Underpotential Deposition of Copper on Pt(S)[n(100)x(110)] Stepped Surfaces

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Introduction

The process of metal underpotential deposition (UPD), that is, the deposition of a monolayer of a metal on a foreign substrate, which takes place at higher potentials than the bulk deposition process, has been widely studied with different aims. First, the initial deposition of the first monolayer can often be understood as the initial stage in the bulk deposition of metals. The structure and growth of this first layer can affect significantly the deposition of the following layers. It should be stressed that the formation of the initial layer is significantly affected by the presence of anions, and both the structure and the kinetics of the formation of the adlayer depend on the anions present on the surface. Secondly, the modified electrodes covered with different submonolayer amounts of foreign metal adatoms have been used in electrocatalysis to improve the catalytic properties of the metal substrate. Since UPD processes markedly depend on the geometric arrangement of atoms on the surface of the substrate, these effects can be more easily understood and rationalized using the simpler basal plane surfaces. For these surfaces, the structure is well characterized at atomic level and the electrocatalytic effects of the underpotentially deposited layer can be easily separated from other possible effects. Additionally, the surface structure of the UPD layer can be investigated in situ using surface probe techniques such as STM or X-ray diffraction, allowing the determination of the structural parameters of the adlayer that are related to the modification of its electronic properties. Thus, it is well known that a single layer of a metal deposited on top of a different metal may have an electrocatalytic activity that is different from that observed for both pure metals, since the electronic structure of the top-most atoms are heavily affected by the presence of the underlying layer of different

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Abstract: The underpotential deposition of Cu on platinum stepped surfaces composed of (100) terraces and (110) monoatomic steps has been studied in different acidic solutions. It has been found that the initial stage of copper deposition on the surface takes place simultaneously on terrace and step sites, irrespective of the nature of the adsorbing anion. During the voltammetric deposition of a full monolayer, several peaks can be observed. The analysis of the dependence of the peak charge with the step density allows assigning the different peaks to different deposition sites. The peak appearing at most positive potentials corresponds to the deposition of Cu on the terrace sites, whereas deposition on the step sites gives rise to different voltammetric contributions depending on the anion present in solution. Additionally, it has been found that the charge transferred upon Cu deposition is very close to 2e and that the anion coverage does not change during this process from that initially present on the platinum substrate.

Key words: Pt single crystal electrodes; copper; underpotential deposition; step decoration

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1 Introduction

The process of metal underpotential deposition (UPD), that is, the deposition of a monolayer of a metal on a foreign substrate, which takes place at higher potentials than the bulk deposition process, has been widely studied with different aims. First, the initial deposition of the first monolayer can often be understood as the initial stage in the bulk deposition of metals. The structure and growth of this first layer can affect significantly the deposition of the following layers. It should be stressed that the formation of the initial layer is significantly affected by the presence of anions, and both the structure and the kinetics of the formation of the adlayer depend on the anions present on the surface. Secondly, the modified electrodes covered with different submonolayer amounts of foreign metal adatoms have been used in electrocatalysis to improve the catalytic properties of the metal substrate. Since UPD processes markedly depend on the geometric arrangement of atoms on the surface of the substrate, these effects can be more easily understood and rationalized using the simpler basal plane surfaces. For these surfaces, the structure is well characterized at atomic level and the electrocatalytic effects of the underpotentially deposited layer can be easily separated from other possible effects. Additionally, the surface structure of the UPD layer can be investigated in situ using surface probe techniques such as STM or X-ray diffraction, allowing the determination of the structural parameters of the adlayer that are related to the modification of its electronic properties. Thus, it is well known that a single layer of a metal deposited on top of a different metal may have an electrocatalytic activity that is different from that observed for both pure metals, since the electronic structure of the top-most atoms are heavily affected by the presence of the underlying layer of different

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composition\(^8\)-\(^{10}\). When submonolayer coverages are obtained, the ensemble of a free substrate site adjacent to an UPD atom can also have different electrocatalytic properties\(^{11}\) and accelerate the desired reaction or block an unwanted side reaction.

When more complex surfaces are used, that is, stepped surfaces, these studies may acquire an additional interest derived from the fact that initial stages of deposition may specifically cover particular sites, resulting in a regular distribution of adatoms on the surface. This is normally the case for the early deposition of copper on surfaces with (111) terraces and (110) or (100) steps\(^{12\text{-}14}\), for which the adatoms preferentially cover the step sites, leaving the terrace sites uncovered. Those "decorated" surfaces are excellent tools to understand the reactivity of both the unmodified and the modified surfaces\(^{15\text{-}17}\). First, the deposited adatom on the step can display special electrocatalytic properties. Second, by selectively blocking the reactivity of the step (or terrace) sites, the reactivity of specific sites can be studied and analyzed without the interference of the other sites on the surfaces, highlighting particular effects\(^{15\text{-}16,18\text{-}19}\). Finally, these types of surfaces can be used to create templates where different structures can be grown.

