to separate the kinetic current from the mass transport current. The kinetic currents obtained were used to construct Tafel plots (see figure 6). Tafel plots for different amounts of Pd deposited on Au(111) electrode surfaces are given with respect to the geometrical area (figure 6) and with respect to the Pd area (figure 7). The latter assumes that only Pd is active in the reaction. The current with respect to the geometric area of the Au(111) surface increases with decreasing amount of Pd from 0.74 to 0.1 ML by about one order of magnitude with a maximum value of 1 mA cm⁻² for an overpotential of 350 mV. The Tafel plot of the specific current density, where the current is normalized to the surface of the deposited Pd, is shown in figure 7. The data indicates that the specific reactivity of Pd increases by about two orders of magnitude with decreasing amount of Pd from 0.74 to 0.1 ML. Hence, current densities of up to 10 mA cm⁻² per Pd area are observed.

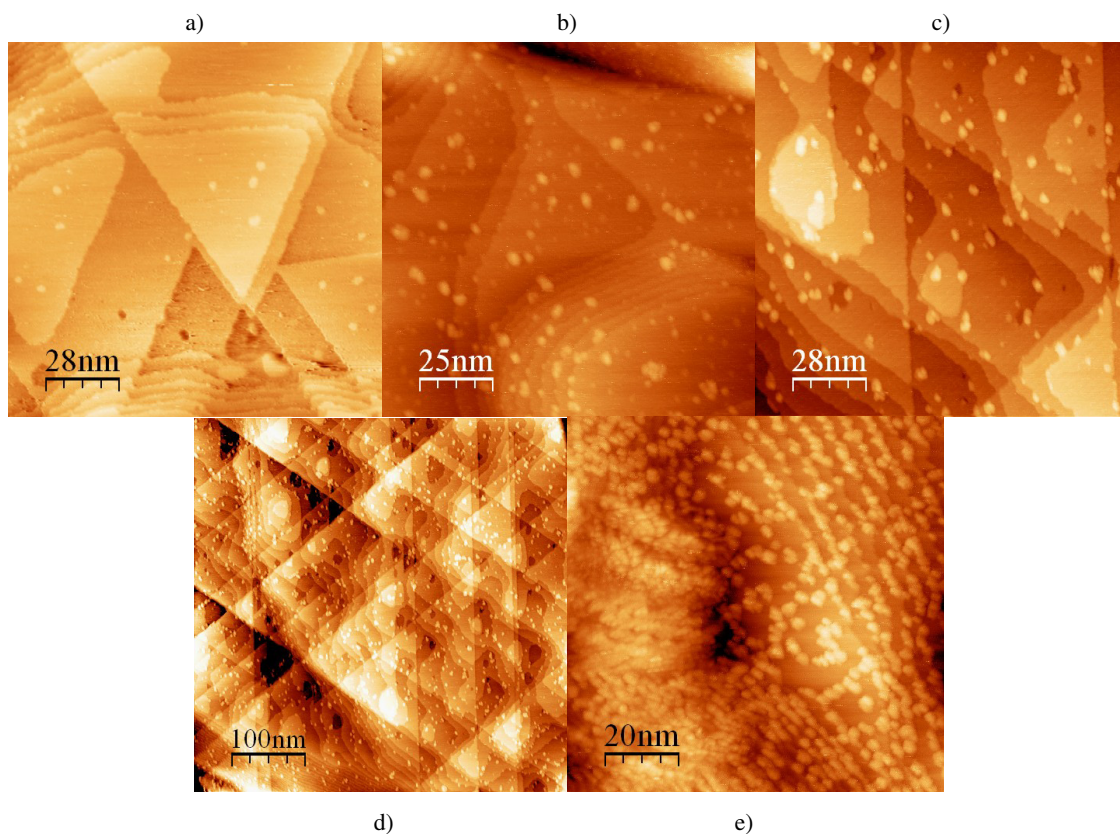


Figure 4. STM image of different Au(111) electrode surfaces nanostructured with Pt. STM pictures were recorded in air with $U_{\text{bias}} = 100$ mV and $I = 1$ nA. The amount of Pt on Au(111) corresponds to (a) 0.025 ML, (b) 0.066 ML, (c) 0.067 ML, (d) 0.13 ML and (e) 0.76 ML of Pt.

