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New insight on the behavior of the irreversible adsorption and underpotential deposition of thallium on platinum (111) and vicinal surfaces in acid electrolytes

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A B S T R A C T

We report, for the first time, the electrochemical behavior of thallium irreversibly adsorbed on Pt (111) and platinum stepped surfaces composed of (111) terraces and monoatomic steps. Similar to the case of thallium UPD, the voltammograms obtained after thallium irreversible adsorption present three characteristic features. After a careful analysis of the effect of the thallium concentration, the concentration and nature of the anion of the supporting electrolyte and the pH of the solution on these voltammetric features, we have been able to ascribe these processes to Tl/Tl$^+$ oxidation and anion adsorption on the Tl-modified surface. In addition, the results obtained with stepped surfaces, indicate that some of the features are clearly associated to the presence of (111) surface domains, and thus they could be used for the quantification of these sites.

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1. Introduction

In order to understand the nature of different heterogeneous processes taking place in the metal-electrolyte interface, it is essential to control the structure of the base metal. The use of single crystal electrodes (with well-defined surface structure) has made this study possible. In the field of the electrochemistry, the use of the cyclic voltammetry with well-defined single crystal electrodes can provide information about the effect of the surface structure on electrochemical reactions. In most cases different geometric sites involve different electrochemical responses for specific reactions. Of special interest is the study of the surface composition of electrodes with well-defined structure on electrochemical reactions. There are two methods that allowed the controlled deposition of adatoms on metal electrodes: underpotential deposition (UPD) [1] and irreversible adsorption [2–5], also called spontaneous deposition [6–9].

UPD is the electrochemical formation of non-bulk surface adlayers at potentials more positive than those of the Nerst potentials corresponding to the bulk deposition of the adsorbate. On the other hand, irreversible adsorption of a foreign adatom occurs when the adatom remains adsorbed on the surface in a wide potential range, despite the fact that the solution does not contain ions of the adatom that could be in equilibrium with the adsorbed species. It could be considered that irreversible adsorption is a particular case of UPD, one in which the adsorbed adatom has a lower oxidation state than the species in solution, within a certain potential window [1,3–5,10]. As a result, the desorption rate would contain an exponential term of the difference of the equilibrium potential and the working potential. Since this difference is negative (see above definition of UPD) and is usually very large, the desorption rate is reduced to a negligible value. The desorption of the adatom occurs during a surface redox reaction involving the oxidation state of the species in solution. In many cases, the adatoms also suffer surface redox reactions on the surface of the metal without desorption of the species.

Most UPD and irreversible adsorption processes are surface sensitive reactions [1]. Also, the effects of anions on the UPD of metals plays an important role [11–16]. The applications of surfaces modified by metals are numerous: from the catalysis of the electro-oxidation of organic substances to the simulation of crystal nucleation and growth [17,18]. The combination of electrochemical and spectroelectrochemical methods has produced interesting studies to of the structure of metallic and anion adsorbates [1,19–21]. In the case of thallium UPD, we report in this paper that the irreversible adsorption of thallium is strongly influenced by the anion in solution. Co-adsorption of perchlorate and sulphate in the UPD of thallium has been reported previously

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[21–23]. Strong changes in the CV of thallium UPD in a solution containing halogen anions indicate co-adsorption with those anions [24]. As far as we know, the behavior of thallium irreversibly adsorbed on Pt (111) surfaces has not been reported before. Only a few electrochemical studies have been published on the stability of thallium adsorbed on Pt step surfaces [25] and on the change in the catalytic effect of polycrystalline platinum surfaces doped with amounts of thallium on the oxidation of formic acid [26].

The aim of this paper is to study the irreversible adsorption of thallium on Pt (111) in 0.5 M H_2SO_4 and 0.1 M $HClO_4$ by means of voltammetric measurements, and to compare it with thallium UPD. The discussion will be based on the surface redox processes undergone by the adatom and the modification of hydrogen and the anion upon the thallium adsorption.

2. Experimental

Platinum single crystal electrodes were oriented, cut and polished from small single crystal platinum beads (2.5 mm diameter) following the procedure described by Clavilier and co-workers [27]. The electrodes were cleaned by flame annealing, cooled down in H_2/Ar (N50, Air Liquid in all gases used) and protected with water in equilibrium with this gas mixture to prevent contamination before immersion in the electrochemical cell, as described elsewhere.

Irreversible adsorption of thallium was performed introducing the electrode into a solution of Tl_2CO_3 with concentrations between 10^{-6} and 10^{-2} M in the presence of a supporting electrolyte (either 0.5 M H_2SO_4 or 0.1 M $HClO_4$). The electrode with a droplet of solution attached was immersed in the cell at 0.1 V. Contamination of the cell by residual thallium ions is negligible for all the experiments shown here. Small amounts of thallium ions in solution are easily detected because they will lead to the blockage of the surface sites of a flame-annealed Pt (111) electrode that is initially free of thallium on the surface. The underpotential deposition experiments were performed as described previously [22,23].

Experiments were carried out at room temperature, 25 °C, using two classical two-compartment electrochemical cells deaerated with Ar and including a platinum counter electrode and a reversible hydrogen electrode (RHE) as references. All potentials in this paper are referred to the RHE scale, except where otherwise stated. Solutions were prepared from H_2SO_4 and $HClO_4$ (doubly distilled, Aldrich), K_2SO_4 (99.998%, Sigma–Aldrich) and recrystallized $KClO_4$ (>99.999%, Aldrich), Tl_2CO_3 (99.99%, Sigma) and ultrapure water from Elga (18.2 MΩ cm^{-1}).

