

# Surface electrochemistry and reactivity

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**Resum.** Els pilars fonamentals de l'electroquímica de la superfície dels elèctrodes de platí són revisats. Aquests pilars es relacionen primerament amb la topografia de la superfície perquè les correctes respostes electroquímiques de les àmplies terrasses i l'efecte dels esglaons de simetria diferent i dels setis ondulats són importants per a la caracterització *in situ*. L'adsorció d'anions té també un paper clau en les característiques selectives associades a la topografia de la superfície. Addicionalment, l'adsorció competitiva d'anions i d'altres espècies en solució té unes conseqüències importants en la reactivitat. De la mateixa manera, l'adsorció d'adàtoms és un procés sensible a l'estructura que afecta la composició de la superfície de l'elèctrode. Es poden considerar dos casos segons si l'adàtom pot formar una capa estable o més en la regió de potencial usualment enregistrada. En el cas de més d'una capa, els resultats es poden comparar amb els elèctrodes monocristal·lins corresponents, i s'obre així la possibilitat de relacionar el comportament característic d'ambdós sistemes.

**Paraules clau:** monocristalls de platí · adsorció d'anions · desplaçament de càrregues · adsorció d'adàtoms · multicapes · potencial de càrrega total zero

**Summary.** Here we review the building blocks of platinum electrodes in surface electrochemistry. These blocks are primarily related to the surface topography because the correct electrochemical responses of wide terraces and the effect of steps of different symmetry and kink sites are important for *in situ* characterization. Anion adsorption also plays a key role in the fingerprint features associated with surface topography. Additionally, competitive adsorption of anions and other species in solution have important consequences for reactivity. Likewise, adatom adsorption is a structure-sensitive process that affects the surface composition of the electrode. Two cases can be considered, depending on whether the adatom forms more than a single stable layer in the potential region usually scanned. In the latter case, when multilayers are generated, the results can be compared with those obtained from the corresponding single-crystal electrodes, with the possibility to compare the characteristic behaviors of the two systems.

**Keywords:** Platinum single crystals · anion adsorption · charge displacement · adatom adsorption · multilayers · potential of zero total charge

## Introduction

Surface electrochemistry is that part of physical electrochemistry that deals with the fundamental properties of the electrode/solution interface, including the role of surface structure and composition in reactivity and selectivity. The aims are similar to those in surface chemistry for solid/gas interfaces but involve a more complex scenario. Thus, the tools for probing surfaces in surface electrochemistry are very similar to the ones used in surface chemistry. However, due to the presence of the solvent (usually water), characterization techniques based on electron beams cannot be used. Also, water interference causes problems for *in situ* spectroscopic characterization techniques, since the water contribution has to be eliminated and a reasonable signal to noise ratio achieved. The usual approach to this problem is to accumulate spectra which are then

subtracted from a reference spectrum. *In situ* scanning tunneling microscopy (STM) and synchrotron techniques can also be used, the latter being limited to a few laboratories. In addition, the stability of the interface limits most of the studies to short temperature ranges, between the boiling and freezing points of the solvent.

In surface chemistry, a clean metal surface in ultra-high vacuum (UHV) environments can be defined as the surface in which only the metal atoms are present on the surface and any other atoms are below the detection limit. In contrast, in surface electrochemistry, the definition must include water and some ions of the supporting electrolyte, as these are in intimate contact with the surface, but no other additional species. This condition is difficult to assess because of the complex nature of the surface response to the applied potential and the only way to achieve it is to define very strict surface conditions and to use ultrapure solution reagents. In this respect, experiments with single-crystal electrodes have the advantage of a known nominal atomic density such that agreement between charge density and atomic density can be achieved with extraordinary precision. In turn, because of the very strict control of surface

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properties, the results of experiments such as those related to reactivity are valid not only with respect to reaction kinetics but also regarding fundamental double-layer thermodynamic parameters. Most of these reactivity-related and interfacial properties are structure sensitive; that is, they depend on the arrangement of the atoms on the surface.

Amongst pure metals, platinum is the most widely studied material in surface electrochemistry and this review will mainly deal with its properties. Accordingly, some of the building blocks of surface electrochemistry are discussed below, while the descriptions are limited as much as possible to criteria derived from purely electrochemical techniques. These experiments have provided information reflecting the *in situ* properties of the interface and they can be performed in most laboratories worldwide. Moreover, the results from other, complementary techniques should be compatible with those obtained in electrochemical experiments if the problem is well defined. In the following sections, the discussion of these experiments is restricted to platinum, although less active metals, such as gold, silver, and copper, have been studied at a fundamental level and the properties of some electrocatalytic metals, such as ruthenium, rhodium, and palladium, have recently received significant attention.