When the initial deposition takes place on a stepped surface, the first deposited adatoms may attach either to the top or to the bottom of step sites, or onto the terrace. On the platinum stepped surfaces with (111) terraces and (110) or (100) steps, the deposition of electropositive atoms, such as Cu, Bi or Pb, takes place on the step, whereas deposition of electronegative atoms such as Se or S occurs on the upper part of the step or on the terrace\(^{12\text{-}20,21}\). This behavior has been interpreted by taking into account the presence of a surface dipole on the step linked to the Smoluchowski effect\(^{22}\). For these stepped surfaces, the value of the dipole is large and leads the initial deposition of the adatom into particular sites. For the surfaces with (100) terraces, this process has been less investigated. For surfaces with (100) terraces and (111) steps, the initial deposition stages of Cu occur simultaneously both on the terrace and step sites\(^{23}\), probably due to a lower energetic difference between both types of sites. In this work, the UPD process on the other series of stepped surfaces with (100) terraces has been studied, to understand how the surface structure of the substrate affects the deposition process, both in the initial stages and during the formation of a full monolayer. The study has been carried out in perchloric and sulfuric acid solutions and also in acidic solutions containing chloride anions to elucidate the effects of the anion specific adsorption on the deposition process.

## 2 Experimental

Platinum surfaces having (100) terraces and (100) monoatomic steps have been studied. The Miller indexes of these surfaces, which belong to the [100] zone, are Pt \((n, 1, 0)\), where \(n\) denotes the number of atomic rows on the terrace. According to the Lang, Joyner and Somorjai notation\(^{24}\), these surfaces can be named as Pt(S)\([(n+1)(100)\times(100)]\). From these series, the surfaces with \(n = 2, 5, 10\) and 20 have been employed in this study. It should be noted that the surface with \(n = 1\) corresponds to the Pt(110) surface, which clearly indicates that the ensemble of the (100) step site and the neighboring (100) terrace site creates a (110) site. For that reason, these surfaces can be also described as Pt(S)\(\[n(100)\times(110)]\).

The platinum electrodes were prepared following Clavilier’s method\(^{25}\). Prior to any experiment, the electrodes were annealed and cooled down in an Ar:H\(_2\) reductive atmosphere. This method produces surfaces with topographies close to the nominal structure\(^{26}\), although some restructuring of the step line may occur\(^{27}\). After the flame annealing, the electrode was protected with a drop of ultrapure water saturated in those gases and transferred to the electrochemical cell.

Experiments were carried out at room temperature in classical two-compartment electrochemical cells de-aerated by using Ar (N50, Air Liquide in all gases used), including a large platinum counter-
electrode and a reversible hydrogen (N50) electrode (RHE) as reference. The voltammetric experiments were recorded with a potentiostat (eDAQ EA 161), a signal generator (EG&G 175) and a recording system (eDAQ e-corder ED401) connected to a computer.

Experimental solutions were prepared with ultrapure water (ELGA PURELAB ultra system, 18.2 MΩ·cm), sulfuric acid (Merck Suprapur, 96%), perchloric acid (Merck Suprapur, 70%), sodium chloride (Merck Suprapur), CuSO₄·5H₂O (Merck Pro-Analysis) and CuO (Merck Pro-Analysis).

3 Results and Discussion
3.1 Voltammetric Behavior of the Pt(S) [n(100)×(110)] Electrodes

Before addressing the study of the effect of the anion and steps on the Cu UPD process, the voltammetric behavior of the stepped surfaces in this series will be analyzed. Although there has not been a detailed study of the surfaces belonging to this zone in acid solutions, the effect on the voltammogram of the increasing step density and the comparison with the behavior observed for the surfaces with (100) terraces and (111) steps allow drawing some conclusions on the origin of the different voltammetric peaks. Fig. 1 shows the voltammetric profiles of the electrodes in the different electrolytes. In the absence of specific adsorption of the anion, Fig. 1B, the voltammogram shows broad peaks and three different regions can be distinguished: below 0.25 V, between 0.25 and 0.50 V and above 0.50 V. From the behavior of the Pt(100) electrode in perchloric acid solutions and the changes observed as the step density increases, the different peaks can be assigned to different adsorption processes. Thus, it is clear that the signals below 0.25 V correspond to hydrogen adsorption on the steps. In fact, a clear contribution at 0.12 V develops for the surfaces with a high step density, which coincides with the main contribution observed for the Pt(110) electrode. Hydrogen adsorption on the terrace occurs in the potential region between 0.25 and 0.5 V where two main contributions appear: the one at the most positive potentials decreases with the step density and can be ascribed to wide terraces, whereas the second one, at ca. 0.30 V, would correspond to the adsorption of hydrogen on terrace sites close to the step (since a peak at identical potential is observed for surfaces with (111) terrace and (100) step, this peak can be assigned to the combination of adjacent (100) and (111) sites). This peak is smaller and wider than that obtained for the Pt(S)[n(100)×(111)] stepped surfaces. On the other hand, the signals above 0.5 V in the voltammogram for the Pt(100) electrode have been ascribed to OH adsorption. These signals shift towards higher potential values and diminish in charge as the step density increases.