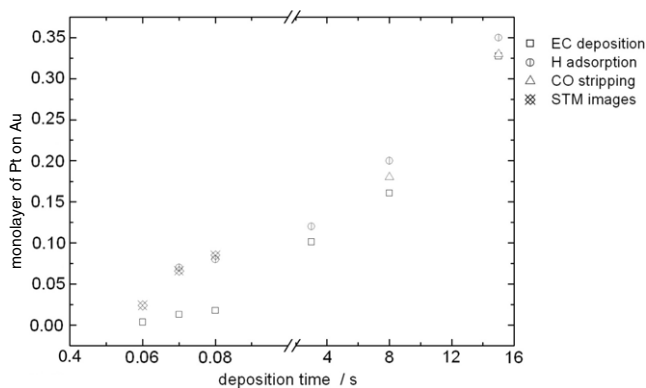


Figure 5. Comparison of different methods, which were applied in order to determine the amount of deposited Pt from 1 M $\text{HClO}_4 + 0.5$ mM K_2PtCl_6 . The monolayer equivalent was calculated by electrochemical deposition (squares), STM images (open squares with cross), hydrogen adsorption (circles with line) and CO stripping experiments (triangles) and normalized to the coverage determined by electrochemical deposition charge. The data is plotted versus the pulse length of the deposition pulses used for the nanostructuring of the Au(111) surfaces.

4.3. Hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) at Pt mono- and submonolayers on Au(111)

On Pt-modified Au(111) surfaces, measurements of the HER and HOR were carried out in H_2 -saturated 1 M HClO_4 using

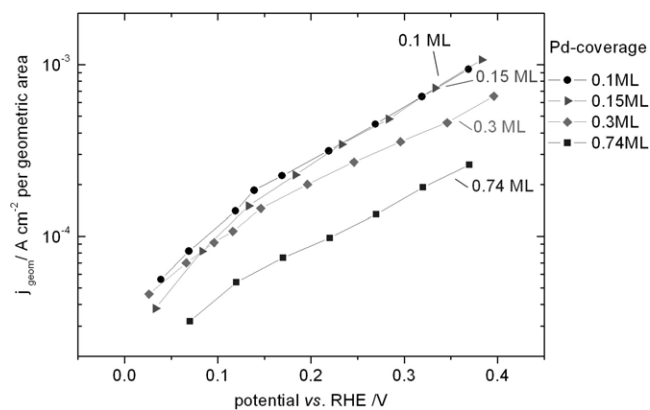


Figure 6. Electrocatalytic activity for the HOR per geometrical area of the Pd/Au(111) system in 0.1 M HClO_4 . The activity for the hydrogen oxidation reaction (HOR), reflected by the observed current density at a given potential, is notably higher for 0.1 ML (circles) and 0.15 ML (triangles) than for larger Pd coverages.

potentiostatic pulses. For the evaluation of the kinetic currents of HOR, the same procedure as described above was used. The HER and HOR for Pt submonolayers on Au(111) are plotted together with a Pt(111) surface (roughness factor = 1.8, based on H-upd) in a Tafel plot in figure 8 where the current refers to the geometrical surface area. An Au(111) surface with a Pt coverage of less than 1% of a monolayer

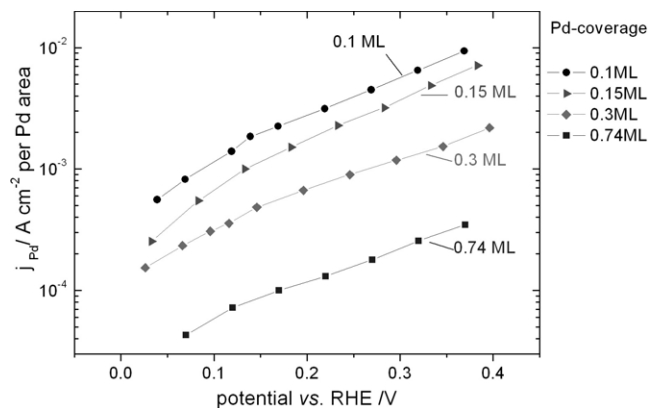


Figure 7. Electrocatalytic activity of the HOR per Pd area of the Pd/Au(111) system in 0.1 M HClO₄. The current density is normalized to the surface area of the deposited Pd.