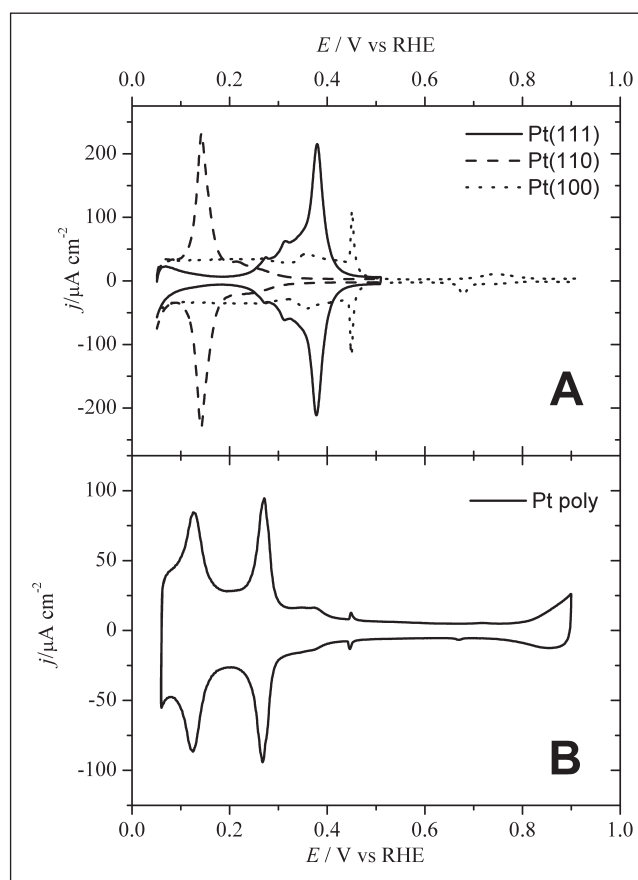
### The surface of the metal substrate

The origin of surface electrochemistry studies on platinum was the quest for the origin of the multiple peaks for hydrogen adsorption that appeared in the voltammetry of polycrystalline samples in contact with a clean test electrolyte, such as 0.5 M sulfuric acid. The characteristic voltammogram of these interfaces was well established in the 1970s, and a general consensus was reached in laboratories throughout the world to accept this fingerprint profile as representative of a clean polycrystalline platinum electrode surface. The voltammetric profile comprises, among other features, two reversible pairs of redox peaks attributed to the underpotential deposition/stripping of a monolayer of hydrogen prior to hydrogen evolution (Fig. 1). The weakly adsorbed couple appeared at 0.12 V, and the strongly adsorbed one at 0.28 V vs. the reversible hydrogen reference electrode (RHE). A third peak, at 0.22 V, was also observed in the positive-going sweep, associated with the use of clean solutions [36]. Will was the first to examine whether these two peaks were related to surface-structure heterogeneity, in experiments using single-crystal surfaces for the first time [118]. After contact with the solution, the electrode/electrolyte interface was cycled between hydrogen and oxygen evolution until a stable voltammogram was reached, *i.e.*, the same procedure used for polycrystalline electrodes. It was observed that the different orientations led to different hydrogen adsorption peaks, which could be then related to the different sites present on polycrystalline platinum. However, the measured charge density was too high compared to the expected value, easily calculated from the surface atomic density. As stated before, this expected value can be readily computed for single-crystal surfaces—unlike polycrystalline samples—from the ideal packing density of each orientation, assuming mono-electronic transfer for each platinum surface atom.

It was consequently proposed that electrochemical cycling induced surface roughness. Then, the goal was to measure the charge density on electrode surfaces not cleaned by this standard procedure, which led to reproducible voltammograms of polycrystalline platinum samples.

Avoiding cleaning of the electrode by cycling it through the oxygen adsorption region turned out to be a serious problem [62,112], as evidenced by the fact that the results reported by the different laboratories were not reproducible. Also, charge densities, in most cases and especially for Pt(111), were compatible with only a small fraction of the hydrogen monolayer. Hubbard's group achieved reasonable charge results but always routinely using one or two oxidation and reduction cycles prior to recording of the characteristic voltammogram [63,64]. It was clear, however, that the voltammetric profile of the hydrogen adsorption region was different for the different electrodes used [63,64,92,110,118].

The situation changed dramatically in 1980, with Clavilier's publication of flame-annealing pre-treatment [29–31]. The charge density under the voltammogram fit well with the surface atomic density and the peaks observed in polycrystalline samples were identified. In fact, the weakly adsorbed hydrogen was shown to be representative of the Pt(110) orientation that also accounts for the third peak, and the strongly bound state was observed with the Pt(100) electrode. In addition, new, unpredicted features appeared in the voltammograms; these were definitely considered as fingerprints of a particular surface



**Fig. 1.** Voltammetric profiles of the Pt(111), Pt(100), Pt(110) and Pt(poly) electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mV s<sup>-1</sup>.

