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Formic acid electrooxidation on thallium modified platinum single crystal electrodes

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ABSTRACT

Formic acid electrooxidation on Tl modified Pt single crystal electrodes has been carried out in sulfuric acid media. Voltammetric experiments demonstrated that Pt(100) modified by Tl displays a significant enhancement towards formic acid oxidation both lowering the oxidation onset potential and increasing the maximum current density in the positive going-sweep. A similar behavior has been observed in Pt(s)[(100)x(111)] stepped surfaces. On the other hand, for Pt(111) surfaces, the incorporation of Tl also induced a shift of the oxidation onset to lower potential values, a diminution of the hysteresis between the positive and negative going-sweep and also an increase of the oxidation currents. These results have been corroborated using in situ FTIR experiments, where the CO adsorption band disappears completely when Pt(100) and its vicinal surfaces are modified by Tl adatom, leading to the formation of CO_2 at lower overvoltages.

1. Introduction

Formic acid oxidation is known to be a very important reaction in electrocatalysis [1,2]. It can be used as a model reaction for more complex organic molecules, given that i) its oxidation process only involves two electrons, ii) an additional oxygen atom is not required to produce CO_2, and finally, iii) it is a clear example of a reaction sensitive to the surface structure of the electrocatalyst. In addition, formic acid has been proposed as a possible fuel for fuel cells with portables and small power applications [1,3,4]. Although this species emerges as a possible fuel in direct formic acid fuel cells (DFAFC), its application is limited by a low power density and the poisoning of the catalyst. Therefore, high active catalysts towards formic acid oxidation are required.

It is well accepted that formic acid oxidation reaction (FAOR) proceeds via two different routes in Pt electrodes: the so-called indirect pathway, where CO (poisoning intermediate) is formed on the electrode surface, being then oxidized to CO_2 at high potentials; and the second route (direct pathway), which involves the formation of an active intermediate, presumably a formate weakly adsorbed species [5,6], and its subsequent oxidation into CO_2 at low potentials. This dual pathway mechanism sets one of the main problems to be solved in order to catalyze this reaction in Pt electrodes, which is suppressing the poison formation route and enhancing the oxidation through the direct pathway.

There are two classical approaches to enhance the activity of the electrocatalyst, namely, modifying the surface structure, or changing the composition of the electrode. The first one consists in preparing electrodes with different atomic arrangement, providing specific surface symmetry that favors the formic acid oxidation by the direct pathway [7,8]. The second one implies the modification of the platinum surfaces with the adsorption of foreign atoms. This second approach has been widely studied over the past years. Adatoms such as bismuth (Bi) [9], antimony (Sb) [10,11], arsenic (As) [11] or palladium (Pd) [12] provide an important improvement in the catalytic activity, not only in terms of maximum current density, but also in shifting the oxidation onset potential to lower values. One reason for this enhancement is the so-called, third body effect [13], in which one of the metals acts with a steric influence to suppress the poison formation, enhancing the activity through the other pathway. However, some adatoms have also an important bifunctional effect [13–15], where the adatom act as a promotor of the active intermediate in a specific configuration, thus decreasing the activation energy of the process through the direct pathway. The case of Bi modification is a clear example of this bifunctional effect [16].

In recent years, an increasing interest has been set on those metals that have been less studied, among them, thallium adatom. In earlier studies, Clavilier et al. [17] perfomed the underpotential deposition (UPD) of Tl^+ on Pt(111) electrode, arguing that there is an equilibrium in the adsorption-desorption process. More recently, Rodriguez et al. [18] has studied extensively either the UPD and irreversible adsorption of Tl on Pt(111) and vicinal surfaces. They were able to ascribe the processes Tl/Tl^+ oxidation and anion adsorption on the Tl-modified surface. Additionally, the results obtained with stepped surfaces indicate that some of the features are clearly associated to the presence of (111) surface domains (terraces).

On the other hand, some few works has studied the FAOR on Tl modified Pt electrodes. For instance, Hartung et al. [19] reported the effect of

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Tl deposition on Pt electrodes towards formic acid oxidation, concluding that Tl catalyzes the direct oxidation of bulk HCOOH. More recently, Tl modified shape-controlled Pt nanoparticles showed an important enhancement of the FAOR [20], concluding that preferentially (100) Pt nanoparticles (cubic shape) modified by Tl were more active than the (111) Pt nanoparticles (octahedral shape) in the entire range of Tl coverages. However, despite these previous contributions, a fundamental study dealing with the activity of Tl modified Pt single crystal electrodes have not been conducted yet. For this reason, in this contribution, an electrochemical and spectroscopic study of formic acid oxidation on Tl modified Pt single crystal electrodes, both using basal planes and stepped surfaces are presented.

2. Experimental

Platinum single crystal electrodes were oriented, cut and polished from small single crystal Pt beads (2.5 mm diameter) following the method developed by Clavilier et al. [21]. Before all the experiments, working electrodes were flame annealed during 30 s, cooled down in a H_2/Ar atmosphere and quenched in ultrapure water in equilibrium with this atmosphere before immersion in the electrochemical cell [22]. Tl deposition on Pt was performed by cycling between 0.06 V and 0.65 V for Pt(100) and Pt(s)[(100x111)] stepped surfaces, and between 0.06 V and 0.50 V for Pt(111) electrodes. The upper potential was chosen in order to preserve the surface order and also to avoid problems of Tl desorption at higher potentials. Diluted solutions of Tl^+ (Tl_2SO_4, Aldrich® 99.995%) with concentrations between 10^{-5}–10^{-6} M in 0.5 M H_2SO_4 were used.