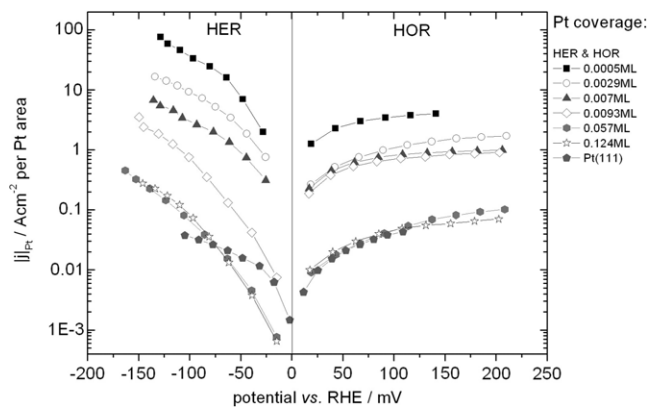


Figure 9. Tafel plot of the HER and HOR with current density per Pt area for Pt submonolayers on Au(111) and Pt(111) in 1 M HClO₄.

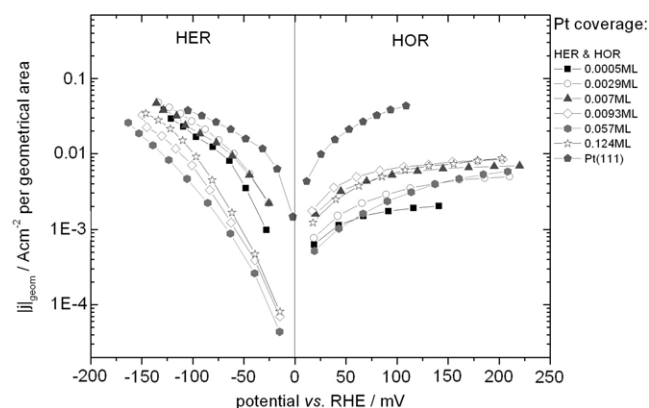


Figure 8. Tafel plot of HER and HOR with current density per geometrical area for Pt submonolayers on Au(111) and Pt(111) in 1 M HClO₄.

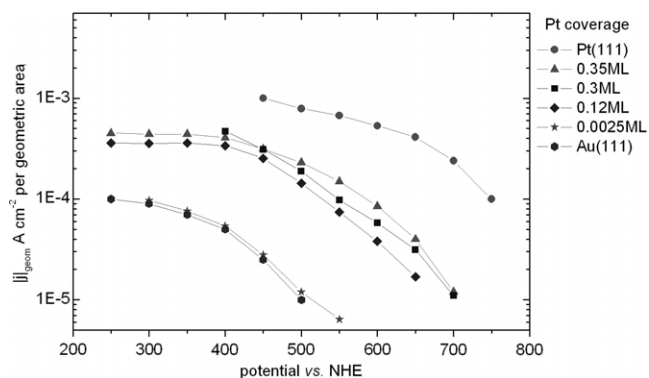


Figure 10. Tafel plot of the ORR at Pt/Au systems, Pt(111) and Au(111) single crystal in 1 M HClO₄. Current densities were derived from cyclic voltammograms. The coverage of Pt (0.35, 0.3, 0.12 and 0.0025 ML) on the Au(111) electrode surfaces is indicated in the figure. The results obtained on a pure Au(111) surface (hexagons) and a Pt(111) surface (circles) are provided for reference.

has approximately the same activity for the HER as Pt(111) for an overpotential only approximately 50 mV larger. Hence, the electrocatalytic activity of Pt submonolayers obviously increases with decreasing amount of deposited Pt. If the current density is referred to the Pt area on the Au(111) electrodes a clear trend of increasing activity of the Pt with decreasing amount of Pt on Au(111) is obtained for the HER and HOR (see figure 9). For the HOR reaction, the potential dependence is not as pronounced as for the HER but the influence of coverage of the Pt on Au(111) has a comparable effect.