orientation (Fig. 1). Thus, flame cleaning explained the origin of the surface heterogeneity of the observed voltammetric features and revealed other features that were never observed previously in polycrystalline samples. Consequently, a new series of problems appeared, namely, the correspondence between voltammetry and topography. The voltammetric profile previously resulting from flame annealing was considered as non-representative of the well-ordered surface, and again electrochemical cycling was proposed to obtain the profile corresponding to well-ordered surfaces [98–100]. The voltammogram after flame annealing was considered to represent a sort of frozen surface state that would evolve to the stable one after cycling. This interpretation was rapidly abandoned in light of data from stepped surfaces [81] and, particularly, when proper UHV-electrochemistry transfer experiments [1,123] were performed using well-defined surface techniques. To make a long history short, it was finally recognized that the electrochemical adsorption/desorption of oxygen led to disordered surfaces in most cases and that this happened especially with the two-dimensionally ordered basal plane electrodes. Definitive confirmation came when in situ STM images showed a flat surface after flame annealing and a disordered surface after a single excursion up to high potentials [18,40,65].

The most important consequence of this study was to realize the power of voltammetry as a surface-sensitive technique. It was evident that a simple examination of the voltammetric profile of a freshly prepared electrode allowed identification of the nature of the platinum surface used and assessment of its quality, in a way similar to that achieved by analyzing low-energy electron diffraction (LEED) patterns. Additionally, it was also possible to detect the presence of surface defects associated with characteristic adsorption states whose charge density would be a direct measure of their relative population on the whole surface. Moreover, as is the case with polycrystalline platinum, the voltammogram profile can be used to detect the presence of surface contamination, since sharp features would be less marked and less reversible because of the adsorption of impurities and subsequent blockage of these states for hydrogen adsorption. Surface contamination could be the result of incorrect preparation of the electrode surface in the flame-annealing/cooling step or of solution impurities. In the first case, the voltammetric profile may not show sharp features, but is stable upon cycling. If contaminants are present in the solution, the first voltammogram usually resembles the correct one but the adsorption charge decreases upon cycling as the impurities reach the surface and block the active sites.

Extensive topographic studies have been carried out with the most packed surface Pt(111) and its vicinal stepped surfaces [57,65,67,109]. Results suggest that cooling down in a reductive atmosphere ( $H_2+Ar$ ) is usually necessary to obtain better ordered surfaces, as thermal oxygen adsorption leads to disordered topographies. Accordingly, bulk electrodes may have the correct orientation on X-ray diffraction, but their surfaces may be completely disordered if the appropriate treatment is not used. This is especially important when stepped surfaces are studied. As a classical example, the voltammogram of Pt(S) [n(111)×(100)] electrodes shows the correct voltammetric pro-

file, with a single step contribution at 0.28 V RHE, only if the cooling step is performed in the absence of air oxygen [87]. In the latter case, a second contribution, in fact the most prominent one, at 0.12 V, corresponding to Pt(110) sites, also appears in the voltammogram. Under the appropriate cooling conditions, the voltammetry of stepped surfaces usually shows sharp peaks whose charge densities are related to the step density (it should be recalled that the density of terrace edge sites is the same as the step density). In a naive interpretation, sharp peaks usually suggest the presence of a single adsorption state on the surface and this is equivalent to the existence of widely ordered, nominally infinite, mono-dimensional surface-adsorption states. In the classical polycrystalline electrodes voltammogram, with the electrodes' surfaces activated by electrochemical cycling, the two main adsorption states are broader than in the preceding case, suggesting that cycling not only breaks the two-dimensional surface order of the terraces but also that of the steps. This was confirmed after preparation of kinked surfaces. In this case, in the absence of an electrochemical cycling step, not only were there two adsorption peaks for the step sites, as expected when two adsorption states having two different symmetry sites are present on the step, but also they were broader than on the corresponding single-stepped surfaces Pt(531) [17]. Kinked surfaces show chiral reactivity although this property should be examined with chiral probes, i.e., other than hydrogen adsorption [2,8,9].

Comparatively speaking, fewer studies have been carried out with Pt(100) [50,67,113]. Different reductive cooling atmosphere treatments of Ar [67],  $Ar+H_2$  [24,80] or, more dangerously, CO [67], are described as suitable to obtain the best possible surface topographies and the corresponding voltammetric profiles. The situation is more dramatic in the case of Pt(110) [79]. The cooling temperature is a key point in the preparation of reconstructed ( $2\times 1$ ) or unreconstructed surfaces [20,77]. In this latter surface, well-defined STM images have not yet been published in spite of serious attempts to achieve this goal. The lack of data points out the difficulties, still unresolved, in characterizing this elusive open surface at the atomic level. Based on trends from stepped surfaces, it would appear that the current flame-annealing standard pre-treatment would result in 85% defect-free Pt(100) [37] electrodes but only 50% defect-free Pt(110) electrodes as compared to nearly 99–100% defect-free in the case of Pt(111) [107].