The presence of adsorbing anions in the supporting electrolyte produces significant changes in the voltammetric profile. Fig. 1A shows voltammetric profiles of some of the electrodes belonging to the [100] zone in 0.1 mol·L⁻¹ H₂SO₄. As before, it is clear that the states above 0.31 V correspond to processes occurring on the terraces sites, since the charge in this region diminishes as the step density increases. On the other hand, the current at potentials below 0.31 V increases as the step density increases, which reveals that the adsorption processes at these potentials could be associated to the step or adjacent sites. When compared to the analogous contribution observed for surfaces having (100) terraces and (111) steps, it should be highlighted that the peak width in this case is wider (60 mV for the (110) steps vs. 40 mV for the (111) steps in surfaces with similar terrace widths, measured at the base of the peak) and the peak appears at slightly higher potentials (0.275 V for the (110) steps vs. 0.285 V for the (111) steps) which reveals the different effect of the step on the energetics on the corresponding neighboring sites. It should be noted that the surfaces close to the (110) pole present in this media peaks at 0.14 and 0.17 V, whereas no other contributions are measured above 0.3 V. Thus, it is expected that all the contributions from the (110) steps
appear at low potential, as it is clearly observed for the Pt(210) electrode.

From the comparison between perchloric and sulfuric acid media, the role of the anion adsorption in the voltammetric behavior can be assessed. For the Pt(100) electrode, the voltammetric profiles in both media below 0.30 V overlap, which indicates that anion adsorption (OH in perchloric acid and sulfate in sulfuric acid solutions) takes place only at higher potentials. As aforementioned, OH adsorption takes place in the region between 0.50 and 0.60 V for perchloric acid solutions. If sulfuric acid is added to the electrolyte, the broad hydrogen + OH adsorption processes on the terraces are replaced by a sharper new peak at 0.38 ~ 0.40 V. This new peak is then ascribed to the competitive adsorption/desorption processes of hydrogen and specifically adsorbed anions. The broad peak at 0.67 V observed in sulfuric acid solutions for the Pt(100) electrode is most likely related to the replacement of sulfate by OH anions on the (100) terrace sites. Thus, the voltammetric zone below 0.31 V could be tentatively ascribed to processes taking place close to (110) step sites. Hence, the competitive adsorption between sulfate and hydrogen on sites adjacent to the step site gives rise to the peak at 0.28 V, as has been proposed previously. On the other hand, the increase in the current observed in the region between 0.1 ~ 0.2 V is most likely related to the hydrogen adsorption on the step site. No anion adsorption has been detected in this region for the structurally similar n(100)×(111) stepped surfaces, and therefore it can be assumed that only hydrogen adsorb at these potentials also for the present surfaces.

In the presence of chloride anions (Fig. 1C), the voltammetric profile resembles that of sulfuric acid solutions. As a consequence of the higher adsorption strength of chloride in comparison with that of sulfate, the peaks in this case are sharper and appear at lower potential values. As in the case of

![Voltammetric profiles](image)

Fig. 1 Voltammetric profiles of the Pt(S)[n(100)×(110)] electrodes in 0.1 mol·L⁻¹ H₂SO₄ (v = 50 mV·s⁻¹) (A), 0.1 mol·L⁻¹ HClO₄ (v = 50 mV·s⁻¹) (B) and 0.1 mol·L⁻¹ HClO₄ + 1 × 10⁻³ mol·L⁻¹ NaCl (v = 10 mV·s⁻¹) (C). Arrows indicate the changes upon the increase of the step density.
sulfuric acid solution, the sharp peaks are related to competitive adsorption processes between hydrogen and chloride anions\[39\]. The peak at 0.29 V is related to these competitive processes on the terrace, whereas the signals below 0.22 V are associated to steprelated processes. The peak at 0.21 V increases with the step density, and thus must be related to adsorption processes on step or adjacent sites. This latter peak is not as prominent as the equivalent peak observed in sulfuric acid solution at 0.275 V.