4.4. Oxygen reduction reaction (ORR) at Pt submonolayers on Au(111)

The deposition and characterization experiments of Pt submonolayers were carried out as described before. After purging the electrolyte with oxygen the initial potential was set to 820 mV versus NHE and cyclic voltammograms for the Pt/Au(111) system were performed between 820 mV versus NHE and 250 mV versus NHE. The obtained results for the Pt/Au(111) system are summarized in a Tafel plot in figure 10. For comparison results obtained on bare Au(111)

and Pt(111) surfaces are added. Lower current densities are observed for lower amounts of deposited Pt on Au(111), and thus the reactivity decreases with decreasing amount of Pt. The Pt(111) surface shows the highest electrocatalytic activity within the series of investigated surfaces. Figure 11 shows the current density referred to the amount of platinum for several submonolayers. The specific current density is approximately the same for all different Pt coverages. This indicates that there is no change of specific electrocatalytic activity (activity normalized to Pt area) for different coverages. In summary, the Pt/Au(111) show an activity decreasing with decreasing amount of deposited Pt, which is in clear contrast to the experiment results for the hydrogen reactions.

5. Discussion

The experimental results for the HOR on monoatomically high Pd nanoislands deposited on Au(111) indicate a specific electrochemical activity that increases with decreasing coverage from 0.74 to 0.1 ML. A similar increase in specific activity was reported for the HER in the same system [6]. The net current densities for the HOR are one order of magnitude

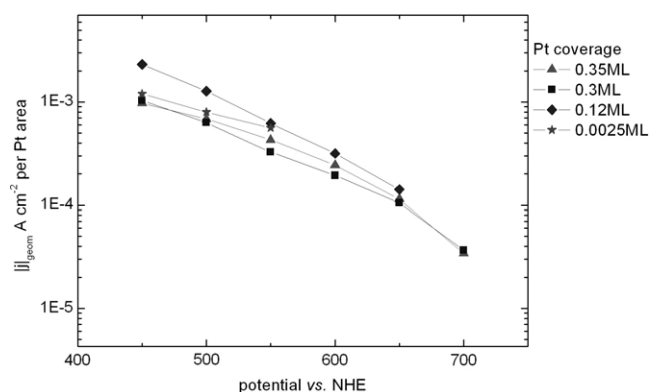


Figure 11. Tafel plot of the ORR at Pt/Au(111) systems in 1 M HClO_4 . Current densities were derived from cyclic voltammograms and were referred to the normalized Pt area.

lower as compared to the HER [6], certainly due to the lower concentration of reactants in the case of the HOR. Nevertheless, the enhancement of the specific current density is nearly two orders of magnitude going from 0.74 to 0.1 ML of Pd on Au(111) for both reactions HER and HOR.

The HER and HOR were also studied at monoatomically high Pt nanoislands deposited on Au(111) electrodes. The current densities for HOR on the Pt/Au(111) system are significantly higher as compared to the Pd/Au(111) system. For small overpotentials the specific current densities were similar for the HOR and HER (figure 9). For higher overpotentials, the specific current densities for the HOR are also smaller compared to the HER, similar to the Pd/Au(111) system. Nevertheless, an obvious enhancement of the specific electrocatalytic activity for Pt on Au(111) with decreasing Pt coverage with respect to the HER and HOR is clearly seen in figure 9. The specific current densities are approximately three orders of magnitude higher for small coverages of Pt on Au(111) as compared to the Pt(111) surface for the HER and more than two orders of magnitude higher for the HOR.

Several studies on Pd- and Pt-modified Au electrodes are reported [5, 6, 43, 49]. Aiming at a general understanding of the HOR and HER activity of Pd- and Pt-modified Au(111) electrodes several parameters have to be considered. One parameter is the influence of the substrate on the lattice constant of the Pd or Pt overlayer. According to the Nørskov model a lateral strain on the metal overlayer causes a shift of the d-band centre [6, 13, 15–21], resulting in a change in the electronic properties of the overlayer. For the Pd/Au(111) system the HER was investigated for Pd coverages ranging from several ML down to approximately 3% of a ML [6]. The enhanced activity of Pd monolayers compared to Pd multilayers on Au(111) can be explained by a strain effect of the gold substrate on the Pd layer. Such strain effects gradually decrease with increasing thickness of the Pd layer [4]. This influence is confirmed by the reverse experiment. In the case of tip-induced Pd particles on Cu(111) no enhancement for HER activity was found [50]. This is in line with expectation, since copper has a smaller lattice constant than palladium. Furthermore, Pt nanoislands electrodeposited on highly oriented pyrolytic graphite (HOPG) also show no

enhanced activity for the HER for mono- and submonolayers of Pt [51]. Both results indicate that neither Cu nor HOPG as support enhance the electrocatalytic activity of deposited Pd or Pt particles. Therefore, strain induced by the support material seems to be an important parameter that enhances the electrocatalytic activity for the HER and HOR. This allows understanding the increase of electrocatalytic activity of deposited Pd as a function of layer or particle thickness.