Recent efforts have led to an improvement in obtaining nearly ideal surface topographies at the atomic level. This means that surfaces having terrace widths of 2–10  $\mu m$  can be prepared [117]. Although this method seems to be restricted to compact Pt(111) fcc surfaces, it will be crucial to study the reactivity of extremely well-ordered domains, which are sometimes masked by the presence of surface defects [54,70,74]. The results of these studies will supply the criteria needed to improve the preparation methods of more open surfaces. It should be stressed that surface order is a key parameter in understanding reactivity and the use of model electrodes should provide data on the role of ordered domains versus surface defects in electrocatalysis. This is particularly important when the reactivity of large molecules is under analysis.

## Charge displacement and anion adsorption

Following the interpretation of the adsorption states in polycrystalline Pt, the low-potential characteristic features observed on platinum single crystals, i.e., those that can be used as fingerprints of their surface state, were originally assigned to hydrogen adsorption at the (sub)monolayer level. This assignment was reinforced by the good correspondence between the experimental charge density and the theoretical atomic packing density of the corresponding surface [29,30,38]. In the case of Pt(111) and its vicinal surfaces, this agreement was extremely good and the small charge excesses measured on Pt(100) and Pt(110) could be attributed to the consequence of surface reconstruction, a phenomenon well-described in UHV for both orientations [38,86]. Following the first studies with flame-annealed electrodes, it was, however, suggested that the high adsorption state of Pt(111) in perchloric acid could not be compatible with the adsorption energies of hydrogen on these surfaces as measured in UHV [112]. A possible explanation was that the strong fields present on the electrode/electrolyte interface were claimed to be responsible for this extraordinary adsorption energy [38,69]. Alternatively, several authors considered that anions, including OH, accounted for a significant fraction of the charge transfer measured in the high-potential region [66,111]. This double interpretation remained for more than ten years in the literature. For characterization purposes, it was clear that the total charge density values agreed reasonably well with the surface packing density and were essentially correct from a quantitative point of view, but interpretation of the origin of the charge transfer, e.g., the species involved in the redox process, remained under discussion. As so frequently happens, the existing set of experimental data could not univocally support a unique interpretation, one that excluded other options.

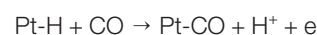
The required new experiment came when other surface probes, such as CO, were studied on Pt single crystals. CO is an important molecule in surface electrochemistry, not only because it is the main surface poison in fuel-cell research but also because it undergoes a characteristic structure-sensitive, anion-dependent oxidative stripping reaction in the adsorbed state:



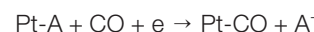
In this reaction, CO is stripped from the surface, which then becomes clean because none of the products can be adsorbed at these potential or concentration conditions. Simple measurement of the stripping charge was used for characterization purposes, since, in principle, it should be twice that measured in the lower potential region, as extensively reported and accepted in polycrystalline Pt samples.

Previously, CO experiments were mainly interested in oxidative stripping of the adsorbed CO layer, which fully covered the single-crystal electrode. The use of single-crystal electrodes, especially Pt(111), enabled the use of other complementary techniques, such as Fourier transform infra-red (FTIR) spectroscopy, radiotracer experiments with radioactive isotopes, and STM in situ images. It was observed that while

the stripping charge of the complete monolayer was close to CO coverage values of almost unity [20,43], the techniques that were sensitive to the molecular nature of the reactant and products supported a considerably lower coverage [15,116]. This contradiction between measured charges and molecular information was not satisfactorily resolved and required arbitrary corrections. The explanation came from the so-called CO displacement experiment, which was first carried out on the Pt(111) electrode, e.g., that in which different coverage was determined, and on the Pt(110) electrode [20]. In the genesis of that experiment, CO was expected to adsorb strongly on Pt(111) because it was able to displace iodine from the surface [123]. Accordingly, it was expected that any species coming from the aqueous solution of the test electrolytes, such as perchlorate and sulfate anions, would be also displaced. In contrast to voltammetry, in which hydrogen adsorption and anion desorption are reductive processes, the displacement experiment was able to prove a difference in the sign of the displaced current: if the potential at which the experiment is carried out corresponds to a surface covered by adsorbed hydrogen, then:



and an oxidation charge is recorded. However, if anions are adsorbed at the potential at which the experiment is made, then:



and a reduction current is observed. The displacement charges correspond to the reverse of the initial charge on the electrode surface at the potential at which the experiment is carried out:

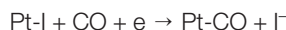
$$q_{\text{disp}} = q_f - q_i \cong -q_i$$

because the final charge density of an electrode covered by adsorbed CO is negligible compared to the charge of the electrode in the absence of CO, in most cases.

The experiment agreed with the existence of (at least) two different adsorbates being responsible for the charge transfer resulting in the characteristic voltammetric features [20,41,53,85]. As a first consequence, the CO stripping experiment, in which the electrode surface becomes clean, needed a significant double-layer charge restoration because anions should be finally fully adsorbed at the upper potential limit of the sweep [20]. Once corrected, the results of the different techniques nicely agreed with the coulometric data and CO coverage was accepted to be about 0.7 on Pt(111).