3.2 Initial Stages of Copper Deposition on the Stepped Surfaces

Fig. 2 shows the initial deposition process of copper in a 0.1 mol·L\(^{-1}\) H\(_2\)SO\(_4\) solution for different Pt(S)\([(n)(100)\times(110)]\) electrodes with \(n = 20, 10, 7\) and 5 terrace atomic rows. To have access to the very initial stages of Cu deposition, a very low Cu concentration (2 × 10\(^{-6}\) mol·L\(^{-1}\)) was used. Under these conditions, the rate of deposition is limited by mass transport, being so low at this concentration that the changes upon deposition can be followed through the changes in the voltammetric profile during the potential cycling. The upper limit of the potential scan was reduced to 0.5 V to avoid any Cu dissolution from the electrode surface. As can be seen in Fig. 2, a new voltammetric peak can be distinguished growing at 0.355 V. This peak splits into two for some surfaces and Cu coverages. Parallel to the development of this peak, the adsorption states assigned to the bare platinum surface diminish. Thus, a diminution is observed of the states at 0.39 V corresponding to the adsorption on the terraces as well as those at 0.275 V corresponding to adsorption on sites close to the step. Also, a small diminution of the adsorption states below 0.2 V, corresponding to the step sites, can be detected. From this behavior it can be concluded that the initial stages of Cu deposition take place simultaneously on both terrace and step sites. Although some preference for deposition on steps can be deduced from the behaviour reported in Fig. 2, the situation is very different to that observed for the surfaces with (111) terraces, where the deposition on the terrace only takes place when the step has been completely decorated\[12, 40\]. For the surfaces studied here, a diminution of the adsorption processes related to the terrace is observed even in the first Cu deposition cycles. Still, the voltammetric behavior of these surfaces is much more complex than that corresponding to the stepped surfaces with (111) terraces, for which the voltammetric contributions from terraces and steps can be easily separated. Hydrogen adsorption on the (111) terrace gives rise to a broad feature between 0.06 and 0.35 V that can be described, according to a Frumkin isotherm, with a large repulsive parameter\[41\]. On the other hand, hydrogen adsorption on the step occurs on a narrow single peak at 0.125 V and 0.26 V for (110) and (100) steps, respectively. Other overlapping contributions between 0.25 and 0.4 V can be associated to the (100) terraces\[28, 42\].

Due to this complex relationship between sites and voltammetry, it cannot be discarded that the deposition of Cu on the step modifies the energetics of hydrogen adsorption on the terrace leading to changes in the voltammetric profile associated with the terraces. In fact, a distribution of the adsorption processes can be observed in the voltammogram, so that the charge between 0.3 and 0.35 V increases significantly. A similar situation has been found for the surfaces with (100) terraces and (111) steps\[29\]. The new peak appearing at 0.355 V can be assigned to anion adsorption processes taking place on adjacent sites to the Cu deposited on the step. Such adsorption processes induced by Cu adatoms have also been detected for copper decorated (110) steps on the Pt(S)\([(n-1)(111)\times(110)]\) surfaces\[12, 40\].

Increasing the potential range to 0.80 V, copper previously accumulated on the surface is stripped at ca. 730 mV, as observed in Fig. 2. For the stripping voltammograms shown in the Fig. 2 corresponding to different stepped surfaces, the Cu coverages were different and for that reason, the Cu stripping peak has different charges.

To gain more insight into the electronic effects that induce the selective adsorption of adatoms on different sites for these surfaces, a similar experi-
ment to those presented in Fig. 2 was carried out with a different adatom, namely antimony. One advantage of antimony is that deposited adatoms show a characteristic peak at 0.65 V, linked to a redox process undergone by antimony on terrace sites (Fig. 3), giving a specific measure of the amount of adatoms on those sites. For this peak, antimony coverage does not change since the dissolution takes place at potentials above 0.8 V. As can be seen in Fig. 3, the initial stages of the deposition of antimony lead to a significant diminution of the peak at 0.39 V, but the peak at 0.29 V, associated to sites close to the step remains unaltered. No other processes can be observed in the region between 0.3 and 0.35 V. In parallel to these processes, the peak at 0.65 V for the redox process of Sb on the terrace appears from the first scan. Thus, it can be concluded that the initial stages in the deposition of these

Fig. 2 Left panels: Slow Cu deposition on Pt(20,1,0), Pt(10,1,0) Pt(710) and Pt(510) electrodes by successively cycling the potential between 0.060 and 0.500 V in 0.1 mol\cdot L^{-1} H_2SO_4 + 2\times10^{-6} mol\cdot L^{-1} CuSO_4 (v = 50 mV\cdot s^{-1}). The dashed line corresponds to the blank voltammogram in the absence of copper. Arrows indicate the evolution of the current during potential cycling.

Right panels: Cu stripping by increasing the upper potential 0.800 V after the experiments in panel A (v = 50 mV\cdot s^{-1}).