3. Results and discussion

3.1. Electrochemical behavior of UPD and irreversibly-adsorbed thallium on Pt (111) in sulfuric solutions

Fig. 1 shows the voltammetric behavior of the thallium UPD on Pt (111) surfaces in 0.5 M $H_2SO_4 + 10^{-2}$ M Tl and 0.1 M $HClO_4 + 10^{-2}$ M Tl. The profiles in absence of thallium are included for comparison. In the UPD profile of Tl, three different regions can be distinguished: (i) at high potentials, above 0.7 V, a pair of peaks appears at around 0.75 V in 0.5 M sulphuric acid and at 0.67 V in perchloric acid, respectively; these pairs of peaks are associated to the deposition/desorption process of Tl/Tl$^+$ [23], in sulphuric acid media, the charge measured under this peak is consistent with a thallium coverage 0.25 [23], (ii) the peaks appearing in the second region, between 0.3 and 0.6 V, are mainly associated to the adsorption/desorption process of the anions (either sulphate in sulphuric acid solution or OH or perchlorate in perchloric acid solutions, respectively) [22,23], in the case of sulphuric acid, SXS
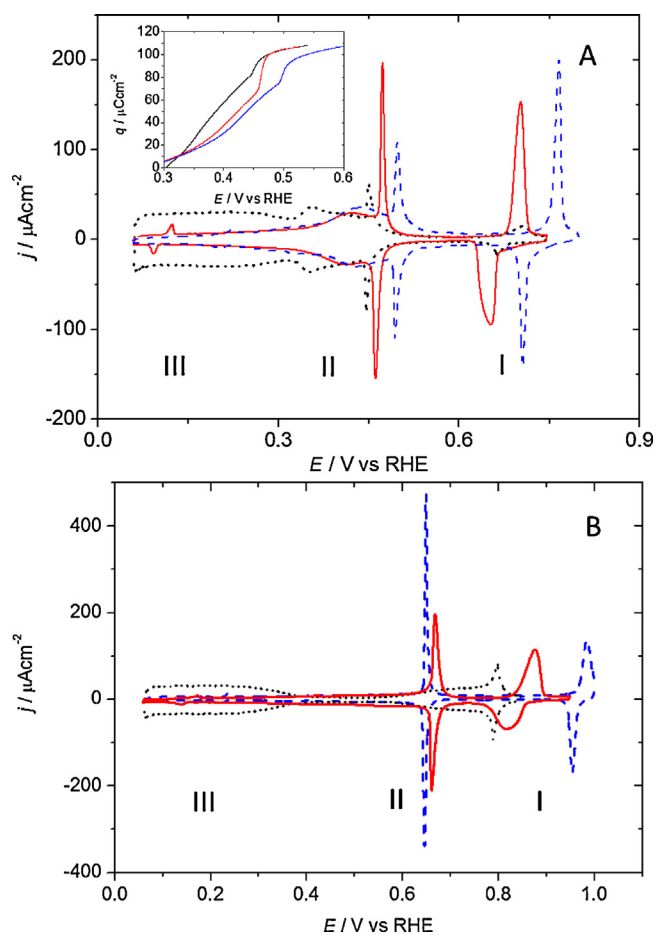

Fig. 1. Voltammetric profile of the Pt (111) electrode in (A) 0.5 M H_2SO_4 and (B) 0.1 M $HClO_4$ in (•••) absence and (– – –) presence of Tl$^+$ 10^{-2} M, and (——)

measurements have revealed the presence of a $\sqrt{3} \times \sqrt{3}$ R30° sulphate adlayer on the thallium UPD layer at 0.7 V RHE [22], the adsorption/desorption of the sulphate adlayer on the thallium-modified surface between 0.6 and 0.3 V gives a voltammetric profile that is similar to that obtained for the adsorption/desorption the sulphate layer on the unmodified Pt(111) electrode, at potentials between 0.5 and 0.3 V, (iii) in the low potential region (below 0.3 V), no significant currents are recorded aside from a small pair of peaks at 0.2 and 0.19 V, this fact implies that the hydrogen adsorption process typical of Pt(111) electrodes has been suppressed by the adsorption of thallium.

From the comparison of the thallium UPD in both electrolyte media, it can be seen that peak potentials of all the processes depend on the supporting electrolyte, indicating that in all cases anion adsorption is involved to some extent in the deposition/dissolution processes of thallium. As will be shown later, a similar situation is found in the case of the irreversibly adsorbed thallium.

In order to obtain a deeper understanding of thallium deposition on Pt(111), the UPD of thallium was carried out in different concentrations of sulphate, different pH's and also different concentrations of thallium. Fig. 2 shows the voltammetric behavior of the Pt(111) electrode in 0.1 M H_2SO_4 (pH 1) with different concentrations of thallium in the solution. As can be observed, the peak at lower potentials (peak III) shifts from 0.19 V to 0.27 V when the concentration of thallium increases from 10^{-4} M to 10^{-2} M. The displacement is ca. 60 mV per unit of thallium concentration, which is the expected value for the redox