A second consequence was the establishment of a correspondence between the displaced charge and the electrode coverage. To achieve this, some essential conditions must be fulfilled: the charge displacement experiment is quantitative if, and only if, the displacing agent behaves as a neutral probe in its adsorption step. This means that the CO adsorption step should not involve charge transfer. To confirm this condition, a monolayer of iodine on Pt(111) whose coverage is precisely known [94]

within the experimental error limits of the displacement experiment was displaced according to the following reaction:



The reduction charge displaced at different potentials corresponded to a reductive process and was the same at different potentials, involving a number of iodine atoms that agreed with the coverage expected from STM experiments [19]. Thus, CO could be considered as a neutral probe and the source of the displaced charges coming only from the other adsorbates. For purposes of consistency, I<sub>2</sub> was also used as the displacing agent, with the results confirming those obtained by CO displacement [58]. Iodine has the advantage that the displacement process is able to directly check the behavior of the OH adsorption step observed on Pt(111) in perchloric acid.

The displaced charges are usually dependent on the potential at which the experiment is carried out. At low potentials, the oxidative process is related to the displacement of hydrogen adsorbed on the surface, while the reductive processes observed at high potentials are related to the displacement of adsorbed anions. Thus, there is an intermediate potential at which the displaced charge is zero. This particular potential was assigned, as a first approximation, to the potential of zero total charge (pztc) of the electrode ( $-q_i = 0$ ). The value of this final charge may be estimated based on several assumptions about Pt(111), with a refined value of the displaced charge then obtained together with a better estimation of the pztc [52,115].

Knowledge of the pztc of the different electrodes is important from a fundamental viewpoint because molecular [7,34] and anion adsorption coverage can be estimated if the formal charge number, the electrosorption valency, is defined [50,82,84]. The effect of step dipoles [52] can be checked as well as the adsorbed adatoms or adlayers. The study also can be extended to other metals [6,120]. The charge displacement method can be used with polycrystalline and dispersed materials [16] and local effects evaluated by comparison with other surface probes such as N<sub>2</sub>O [10,34]. Moreover, macroscopic determinations of the pztc values can be compared to pulsed-laser microscopic determinations of the potentials of maximum entropy of the double layer [32,33,45–49]. Relevant data to quantitatively explore and model the metal/electrode interface of hydrogen adsorbing electrodes can then be obtained.

### Foreign adatom layers

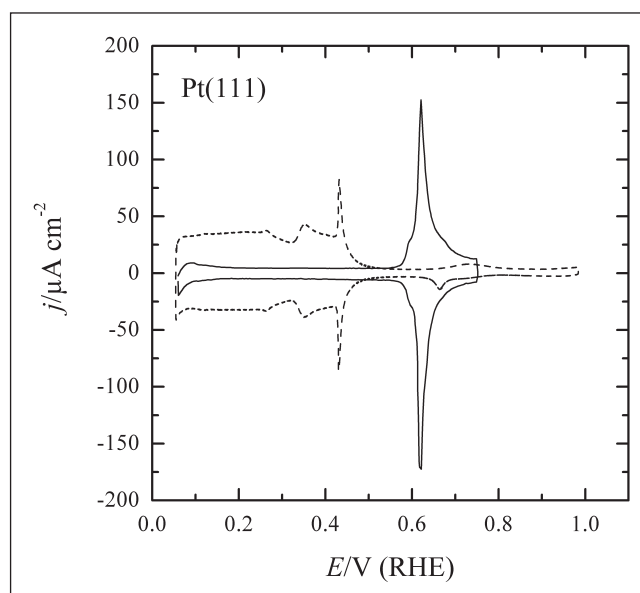
Once the main problems, i.e., those related to the control of surface order and determination of the relevant surface species transferring the charge, are solved, the surface composition is checked. Strictly speaking, surface composition effects should be studied on well-defined alloy electrodes. However, the difficulty in this experimental framework is enormous. As is well known, the surface may be different from the bulk composition, which is the parameter that can be easily controlled. This effect will be more evident if one considers that flame annealing or any other high-temperature cleaning method is required. To prop-

erly characterize alloy surfaces, UHV techniques should be used and the electrode safely transferred to the cell prior to any electrochemical experiment; that is, it is not possible to perform the flame-cleaning step routinely because the surface composition may change after each treatment and the surface would continuously become enriched in one of the components.