Fig. 3 Slow Sb deposition on the Pt(710) electrode by successively cycling the potential between 0.060 and 0.800 V in 0.1 mol\cdot L^{-1} H_2SO_4 + 1\times10^{-6} mol\cdot L^{-1} SbO_2 (v = 50 mV\cdot s^{-1}). The dashed line corresponds to the blank voltammogram. Arrows indicate the evolution of the current during potential cycling.
surfaces take places almost exclusively on the terrace sites. Also, the diminution of the peak at 0.39 V should be assigned unequivocally to the deposition on the terrace sites. This behavior is similar to that observed for As on Pt(19,1,1), a surface with a (100) terrace symmetry and monoatomic (111) steps. When compared with the observed behavior for Cu deposition, the differences are clear, and thus, it can be concluded that the initial stages of the Cu deposition process take place simultaneously on the terrace and step sites, since the signals associated with all these sites diminish upon Cu deposition.

The stripping of the deposited Cu submonolayer is shown in the right panels of Fig. 2. As can be seen the stripping process takes place on a single peak, independently of the step density or Cu coverage. In the particular experiment shown for the Pt (710) surface, the number of deposition cycles was larger than those recorded for the other electrodes. For that reason, the charge is higher. However, the peak potential is the same, which is in agreement with the fact that the Gibbs energy change for the deposition on the terrace and step sites is very similar.

In order to analyze the effect of the specifically adsorbed anions on the initial stages of Cu deposition, experiments were carried out in perchloric acid solutions. As can be seen in Fig. 4, the initial stages of Cu deposition lead to a diminution in the current density throughout the voltammogram, without the appearance of any new peaks, unlike the observed behavior for the surfaces with (100) terraces and (111) steps. In fact, it is difficult to distinguish whether the deposition is taking place on the terraces or on the steps. Also, double peaks are obtained for the stripping process when the upper potential limit is increased to 0.8 V, independently of the amount of deposited Cu, which also supports unspecified deposition sites for Cu on these stepped surfaces. Thus, also in this case, the deposition takes place simultaneously on the step and terrace sites.

The addition of chloride has similar effects in the Cu deposition process, and the behavior is parallel to that observed in sulfuric acid solutions. As shown in Fig. 5, the signal associated with the adsorption of hydrogen and chloride on the sites close to the step (peak at 0.22 V) diminishes during the initial stages of the deposition. Also, there is a decrease of the adsorption processes on the terraces. In parallel to these diminutions, a new peak appears at 0.25 V, whose maximum intensity is proportional to the step density of the surface. This new peak is most likely associated, as already proposed for the

Fig. 4 Slow Cu deposition on the Pt(20,1,0), Pt(10,1,0) and Pt(510) electrodes by successively cycling the potential between 0.060 and 0.500 V in 0.1 mol·L⁻¹ HClO₄ + 2×10⁻⁶ mol·L⁻¹ CuO (v = 50 mV·s⁻¹).
peak 0.35 V in sulfuric acid solutions, with the adsorption of the anion induced by the Cu deposited on the step. In summary, it can be concluded that for these surfaces, the initial deposition stages of Cu occur simultaneously on the terrace and step sites, irrespective of anion specific adsorption.

3.3 Effect of the Step Density on Copper UPD

Fig. 6 shows the effect of the step density in the Cu UPD process on this series of stepped surfaces. In these experiments the Cu$^{2+}$ concentration was increased up to 1 mmol·L$^{-1}$ in order to fully cover the electroode surface in a single sweep. As can be seen, copper UPD on the Pt(100) electrode shows a well characterized pair of peaks at 0.730 V for the deposition process and 0.775 V for the corresponding dissolution, as has been already reported\cite{23}. No other additional processes are observed for this electrode until bulk deposition starts at potentials below 0.28 V (not shown in the Fig. 6 for clarity). A clear influence

Fig. 5 Slow Cu deposition on the Pt(20,1,0), Pt(10,1,0) and Pt(510) electrodes by successively cycling the potential between 0.060 and 0.500 V in 0.1 mol·L$^{-1}$ HClO$_4$ + 2×10$^{-6}$ mol·L$^{-1}$ CuO + 1×10$^{-3}$ mol·L$^{-1}$ NaCl. Arrows indicate the evolution of the current during potential cycling. For clarity, the bottom right hand panel shows the cycles 1, 35 and 75 for the Pt(510) electrode. $v = 50$ mV·s$^{-1}$.
of the lower limit of the voltammetric scan in the shape and potential of the dissolution at 0.775 V can be observed in Fig. 7. If the lower potential limit is close to 0.6 V, a single UPD dissolution peak appears at ca. 0.75 V. As the lower limit is made more negative, this peak shifts progressively to higher potential values while a shoulder remains at ca. 0.75 V. Since the only observed current between 0.6 and 0.3 V can be assigned to the double layer charging process, it is clear that the adlayer suffers some modification in this potential range although the charge involved in this process is negligible. A similar observation has been already described for Cu UPD on Pt(111) electrodes. In this case, the changes were assigned to the formation of copper oxide centers on the electrode surface at potentials higher than 0.55 V, which accelerates deposition or dissolution of the adlayer, making the voltammetric peaks appear more reversible. An alternative interpretation could be that, as the potential is made more negative, the defects between the different domains formed in the copper adlayer heal, forming a larger ordered domain. Since the dissolution process is probably initiated at the defects, the lower the concentration of defects the higher the potential is for the dissolution peak.