Experiments were carried out at room temperature (25 °C), in a classical electrochemical cell, including a large platinum counter electrode and a reversible hydrogen (N50) electrode (*RHE*) as reference. All potentials used in this work are referred to *RHE*. The solutions were prepared by using H_2SO_4 (Merck KGaA Suprapur® 96%), formic acid (Merck KGaG 98%) and ultrapure water (Elga PureLab Ultra 18.2 MΩ cm), preparing 0.1 M HCOOH + 0.5 M H_2SO_4 solution. Ar (N50, Air Liquide) was used for deoxygenating the solutions. All the electrochemical measurements (cyclic voltammetry) were performed using a waveform generator (EG&G PARC 175) coupled to a potentiostat (eDAQ EA161) and a digital recorder (eDAQ ED401).

In situ FTIR measurements were performed in a Nicolet 8700 spectrometer equipped with a mercury cadmium telluride (MCT) detector, according with the external reflection configuration for a transparent prism of CaF_2 beveled at 60° [23] and coupled with the spectroelectrochemical cell. For each spectrum, 100 interferograms were averaged to increase the signal-to-noise ratio, using a resolution of 8 cm^{-1}. For all the experiments, p-polarized light was used, allowing the detection of species adsorbed on the electrode surface and other species in the electrolyte solution. Spectra were presented in absorbance units, $A = -\log(R_1 - R_2)/R_1$, in which R_1 and R_2 are the reflectance values for the single-beam spectra recorded at the sample and the reference potential respectively. Positive bands in spectra are related to species formed at the sampling potential with respect to the reference potential, whereas negative bands correspond to species consumed. IR spectra were collected at intervals of 50 mV between 0.05 V and 0.5 V, and 100 mV between 0.5 V and 0.9 V vs. *RHE*. Spectrum taken at 0.05 V was used as a reference in all spectra presented.

3. Results and discussion

3.1. FAOR on Tl modified Pt(100) and Pt(111) electrodes

Fig. 1 shows the voltammetric profiles corresponding to a) Pt(100) and b) Pt(111) modified with Tl at different coverages in 0.5 M H_2SO_4. In the case of Pt(100), two different regions can be distinguished: the first one, located between 0.06 V and 0.20 V, where a new peak centered at 0.17 V appears for increasing thallium coverages and a second one involving the decrease of the contributions from 0.2 V to 0.5 V, related to the competitive adsorption between hydrogen and sulfate anions on the Pt surface. In order to find out the nature of the peak at 0.17 V, the peak potential position (in the hydrogen electrode scale (SHE)) was plotted against solution pH (Fig. 2). A slope value of 52 mV was obtained, very near to 59 mV, which implies that one proton is exchanged per electron in the surface redox reaction. Since the charge of this process is small and the peak is only well defined at high coverages, it can be proposed that the reaction is associated to the hydrogen adsorption process on a Pt site surrounded by Tl adatoms. Thus, considering Tl as an electropositive adatom, this finding suggests that its presence modifies the adsorption of hydrogen profile, lowering the potential where the adsorption starts to occur.

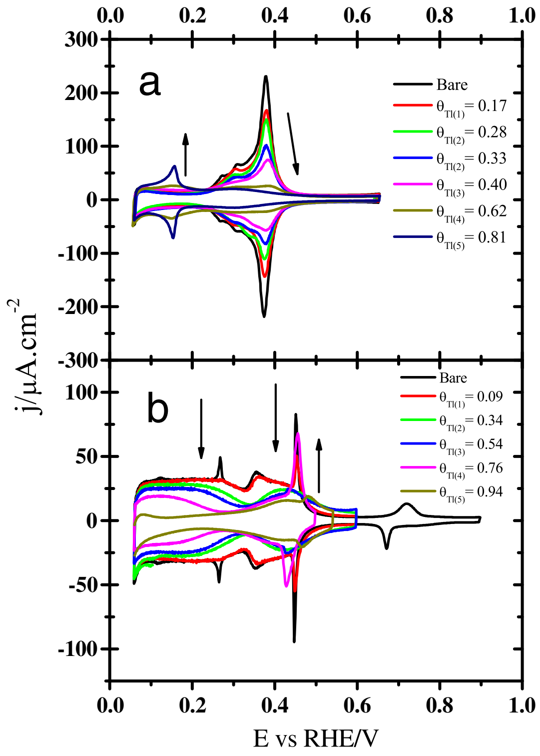

Fig. 1. Cyclic voltammetry of Tl modified Pt single crystal electrodes taken in H_2SO_4 0.5 M at different Tl coverages. (a) Tl modified Pt(100) electrode; (b) Tl modified Pt(111) electrode. Scan rate 50 mV·s^{-1}.

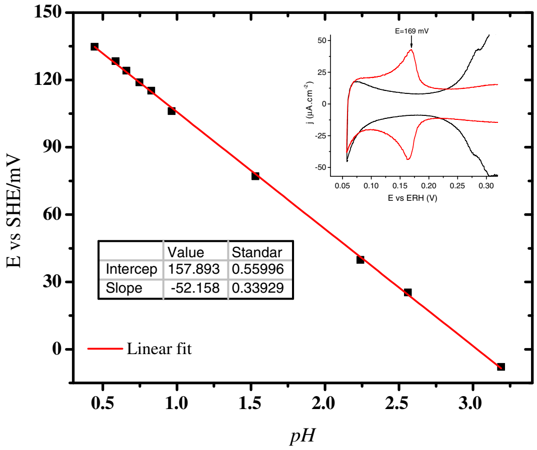

Fig. 2. Linear relationship between the peak potential of the reversible feature in Tl modified Pt(100) electrode (inset) and the solution pH.