To solve this problem in a first approach, the deposition of (sub)monolayers of foreign atoms on a well-defined single-crystal substrate electrode has been fruitful. The optimal situation is that in which adatom coverage remains stable on the substrate surface over a wide range of potentials, even if the adatom ions are not in solution. This is achieved in those cases in which there is irreversible adsorption of the adatom [28,44]. The irreversibility of the adsorption step guarantees that the surface composition remains stable in the absence of other ions in solution that could adsorb and therefore modify the composition. A second, quite important property is that in which the adsorbed adatom undergoes a surface process whose charge density is proportional to its surface concentration (Fig. 2). This occurs when the adatoms are subjected to a surface redox process in a well-defined range of potentials, one that is likely different from that in which the substrate adsorption states appear. A comparison between the two signals is an internal test to check the presence of uncontrolled contaminants in the adatom dosing step. In these cases, it is possible to continuously vary the surface composition of a single-crystal electrode and to compare the change in reactivity of a particular reaction by varying the surface composition. Once the reactivity step is performed, the electrode surface may be studied again in a clean cell to check whether the composition of the electrode is the same as at the beginning of the experiment.

Among the best characterized, irreversibly adsorbed systems, As on Pt(111) can be considered as a simple system in which charge density is conserved over the entire range of potentials between 0.7 V and the beginning of hydrogen evolution [13,22,83]:

$$q_{(111)} = q_{\text{Pt}} + q_{\text{As}}$$



**Fig. 2.** Comparison of the voltammetric profiles of a Bi covered Pt(111) (full line) and an unmodified Pt(111) electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mV s<sup>-1</sup>.

where the value of  $q_{(111)}$  is  $241 \mu\text{C}\cdot\text{cm}^{-2}$ ,  $q_{\text{Pt}}$  is the charge under the remaining adsorption states of Pt, and  $q_{\text{As}}$  is the charge of the surface redox process of adsorbed As. Diminution of the substrate charge reflects adsorption of the adatom as it progressively covers the surface. The adatom redox process remains constant in the RHE scale while the solution pH is varied, thus supporting the formation of surface oxygenated species. Finally  $q_{\text{As}}$  amounts to  $241 \mu\text{C}\cdot\text{cm}^{-2}$  at full substrate blockage. It was shown that this value is independent of the anions present in solution, and any contribution of anion adsorption to the redox surface reaction of adsorbed As was discarded by FTIR spectroscopy [59,83]. The linear relation described above, together with As chemistry and the fact that As atoms are bigger than Pt atoms, suggests a surface stoichiometry in which each As adatom blocks three surface sites. In the redox process, As exchanges three electrons to maintain the charge balance. This model implies a  $(\sqrt{3}\times\sqrt{3}) R30^\circ$  structure of adsorbed As on the surface, as shown by STM [83]. It was also shown that the redox process involved the formation of As III oxygenated species [122], as inferred by simple electrochemical measurements. Since no other solution species, except water, participates in the redox process, temperature effects could be analyzed (thermodynamically), with the data supporting the formation of  $\text{As}(\text{OH})_3$ , at potentials higher than that of the redox process, prior to further oxidation to soluble As (V) species [22].

In contrast to As, the case of Bi on Pt (111) yielded more elusive results. In this case, the charge densities led to a calibration curve whose slope suggested that the number of electrons per Bi adatom is 2, a number not usual in bismuth chemistry [25,42]. Electrochemical results suggested that the surface structure of the adlayer was the same as in the case of As at full Bi coverage, with the pH shift pointing to the formation of hydroxylated species. The possible contribution from other species such as anions may in this case be problematic [35]. Nonetheless, Bi-Pt has been shown to be an extremely good electrocatalytic system to oxidize formic acid [24,26,27,60, 61,71,95–97,101–103]. This has led to a series of studies that finally achieved the preparation of intermetallic Pt-Bi compounds serving as practical electrocatalysts [14,93]. Moreover, the intermetallic compound Pt-Pb was also prepared [78] and was shown to be more active than Pt-Bi in formic acid oxidation, as suggested in earlier studies on polycrystalline platinum substrates [114,119]. The problem is that irreversibly adsorbed Pb on Pt(111) is not stable, with the main redox process always leading to adatom dissolution in acid medium [23,42]. Therefore, in fundamental studies performed with single-crystal electrodes the system has been less explored than the one involving irreversibly adsorbed Bi.

One interesting aspect of irreversibly adsorbed adatoms is the preferential adsorption on step sites over terrace sites. This allows modification of step composition while keeping the terrace sites free of adatoms. This has led to reactivity studies on defects generally considered to be the most reactive surface sites. It was shown that step decoration requires the use of electropositive adatoms, as electronegative ones also adsorb to the terrace [56]. These decorated surfaces have been useful to demonstrate that Pt(111) terraces are almost inactive to-

wards several technologically important reactions, such as the self-poisoning of HCOOH, which only takes place on step sites, preferably those with (110) symmetry, and not on (111) terraces, which, in turn, are very sensitive to the direct oxidation of formic acid when modified by irreversibly adsorbed Bi [74–76]. This inhibition of poisoning may also explain the origin of the extremely high enhancement of reactivity towards HCOOH oxidation observed in this particular (Pt(111)-Bi) case (a 40-fold increase in the current measured at 0.5 V).