The presence of steps leads to the modification of the copper UPD voltammetric profile. First, the pair of peaks at 0.73 ~ 0.77 V diminishes, which clearly indicates that this process is related to Cu deposition/dissolution on the wide (100) terraces. On the other hand, two new pairs of peaks (peaks 2 and 3 in Fig. 6) appear and increase with the step density, a clear indication that they are related to step or adjacent sites. These pairs of peaks show a clear irreversibility since the difference in the potential value between the deposition and dissolution peaks is ca. 100 mV. In this respect, it should be noted that the Pt(210) surface, the turning point surface in the series with 2 (100) terrace sites and a (110) step site shows very broad peaks that can be easily mistaken with the typical double layer charging process and only an enlargement of these currents allows distinguishing the peaks (Fig. 6, bottom panel). It is also worth mentioning that these peaks are different from those observed for the stepped surfaces with (100) terraces and (111) steps. In this latter case, only one pair of peaks is observed for processes on the steps, involving a higher charge density. These results confirm that the step structure from both series of surfaces is significantly different, although some reorganization of the step line has been previously observed by STM.
When chloride anions are added to the solution, four clear contributions for these electrodes, termed as peaks 1, 2, 3 and 4 can be seen in Fig. 8. Peaks 1, 2, 3 and 4 appear at 0.710, 0.580, 0.505 and 0.375 V respectively on the positive going sweep at 10 mV·s⁻¹. The corresponding deposition counterpeaks 1', 2', 3' and 4' on the negative going sweep are observed at 0.675, 0.570, 0.495 and 0.350 V, respectively. Clearly, these peaks are related to those reported before in the presence of sulfate in the supporting electrolyte, although a new peak (4) appears now at potentials close to the onset of bulk deposition. The sharp peak at 0.3 V is most likely related with the stripping of the second or further layers of copper that took place in the negative scan. As before, the peak at 0.710 V is related to the stripping of copper deposited on the terraces whereas deposition on the sites close to the step occurs under the other three peaks. Similarly to the result observed in sulfuric acid solution, the voltammetric profile for the surfaces with high step density is not well resolved, giving rise to an apparent large double layer current. The shape and potential of these peaks are also different from those obtained in the
other series of stepped surfaces with (100) terraces, confirming the different geometry of both step sites. As can be seen by comparing Figs. 6 and 8, the presence of chloride in the solution leads to a shift of the peaks to lower potential values. Chloride anions can induce a weakening in the adsorption strength of the copper adatoms to platinum as was reported in reference [40]. Weaker bonds between copper and platinum means that the stripping (oxidation) of copper atoms occurs at lower potentials, and copper is less stable on the surface when the solution contains strongly adsorbed anions.

Also, chloride adsorption plays a significant role in the energetics of the process. For that reason, the effect of both copper and chloride concentration are examined (Figs. 8 and 9). When the copper concentration is increased, there is a significant shift of the peaks towards more positive potentials, as expected, also in the bulk deposition process. In addition, there is a diminution of the irreversibility of the deposition/dissolution process, since the peak potential difference between the related pair of peaks diminishes. As the concentration increases, the deposition peaks become sharper and better resolved, a clear indication that this irreversibility is mainly related to the slow diffusion of Cu^{2+} ions to the surface. From the slopes of the peak potential vs. the logarithm of the concentration, the apparent number of electrons can be obtained. As can be seen in Tab. 1, these values are close to 30 mV, which is the expected value for a Nernstian process exchanging two electrons such as the Cu^{2+}/Cu process. For the deposition peaks, slopes are slightly higher, affected by the diffusion process of Cu^{2+} from the bulk solution to the surface. For some peaks, the slopes are around 20 ~ 25 mV, which would imply that the number of electrons transferred during the dissolution process is higher than 2. Since values higher than 2 are not possible, the lower than expected slope values should be then associated with some irreversible

Fig. 9 Effect of the copper concentration in Cu UPD on the Pt(20,1,0), Pt(10,1,0) and Pt(510) electrodes in 0.1 mol·L⁻¹ HClO₄ + x mol·L⁻¹ CuO (x = 10⁻⁴, 10⁻³, 10⁻²) + 1×10⁻³ mol·L⁻¹ NaCl (ν = 10 mV·s⁻¹).
process that is taking place during the formation of the adlayer or to anion coadsorption phenomena. It should be stressed that the number of electrons transferred during the process does not necessarily imply that copper layer is neutral. In fact, some charge distribution between the substrate and the copper layer has been observed in the case of copper UPD on Pt(111)\textsuperscript{[46]}, in which the copper has an electronic structure similar to Cu\textsuperscript{+}. On the other hand, no peak shifts are observed when the chloride concentration is changed (Fig. 8). Since chloride is already adsorbed at 0.75 V on the platinum surface, the constant peak potential indicates that the chloride coverage remains constant during the deposition process. It should be mentioned that adsorption of anions on copper is stronger than on the platinum substrate since the presence of adsorbed sulfate on copper can be detected at potentials at which this anion has been already desorbed on gold or platinum\textsuperscript{[47]}.

