



Electrodeposited platinum thin films with preferential (100) orientation: Characterization and electrocatalytic properties for ammonia and formic acid oxidation

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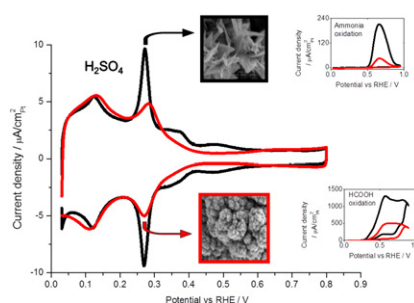
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HIGHLIGHTS

- ▶ Porous and preferentially oriented {100} Pt thin films are prepared.
- ▶ The surface of these electrodes is composed of up to 47% of (100) Pt sites.
- ▶ The current for the electro-oxidation of ammonia is 4.8 times higher than on polycrystalline Pt.
- ▶ The current for the electro-oxidation of formic acid is 2.6 times higher than on polycrystalline Pt.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 July 2012

Accepted 26 September 2012

Available online 27 October 2012

Keywords:

Electrodeposition
(100) surfaces
Bismuth adsorption
Ammonia oxidation
Formic acid oxidation

ABSTRACT

The electrocatalytic activity of preferentially oriented {100} Pt electrodes for the electro-oxidation of ammonia (0.2 M NaOH + 0.1 M NH₃) and formic acid (0.5 M HCOOH + 0.5 M H₂SO₄) was assessed. They were prepared without using any surfactant through potentiostatic deposition ($E_d = -0.10$ V vs RHE, [HCl] = 10 mM and [Na₂PtCl₆ · 6H₂O] = 0.5 mM) and by varying the deposition charge. For comparison, polycrystalline Pt thin films were prepared using the same solution but with $E_d = +0.10$ V vs RHE. Quantification of the fraction of (111) and (100) sites was performed by bismuth irreversible adsorption and deconvolution of the hydrogen region, respectively. Samples with as much as 47% of (100) surface sites were obtained. The preferential orientation was further confirmed by CO stripping voltammetry that exhibits similar characteristic features, as well as a similar potential of zero total charge than those expected for a preferential (100) surface. As compared to polycrystalline Pt, the occurrence of Pt (100) surface sites leads to an electrocatalytic activity enhancement by a factor of 4.8 and 2.6 (expressed as $\mu\text{A cm}^{-2}$) for the oxidation of ammonia and formic acid, respectively.

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1. Introduction

Platinum is one of the most studied elements in electrocatalysis and was investigated for several reactions including the electro-oxidation of hydrazine [1], ammonia [2], formic acid [3] and

a variety of alcohols [4]. In the last decades, improvements of the activity and the poisoning resistance of platinum-based catalysts have been obtained by increasing the electrochemically active surface area (EASA) and by mixing platinum with various elements to form alloys and core/shell nanostructures [5,6]. Optimization of the EASA was achieved by preparing 0D (nanoparticles) and 1D nanostructures (nanowires and nanotubes), both approaches resulting in an enhancement of the surface to mass ratio [7–13], while improvement

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of both the activity [14,15] and the resistance to poisoning [16] could be reached by preparing platinum alloys and core–shell structures. Also, these later approaches allow a reduction of the platinum content [17,18] and therefore a reduction of the cost of materials.

More recently, a new approach has started to emerge to improve the performances of a catalyst that consists in the preparation of electrodes with a specific surface crystallographic structure [19]. The impetus to follow that approach comes from several studies on single crystals that have shown that several electrochemical reactions of interest are structure-sensitive. For example, in alkaline medium, the electro-oxidation of ammonia on Pt occurs almost exclusively on surface sites with (100) symmetry [3,20,21]. Likewise, in acidic medium, platinum (100) single crystals have the highest intrinsic activity for formic acid oxidation, even though their resistance to poisoning is lower than onto (111) surfaces [4]. Therefore, careful tuning of the crystallographic surface orientation of an electrode can lead to drastic improvements in the activity, selectivity and stability of the catalyst.