One of the advantages of irreversibly adsorbed Bi over As is that the surface redox process on Pt(111) takes place within a potential range that is selectively different from the one on other planes [28]. If stepped surfaces are used, the charge density involved in the Bi redox process can be confirmed as being linear with the terrace atomic density at full substrate blockage [89,90]. This charge is not influenced by contributions from any other orientation in which Bi also adsorbs. It can be concluded, also using stepped surfaces, that the charge density involved in the Bi redox process is linear with the terrace atomic density at full substrate blockage. This charge is not influenced by contributions from other orientations in which Bi is also adsorbed, which has the advantage that Bi can be used as a probe to determine the fraction of terrace sites with (111) symmetry on polycrystalline platinum samples [90,104]. Similar properties have the redox process coming from irreversibly adsorbed Ge [91,104]. In this case, the relevant orientation is that of Pt(100) terrace domains, which are proportional to the charge density under the adatom-related signal at full coverage. Incidentally, Te adatoms could be used as probes for simultaneous calibration of (111) and (100) sites, because the characteristic redox reactions are observed in different potential ranges, provided that the substrate-characteristic hydrogen-anion adsorption region suggests that signal overlap for intermediate surface structures is unlikely [89]. In any case, Te can be used as a second probe to verify the predictions from both Bi and Ge on a particular type of site as well as to check the overall result. Irreversibly adsorbed Te has been satisfactorily characterized by STM and the adlayer structures found to be compatible with the electrochemical determinations [88,121].

These three surface probes (Bi, Te, and Ge) have been used to determine the fraction of (111)- and (100)-ordered domains present in different samples of nanoparticles [89,104]. Also, deconvolution of the voltammetric profile in the low-potential region has been applied for the same purposes. The results obtained with the two procedures are in good agreement, which supports the consistency of both experimental charge-density measurements to obtain relevant surface-structure information. The relative fraction of the different sites is very important when the electrocatalytic results of the different nanoparticle samples have to be rationalized with respect to surface structure [55,105,106,108] and it is always convenient to determine the site distribution by *in situ* methods.

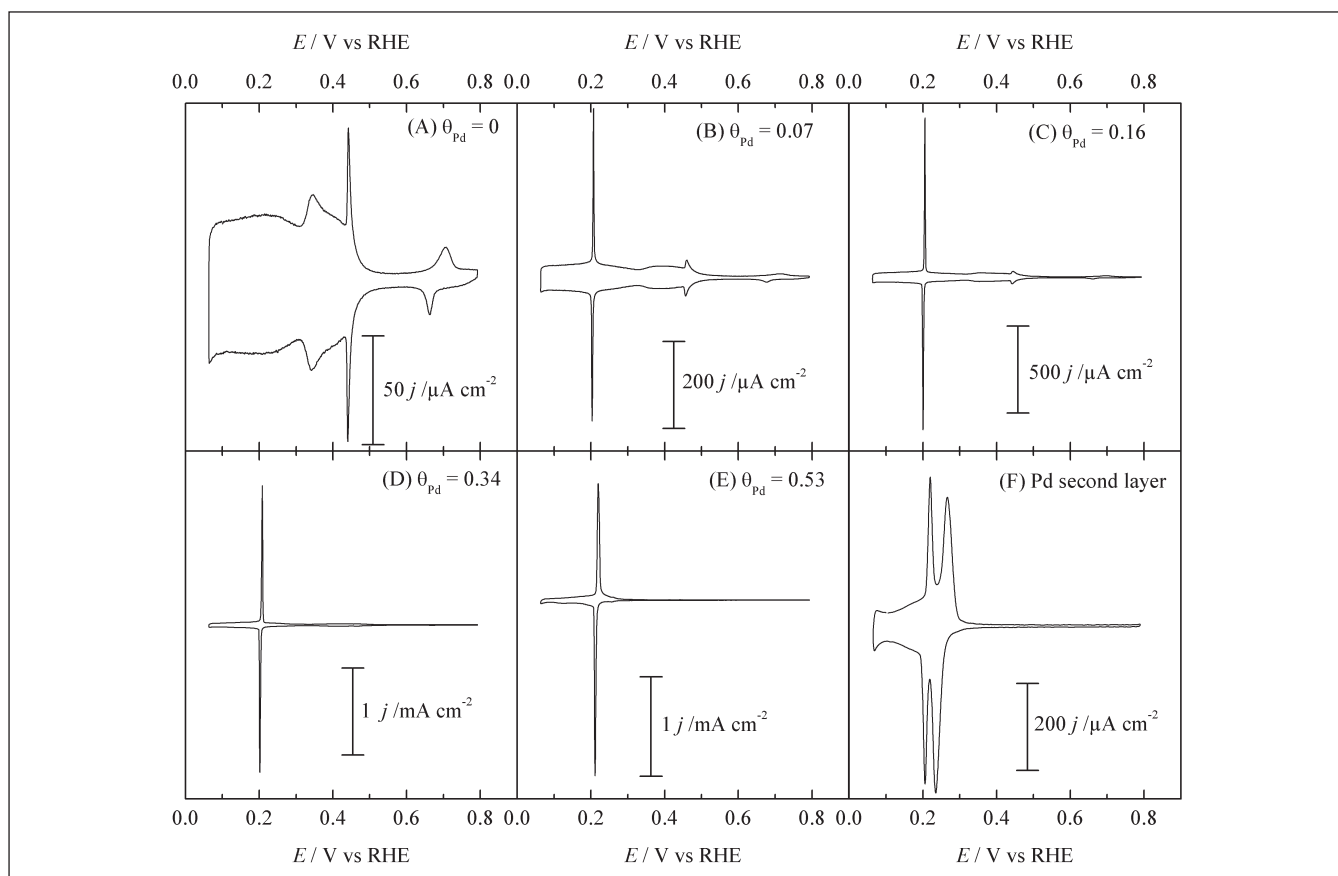
An important group of adatoms are noble metals, which also deposit on the platinum surface as a (sub)monolayer. In this case a driving force is usually necessary to fully achieve the surface process, *i.e.*, either chemical (such as hydrogen) or electrochemical deposition. As a function of the adatom