### 3.4 Charge Analysis

To determine the relationship of the different peaks with terrace or step sites and also the stoichiometry of the reaction on those sites a charge analysis will be attempted. The charge analysis follows those previously done for surfaces with (100) terraces and different anions\textsuperscript{[27, 29]}. For these stepped surfaces, at least 3 different adsorption sites can be distinguished, as marked in Fig. 10. This Fig. illustrates the different position at which a Cu atom can be deposited for the Pt(510) surface, which has 5 rows of atoms on the terrace and a monoatomic (110) step. First, the position 1 corresponds to the adsorption on the step. In principle, this should be the most favorable position for the deposition of Cu. It maximizes the interaction with the platinum surface, since the Cu is surrounded by 6 Pt atoms. However, the results of section 3.1 indicate that the initial stages of the deposition take place both on the step sites and on the terrace sites (position 2). In position 2, the deposited Cu atom has 4 platinum neighbors. The absence of preferential deposition on the step, then, suggests that the energetics of the deposition on position 1 and 2 should be similar. Position 3 is associated with deposition on the top part of the step, in which the interaction with the Pt surface is reduced (only 3 Pt nearest neighbors) and for that reason, it is expected that this is the most energetically unfavorable position for the deposition.

The equations that relate the charge density with the step density will be deduced using the hard sphere model. According to the model, the charge associated to the transfer of one electron per surface unit cell (or, what is equivalent, for a single row of atoms parallel to the step), \( q_{\text{row}} \), is\textsuperscript{[27]}

\[
q_{\text{row}} = \frac{q_{\text{Pt(100)}}}{n} \cdot 209 \text{ \mu C \cdot cm}^{-2} \tag{1}
\]

Fig. 10 Hard sphere model of the (510) \( (n = 5) \) surface. Terrace, terrace edge and step sites have been marked in the plot (see text for details).

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Tab. 1 Slopes of the linear fits of peak potential against logarithm of the copper concentration in mV·dec\textsuperscript{-1} for the different electrodes in 0.1 mol·L\textsuperscript{-1} HClO\textsubscript{4} + x mol·L\textsuperscript{-1} CuO \( (x = 10^{-4}, 10^{-3}, 10^{-2}) + 1 \times 10^{-3} \) mol·L\textsuperscript{-1} NaCl solutions

<table>
<thead>
<tr>
<th>Electrode ( (m,n) )</th>
<th>( dE_{\text{p}} )/d( \log([\text{Cu}^{2+}]) )/mV</th>
<th>1</th>
<th>1’</th>
<th>2</th>
<th>2’</th>
<th>3</th>
<th>3’</th>
<th>4</th>
<th>4’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (20,1,0)</td>
<td>22</td>
<td>37</td>
<td>26</td>
<td>-</td>
<td>28</td>
<td>50</td>
<td>31</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Pt (10,1,0)</td>
<td>22</td>
<td>46</td>
<td>-</td>
<td>-</td>
<td>26</td>
<td>46</td>
<td>32</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Pt (510)</td>
<td>18</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>35</td>
<td>22</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>
where $q_{Pt(100)}$ is the charge associated to the transfer of 1 electron per platinum surface atom for the Pt (100) electrode, $q_{Pt(100)} = e/2F$. Since 2 electrons are transferred for the Cu deposition, equation (1), is then transformed in

$$q_{row} = 2 \frac{q_{Pt(100)}}{n} = \frac{418}{n} \mu C \cdot cm^{-2}$$

(2)

This equation is then valid for the deposition on positions 1 or 3, since they consist of a single row of atoms parallel to the step. For the deposition on the terrace, position 2, the charge $q_t$ can be calculated assuming that the surface has $n$-2 pure terrace sites as:

$$q_t = ((n-2)q_{row}) = 2 \left( \frac{q_{Pt(100)} - 2q_{Pt(100)}}{n} \right)$$

$$= \left( 418 - \frac{836}{n} \right) \mu C \cdot cm^{-2}$$

(3)

The charge corresponding to the simultaneous deposition on sites 1 and 2 takes is given by

$$q_{t+1} = ((n-1)q_{row}) = 2 \left( \frac{q_{Pt(100)} - q_{Pt(100)}}{n} \right)$$

$$= \left( 418 - \frac{418}{n} \right) \mu C \cdot cm^{-2}$$

(4)

