Formic acid electrooxidation on Bi-modified Pt(1 1 0) single crystal electrodes

Ana López-Cudero, Francisco J. Vidal-Iglesias, José Solla-Gullón, Enrique Herrero,
Antonio Aldaz, Juan M. Feliu *

Instituto de Electroquímica, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain

ABSTRACT

Bi-modified Pt(1 1 0) single crystal electrodes have been prepared and characterised. As previously reported for Pt(1 0 0) and Pt(1 1 1) electrodes, the presence of Bi on the Pt(1 1 0) surface greatly enhances formic acid electrooxidation. In addition, the study of the spontaneous formation of CO from formic acid dehydration is also reported in the whole Bi coverage range. The results obtained show that the surface cannot spontaneously form CO at high Bi coverage. Nevertheless, it has also been proved that, even at the highest Bi coverage, CO can be directly adsorbed on the residual free Pt sites, and it is oxidised in two distinct steps. The first one appears only when the Bi coverage is below saturation, and has been identified as CO adsorbed in relatively open sites, while the second one appears after Bi dissolution, and has been assigned to CO in less accessible sites. Finally, a comparison between the changes found in electrochemistry and the Bi adlayer structures reported in UHV is attempted.

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1. Introduction

The oxidation of formic acid on platinum electrodes is a very important reaction mainly due to two facts: it is a two electron process that can be used as a model to understand fundamental aspects in electrocatalytic reactions, and moreover, it has potential application in fuel cells. It is known that formic acid oxidation follows at least a two parallel path mechanism, one step leads to the direct oxidation to CO_2 while the other path mediates by poisoning the surface by the formation of adsorbed CO [1,2]. Besides, it was well-established that the surface structure of the electrode influences both paths of the mechanism in a different extension [3–8]. In this way, in order to simplify the understanding, have a general vision of the whole process and evaluate the weight of the different contributions to the overall process, the reaction has been extensively and intensively studied on well-defined platinum electrodes [9–15]. In addition, the oxidation of the poison formed in the second path, adsorbed CO, is also known to be a structure-sensitive process widely investigated as well as a model of electrocatalytic surface reactions [4,16–20].

In earlier studies it was also reported that the presence of different adatoms adsorbed on the surface of platinum improved its electrochemical reactivity. Motoo's group carried out a series of remarkable studies on polycrystalline platinum describing the effect of several adatoms on the electrode surface towards different

reactions such as hydrogen evolution, CO oxidation or formic acid and methanol oxidation [21–26]. They included fundamental concepts involving third-body effects, the number of sites blocked by the adatom and the existence of different surface domains 3required for both paths, in addition to bifunctional electrocatalysis for CO oxidation through adsorbed oxygen species and poison formation.

To simplify the understanding of the electrocatalytic effects played by the adatoms, the use of well-defined electrode surfaces is required. Consequently, systematic studies on single crystal electrodes with basal orientations, Pt(1 1 1) [9,14,15,27] and Pt(1 0 0) [1,2,9,10,12,28] were performed. Among the different employed adatoms, Bi has shown to be of great relevancy [5,6,29]. For Pt(1 1 1) it was observed that the adsorption of Bi enhanced the activity of the platinum sites for the direct oxidation whereas the poisoning was almost completely suppressed, even at low Bi coverage [6,9]. A model was fitted with the assumption that the active sites were those on which a Pt site was a close neighbour of a Bi-covered site. It was evident that free Pt sites were required. The poisoning was studied also on stepped surfaces [14,15] and it was remarked that the poisoning path was markedly inhibited when Bi starts to be adsorbed on the (1 1 1) terraces.

The study on Pt(1 0 0) revealed two different responses depending on the surface treatment, which indeed reflects different surface arrangements on this electrode [10,30]. In both cases, the presence of Bi led to the enhancement of the electrode activity and the effect on poisoning fitted with a third-body effect, but

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electrodes having wide terraces required free Pt sites and reached the maximum activity at coverage below saturation, as in the case of Pt(1 1 1), whereas the disturbed electrodes, as those that resulted from the flame annealing treatment and cooling in air, that are heavily stepped, displayed a continuous increase in current with increasing Bi coverage, including full electrode blockage. This result means that all the reactive sites could be almost fully covered by the adatoms and maintains high reactivity in this particular surface. The activity of the latter electrodes, however, was slightly lower than that of Pt(1 0 0) electrodes having wide two-dimensional domains.

The Pt(1 1 0) surface is much less compact than the Pt(1 1 1) and the Pt(1 0 0) surfaces. The coordination number of the surface atoms is seven, being only two of them contiguous. Owing to this low coordination number, the Pt(1 1 0) usually reconstructs. For Pt(1 1 0), and in a similar way that for Au(1 1 0) or Ir(1 1 0), the main reconstructed structure in UHV is (1×2), known as missing row, because every two rows of atoms in the $\langle 0\,0\,1 \rangle$ direction one is missing, while distances in the $\langle 1\,1\,0 \rangle$ direction are kept constant. The introduction of species such as CO or adatoms on the surface lifts the reconstruction [31–33]. At present there are not conclusive reports about the surface topography of Pt(1 1 0) in electrochemical environments [34,35].