amount, several characteristic features appear in the voltammogram, which can then be used to precisely define the surface composition and to evaluate the surface coverage, analogous to non-noble adatoms, but usually in the low-potential range, e.g., particularly linked to hydrogen adsorption.

A paradigmatic example is palladium deposited on Pt(111), a system in which epitaxial growth was anticipated because of the almost identical lattice parameters of the two metals [3–5,12,21] (Fig. 3). From the electrochemical viewpoint, during the first stages of Pd deposition a new adsorption state appears at 0.205 V, while the characteristic voltammetric features of the substrate diminish. As deposition proceeds, the palladium state becomes larger and extraordinarily sharp but, unlike the irreversibly adsorbed non-noble metal, the sharp spike at 0.45 V characteristic of wide Pt(111) terraces is still observed. This fact suggests that Pd deposition takes place in islands, likely stabilized by anion adsorption on the substrate and on the foreign adatom layer. Island growth was corroborated by FTIR spectroscopy of adsorbed CO, showing absorption bands at  $1910\text{ cm}^{-1}$  (Pd) and  $2060\text{ cm}^{-1}$  (Pt), irrespective of the palladium coverage and therefore suggesting a uniform neighborhood at the atomic level [39,51]. Characterization may be achieved by plotting the charge density under the palladium-related signal against the remaining substrate charge density, but in this case it is also possible to perform CO charge-displacement experiments that evaluate the role of the anions and of the pzfc (or the potential of zero free charge, pzfc, after the same assumptions necessary for the platinum substrate) [4,6].

Interestingly, once the first adatom-related peak develops, a second adsorption state starts to appear at potentials lower than the first one [3,73]. This suggests the growth of a second layer—actually of several layers, as determined by UHV techniques—that start to deposit on the surface [11]. In this respect, the noble metal atoms deposited on platinum (or other noble-metal single-crystal surfaces, such as gold) constitute a unique group in which it is possible to compare differences, at fundamental or applied levels, between the first layer on top of the substrate and further layers, eventually reaching the behavior of the bulk material which, in turn, can be compared with the same characteristic parameters of the corresponding single-crystal electrode. This comparison cannot be made with the previously discussed non-noble adatom adlayers, in which the stability of the deeper layers, or even that of a compressed first adlayer, is much lower in the potential range used to characterize the surface. Conversely, the stable layers, usually involving a coverage value between 0.33 and 0.50, can be safely studied.

In the case of Pd on Pt(111), the pzfc, measured by extrapolating the free charge in the apparent double-layer region, leads to a value lower than that of Pt(111) and the difference between the two pzfc values coincides with the work-function differences of the two metals [4]. This serves as an additional test, albeit an indirect one, of the free charge estimation procedure. Contrarily, the pzfc of the first Pd monolayer lies between the two extreme values, which can explain the electrocatalytic properties of the single adlayer [72]. In this type of system, more experiments are required to confirm the observed trends. Palladi-



**Fig. 3.** Evolution of the voltammetric profile of the Pt(111) electrode upon deposition of a Pd layer in 0.5 M  $\text{H}_2\text{SO}_4$  at  $50\text{ mV s}^{-1}$ .

um adlayers are also important to check substrate effects, as they can be deposited on single-crystal gold electrodes and other metal surfaces [6,68]. This would offer a unique system in which full monolayer adsorption may be performed under controlled conditions and the properties compared for a particular structure-sensitive reaction. It is evident that additional studies are needed in this area in order to discover all the possible interfacial and reactivity effects associated with these single layers.

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