Nevertheless, it is important to consider that the most pronounced increase in HER activity was observed for submonolayers of Pd on Au(111) [6], which is similar to the behaviour for the HOR reported here. Previously, Meier *et al* reported on nanoscale effects of single Pd particles which were deposited with a STM tip on Au(111) surfaces [35]. On such nanostructured surfaces with single particles, the catalytic activity for the HER is drastically reduced depending on the height of the particles. The activity of Pd nanoislands increases by about two orders of magnitude going from tip-induced particles with a height of 10 layers to particles of approximately two layers in height. Structural and thus electronic effects induced by the substrate depend on the height of the deposited particles as discussed above. The argument of modified electronic properties due to a lattice strain of an isomorphic overlayer is applicable to Pt islands as well as to Pd islands. Since the lattice mismatch between gold (0.408 nm) and platinum (0.392 nm) is 4%, and between gold and palladium (0.389 nm) 4.8%. Therefore, it is expected to see a similar increase in activity based on the Nørskov effect for the Pt/Au(111) as well as for the Pd/Au(111) system. For further understanding, it has to be considered that tip-induced Pd islands on Au(111) were varied in height. The electrochemically deposited monoatomic Pd islands on Au(111) were varied in coverage; nevertheless, in both cases an enhanced activity is observed. The increasing activity for submonolayers of monoatomically high Pd and Pt with decreasing amount of deposited metal may not only be ascribed to a lattice mismatch but to a different effect. According to the Nørskov model alone, the specific activity of nanoislands of various coverages should be identical.

Recently, Eikerling *et al* [14] have described a spillover model, where the catalytic activity of Pd nanoislands is enhanced due to a spillover of atomic hydrogen from the Pd sites to the gold surface. A kinetic model was developed in order to explain the observed activity of single particles on Au(111) surfaces. A spillover of atomic hydrogen from Pd islands with a high coverage of hydrogen to a nearly hydrogen-free gold surface can energetically be a down-hill process [40]. Thus a process where the charge transfer takes place at the Pd islands and the recombination occurs on the Au(111) seems possible. The reverse reaction (HOR) involving both surfaces can also be imagined. Thus, the increase of catalytic activity for monoatomic submonolayers of Pd and Pt on Au(111) compared to monolayers could be understood by the involvement of the Au(111) surface in the reaction.

An alternative explanation for the observed increased electrocatalytic reactivity of submonolayers could be based on a possibly higher activity of low coordinated surface atoms such as step sites as reported by Hernandez and

Baltruschat [29, 30]. Hernandez *et al* studied the HER on Pd/Au(332) with Pd multilayers and submonolayers down to 0.2 ML. It was found that a Pd monolayer is more reactive than a Pd multilayer, which is in good agreement with a strain effect induced by the Au surface. For submonolayers of Pd down to 0.2 ML the exchange current density is not dependent on Pd coverage. Furthermore, it was demonstrated that co-deposition of copper at Pd submonolayers results in a suppressed HER activity. It is suggested that the Pd at the steps controls the kinetics of hydrogen evolution on stepped gold surfaces modified with Pd. In the case of Pd nanoislands on Au(111) the reactivity of HER is significantly larger, by approximately a factor of five, e.g. at an overpotential of 50 mV. In an analysis of nanostructured Au(111) electrode surfaces recently reported by Pandelov and Stimming [6] no correlation of the current density for the HER with the number of Pd edge versus Pd terrace atoms on Au(111) was found. The same result was found by Meier *et al* [4] from an analysis of single Pd particles on Au(111). Hence, the number of low coordinated atoms such as edge atoms does not seem to be a dominant factor controlling HOR and HER activity on nanostructured Au(111) surfaces. Based on the experimental results reported, it remains difficult to develop a complete model for the HER and HOR on nanostructured Pd/Au(111) and Pt/Au(111) surfaces in spite of the strong effects observed.