Thus, the total charge for the copper UPD on these surfaces is then:

$$q_{total} = q_{row} + q_{t+1} = 418 \mu C \cdot cm^{-2}$$

(5)

The charge densities defined in the previous equations are referred to the projected surface over the (100) plane. However, the current densities in the voltammograms are referred to the geometric area of the electrode. In order to compare experimental values with the previous equations, the integrated charges in the voltammogram should be projected on the (100) plane, dividing them by the cosine of the angle ($\alpha$) between the stepped surface and the (100) plane:

$$\cos(\alpha) = \frac{n}{\sqrt{n^2+1}}$$

(6)

Fig. 11 shows the charge for peaks 1, 2 and 3 measured for the different stepped surfaces and also the total charge plotted vs. 1/n, since all the equations are linear with 1/n. As can be seen, the hard sphere model is able to reproduce the observed behavior although some differences are found. First, the total charge for peaks 1, 2 and 3 is slightly lower than that predicted by the model, but the value of the total charge is almost independent of the step density, as predicted by the model. The difference is probably related to the effect of sulfate adsorption on the total charge or to the presence of defects on the surface. The equations are only taking into account the charge associated to copper deposition. However, adsorbed sulfate is always present on the adlayer. Changes in the coverage and/or the electrosorption valency of adsorbed sulfate upon the formation of the copper layer can lead to values different from those predicted by the model. In this case, the slightly lower values may indicate that either the coverage of sulfate is slightly lower or that the number of electrons transferred per adsorbed sulfate molecule is lower on the Cu layer. This effect is also visible for peak 1. As can be seen, the fitted line has a slope similar to that predicted in equation (4) ($440 \pm 30 \mu C \cdot cm^{-2}$), although the intercept value at zero step density is lower. The fact that the experimental results follow the slope deduced from equation (4) clearly indicates that $n$-1 rows on the stepped surface are involved in this peak. This means that this peak is associated with the deposition on positions 1 and 2, that is, on the terrace and the lower step sites, in agreement with the results obtained in Fig. 2. In the initial deposition stages, this process takes place simultaneously on step and terrace sites. Moreover, when copper is stripped from the surface, a single dissolution peak is obtained (Fig. 2).

Peaks 2 and 3 are then clearly related to the deposition in position 3, since the sum of the charge of these two peaks follows equation (2). Except for the Pt(210) surface, charges of peaks 2 and 3 are almost equal, which indicates that deposition on the upper part of the step is taking place in two different stages involving half of the step sites in each peak. As aforementioned, deposition in this position is the least favorable, since the interaction between the Cu
adatoms and the Pt surface is the lowest. It should be reminded that the UPD process is related to the higher interaction energy between a Cu atom and the Pt surface when compared to that measured for a Cu atom and a Cu surface. Thus, the lower number of Pt nearest neighbors for Cu deposited on position 3 should lead to a lower interaction energy and thus, a lower deposition potential.

4 Conclusions

The results presented here for the Cu UPD on the stepped surfaces having (100) terraces and (110) steps clearly indicate that the initial deposition stages of copper on these surfaces take place simultaneously on the terrace and step sites. This conclusion is maintained for the different electrolyte solutions studied here irrespective of the nature of the adsorbing anion. When a full monolayer is deposited, several peaks can be observed in the voltammogram. The analysis of the dependence of the peak charge with the step density has allowed assigning the different peaks to different deposition sites. An attempt has been made to identify these sites on a hard sphere model of the surface. Thus, the peak appearing at most positive potentials corresponds to the deposition of Cu on the terrace and step sites, whereas deposition on the top part of step sites gives rise several contributions depending on the anion present in solution. Additionally, it has been found that the charge transferred upon Cu deposition is very close to 2 and that the anion coverage does not change upon the deposition of Cu.

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References:


Pt(S)[n(100)×(110)]表面 Cu 欠电位沉积

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摘要: 本文研究了 Cu 在 Pt (100)台阶面和(110)单原子台阶的欠电位沉积. 发现若不考虑阴离子吸附, 初始阶段 Cu 在台阶面和台阶处的电沉积同时进行. 在电沉积满单层的伏安曲线上, 可以观察到若干峰. 通过对峰电荷与台阶密度关系的分析, 可认为这些峰分别对应于不同的沉积位点. 较正电位的峰对应于 Cu 在台阶面上的电沉积, 而在台阶处 Cu 的电沉积则因溶液中的阴离子而具有不同的伏安性质. 此外, 还发现 Pt 电极表面的 Cu 沉积电荷转移数接近 2e, 且沉积初始阶段阴离子覆盖度不变.

关键词: Pt 单晶电极; Cu; 欠电位沉积; 台阶修饰