Previous studies aiming to the Bi influence in the CO adsorption on Pt(1 1 0) have been made by Hayden et al. in UHV for a (1×2) reconstructed surface [31,36,37]. Different ordered structures were observed depending on the Bi coverage and temperature annealing, which was necessary to obtain ordered adlayers. These authors reported that more complete ordering and the formation of a series of ordered bismuth overlayers on Pt(1 1 0) $- (1 \times 1)$ after annealing the surface above 350 K, while high annealing temperatures induced surface reconstruction at low Bi coverage. At very low Bi coverage (below 0.15) the surface reconstruction remained, and the Bi adopted the same structure as the substrate, shown by an attenuation of the (1/2) order reflexes of the (1×2) LEED pattern. At coverage just below 0.3, Bi lifted the reconstruction, and annealing the surface resulted in a higher ordering of the adlayers. At low coverages, below 0.55, Bi was preferentially adsorbed in fourfold hollow sites adopting a $c(2 \times 2)$ structure, whereas at higher coverages (above 0.55), repulsion between Bi atoms displaces them to bridge sites, and the spot pattern of the $c(2 \times 2)$ splits. At coverages higher than 0.7, a streaked (3×1) structure is formed which evolved to a (4×1) structure at coverage 0.75, which was the maximum saturation coverage [31]. Hayden et al. also studied the influence of Bi on hydrogen and oxygen adsorptions as well as on the electrooxidation of CO, all of them in UHV [31] and in electrochemical conditions [36]. Results showed that the coadsorption of CO and Bi in UHV produced mixed phases [31], and that the amount of adsorbed CO decreased linearly with increasing Bi coverage until reaching the Bi saturation coverage where the CO adsorption was fully inhibited. Similar experiments were also performed in electrochemical conditions [36]. The authors observed, in agreement with the UHV studies [31], that the amount of CO adsorbed also decreased with increasing Bi coverage, and furthermore, the oxidation potential of CO shifted towards higher potentials [36].

To our knowledge, systematic electrochemical studies related to the dissociative adsorption and the oxidation of formic acid with increasing Bi coverage on a Pt(1 1 0) surfaces have not been reported. Thus, in the present paper, we perform similar experiments to those previously reported with Pt(1 1 1) [9] and Pt(1 0 0) [10] regarding formic acid oxidation for increasing Bi coverages on a Pt(1 1 0) surface. This would complete the picture of the effect of Bi on the three platinum basal planes and would supply a full set of fundamental data that could be eventually applied to understand the reactivity of polycrystalline materials.

2. Experimental

The Pt(1 1 0) single crystal electrode was oriented, cut and polished from small (2–3 mm diameter) single crystal beads as reported [38,39]. Before each experiment, the electrode was flame annealed and cooled down in a reducing atmosphere containing $H_2 + Ar$, and protected with water in equilibrium with this gas mixture to prevent contamination before immersion in the electrochemical cell. It is reported that this treatment leads to the unreconstructed (1×1) surface [40]. In addition, the so-treated Pt(1 1 0) surface was subjected to a CO adsorption-stripping. For that, CO(g) was bubbled through the electrolyte at an admission potential of 0.05 V until the complete blockage of the surface was reached, which was monitored by cycling the electrode between 0.05 and 0.3 V. After that, CO was removed from the solution by bubbling argon (N50, Airliquide®), for at least 20 min. CO stripping voltammograms were registered at 20 mV s^{-1} in order to oxidize the CO molecules adsorbed on the surface in a single sweep. Despite these careful pre-treatment avoiding molecular oxygen, it has been concluded that several surface domains exist on the Pt(1 1 0) surface, which is less ordered than the other basal planes [41].

The electrode potential was controlled using a PGSTAT30 AUTO-LAB system. The counter electrode was a platinum spiral wire. Potentials were measured against a reversible hydrogen electrode (RHE) connected to the cell through a Luggin capillary. The voltammetric experiments were carried out in two classical three electrode electrochemical cells, one of them containing the blank solution (namely 0.5 M H_2SO_4), and a second one containing 0.5 M H_2SO_4 + 0.25 M HCOOH. This solution composition was chosen to compare the results obtained with those previously reported [9,10]. Electrolyte solutions were prepared from Milli-Q® water and Merck "p.a." sulphuric and formic acid. All the experiments were made at room temperature.

Bi was adsorbed on the electrode surface by simple contact of the electrode surface at open circuit with a solution containing Bi_2O_3 dissolved in 0.5 M H_2SO_4 for a given time. The electrode was then rinsed with ultrapure water and transferred to the cell containing the supporting electrolyte (0.5 M H_2SO_4) where the voltammogram was recorded at 50 mV s^{-1}. By changing the Bi concentration as well as the immersion time, different Bi coverage can be achieved. To analyse the surface composition, the charge involved in the so-called hydrogen adsorption–desorption region, which is related to the free Pt surface sites and the charge involved in the oxidation of the Bi adlayer were measured. The adsorbed Bi was oxidatively stripped by cycling the electrode from 0.5 to 0.95 V at a sweep rate of 2 mV s^{-1}.

For the formic acid electrooxidation experiments, the electrode, after coverage characterization, was transferred to a second cell, containing the formic acid solution (0.5 M H_2SO_4 + 0.25 M HCOOH) in which at least three cycles, at 20 mV s^{-1} were recorded up to 0.75 V, to keep constant the surface composition. After that, the electrode was rinsed with water and transferred back to the first cell to evaluate whether the electrode surface had suffered modifications and if the electrode coverage remained stable. Once the stability and cleanliness were checked, the electrode was put again in contact with the Bi^{3+} solution in order to increase the bismuth coverage. All this protocol was repeated as many times as necessary until the maximum coverage was reached.

For the spontaneous poison formation experiments, the electrode was put in contact with a solution containing 0.5 M H_2SO_4 + 0.1 M HCOOH for 2 min at open circuit potential ($\sim$0.1–0.2 V), which simulates the state of a hypothetical formic acid fuel cell anode at rest. After that, the electrode was transferred to the first cell, where it was put in contact with the solution at 0.05 V and the droplet containing the formic acid solution was dispersed.