Comparing the results for the ORR with HOR and HER, a completely different picture is found. No enhancement effect of the electrocatalytic activity for the ORR on submonolayers of Pt deposited on Au(111) was found [52]. The observed current densities linearly decrease with decreasing coverage of Pt on Au(111). Furthermore, the onset of the Faradaic current is shifted to negative potentials, for smaller amounts of Pt, which indicates a lower electrocatalytic activity of the surface. These results for the Pt/Au(111) system show similarities to the results from Schmidt *et al* [42], who investigated the Pd/Au system in alkaline electrolytes. A possible explanation for a decreased electrocatalytic activity for the Pd/Au system is a strong binding between oxygen and Pd due to the d-band centre shift of Pd on Au which was recently suggested by Shao *et al* [39]. This trend was not found from earlier work by Naohara *et al* [11] where 0.9 and 8 ML were compared.

Nevertheless, our experimental findings for the extended surface are in agreement with those reported in the literature [38, 39, 42, 46]. Briefly summarized, the kinetics of the ORR is obviously not influenced by the same structural parameters as for the HOR and HER and it remains important to understand the origin of these differences. Although Pt is among the best catalysts for hydrogen-related reactions and the oxygen reduction reaction, there is still a potential for improvement. Based on our experimental results it can be stated that the positive effect of the Pd and Pt lattice expansion on Au(111) for the hydrogen-related reactions does not work for the ORR.

6. Conclusions

The influence of the gold substrate on Pd and Pt nanoislands was investigated regarding the HOR, HER and ORR. The

observed strong increase in specific activity for the HOR is shown for Pd on Au(111) in figure 7 and the increased specific activity for the HOR and HER for Pt on Au(111) is shown in figure 9. This effect is so strong that, in some cases, even the current density related to the geometric surface area increases for decreasing amount of deposited Pd or Pt on Au(111). Several explanations can be considered in order to understand the influences on reactivity. A theoretical model based on a spillover concept is currently under consideration. It could explain, for instance, that reactivity of monoatomic Pt or Pd nanoislands increases with decreasing coverage and thus distance of the particles on the Au surface. The influence of steps and defects sites may also play an important role for an enhanced electrocatalytic activity but, in our case, no indication was found. An influence of the substrate material on the electronic properties of Pd and Pt seems to be a likely explanation [6, 13, 15–21].

A strain effect on Pd and Pt overlayers on Au(111) seems to be advantageous for hydrogen reactions. With decreasing layer thickness enhanced catalytic activity of Pd islands and Pd layers can be observed [6]. Furthermore, the substrate itself seems to be involved in the electrocatalytic reactions such as the HER and HOR and thus submonolayers of Pt and Pd are far more active than their respective monolayers. Understanding the influence of substrate materials, such as the effect of lattice strain or stress [19] or even a direct interaction of the substrate [14] within the reaction, can result in a better understanding of electrocatalysis. Therefore, it remains a task to develop an integrated structure–reactivity model for the HOR and HER on nanostructured surfaces. An interesting direction of research is to investigate the charge transfer reaction at defined nanoparticles of Pd and Pt on model surfaces different from gold. So far, using copper instead of gold yields no enhancement [50]. This is in line with the Nørskov model, since copper has a smaller lattice constant as compared to Pd and Pt. Possible candidates in order to understand the influence of the substrate material with respect to a bond formation with the noble metal are HOPG and highly doped diamond. The carbon atoms of HOPG have sp^2 hybridization whereas the carbon atoms of highly doped diamond have sp^3 hybridization, and thus for the latter support a larger interaction with the deposited noble metal can be expected. Such systems would allow identifying the influence of the interaction of the nanoparticle with the substrate on their reactivity.

Studies of the ORR at Pt/Au(111) systems show no enhancement in specific reactivity for submonolayers of deposited Pt on Au(111) with respect to Pt(111). A decrease of the amount of deposited Pt is connected with a decrease in the electrocatalytic activity. The strain effect, which positively influences the reactivity for the hydrogen-based reactions, does not seem to be beneficial for the ORR. Furthermore, the constant specific activity for the ORR shown in figure 11 allows us to conclude that the gold surface is not involved in the electrocatalytic process.

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