In the early 1970s, experiments made by Arvia's group described an electrochemical method to modify bulk polycrystalline platinum to obtain surfaces with preferential orientation via the use of repetitive potential sweeps at high frequency under carefully-selected potential perturbation conditions [22–24]. However, because of the low roughness factor, even if the electrocatalytic activity, expressed in terms of current per Pt surface atom, was high, the resulting activity, expressed in current per geometric surface area, was low [22]. More recently, platinum nanoparticles with a preferential orientation were successfully prepared, exhibiting both a specific surface structure and a high EASA [25]. This was achieved using a capping agent, sodium polyacrylate, and hydrogen gas as a reducing agent. High resolution transmission electron microscopy confirmed that cubic Pt nanoparticles were obtained with (100) facets [26]. Further confirmation of the specific surface orientation was obtained by other groups as these nanoparticles exhibit characteristic hydrogen adsorption/desorption peaks [27], as well as a second peak during CO stripping experiments [28,29], and clear oxidation response of germanium adsorbed on platinum (100) sites [27]. However, the preparation of these shape-controlled nanoparticles by colloidal methods implies the use of organic ligand stabilizers, which can be challenging to remove without altering the surface orientation of the particles. In contrast, it was shown that electrodeposition can allow the preparation of platinum surfaces with a preferential (100) orientation without the use of surfactants, assuming that the deposition parameters have been carefully set [30,31]. This method, as the colloidal methods, allows the preparation of electrodes with a specific crystallographic surface structure and a high electrochemically active surface area, both in the form of thin films or nanowires, using a template-assisted deposition method in that later case [31].

In the present study, highly {100} oriented Pt thin films were prepared by electrodeposition. The deposition charges used in the preparation of the films were varied. The occurrence of (100) surface sites was assessed through a semi-quantitative analysis of cyclic voltammetric and CO stripping curves. The fraction of (100) and (111) surface sites was quantitatively assessed by deconvolution of the hydrogen desorption region and an analysis of the bismuth redox peaks, respectively. The results will then be correlated with the electrocatalytic activity of the electrodes for the oxidation of ammonia and formic acid. It will be shown that an increased fraction of (100) surface sites leads to an improvement of the electrode activity for both reactions.

2. Experimental

Platinum thin films were prepared by electrodeposition on titanium substrate (Alfa Aesar, 99%, 0.2 mm) pretreated according to

the procedure described elsewhere [32]. The electroplating solution consisted of 10 mM HCl (Fisher Scientific, ACS) and 0.5 mM $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar). All depositions were achieved under potentiostatic conditions using a VMP3 multipotentiostat (BioLogic), with the deposition potential referred to the reversible hydrogen electrode (RHE). After deposition, the samples were rinsed with de-ionized water (Millipore, specific resistivity 18.2 M Ω cm).

Electrochemical characterization was performed in a standard two-compartment cell using the RHE as reference electrode and a platinum wire as a counter electrode. A Luggin capillary was used to minimize the iR drop. Prior to the measurements, all glassware and cells were cleaned by first immersion in potassium permanganate solution overnight, and then rinsed with water and a solution of hydrogen peroxide in sulfuric acid. Finally, the glassware and the cells were thoroughly rinsed with de-ionized water, boiled for 30 min and rinsed again several times with de-ionized water. All solutions used were de-aerated using argon (N50, Air Liquid).

The electrochemically active surface area (EASA, expressed as cm^2_{Pt}) was determined from integration of the hydrogen desorption region (after subtraction of the double layer contribution) measured in 0.5 M H_2SO_4 Fisher Scientific, Trace Metals Grade, considering that the charge associated with one monolayer of hydrogen adsorbed on platinum is 230 $\mu\text{C cm}^2_{\text{Pt}}$ [33].

Bismuth irreversible adsorption was performed in a saturated bismuth solution (Bi_2O_3 , Sigma Aldrich, 99.999%) in 0.5 M sulfuric acid. After adsorption, Bi was oxidized at the Pt surface by scanning the electrode potential from 0.03 V to 0.75 V at 5 mV s^{-1} . The subsequent deconvolution of the hydrogen desorption region was performed with MagicPlot Student 1.5 using Lorentzian peak profile [27].

Carbon monoxide (N47 Air Liquid) adsorption was performed by bubbling CO gas in the electrolyte whilst the potential of the electrode is held constant at 0.15 V. This was done during 3 min, before the excess of dissolved CO was removed by bubbling Ar in the electrolyte for 30 min. Following that, three successive CO stripping voltammograms were recorded at 5 mV s^{-1} between 0.03 and 0.80 V.

Formic acid (Merck 98–100%, pro analysis) oxidation was done in 0.5 M HCOOH + 0.5 M H_2SO_4 . The oxidation of ammonia was performed in 0.05 M $(\text{NH}_4)_2\text{SO}_4$ (Merck, Pro analysis) + 0.2 M NaOH (Merck, Pro analysis). The ohmic resistance (iR drop) was evaluated from the high frequency (~ 100 kHz) intercept of the impedance spectrum (Nyquist plot, recorded at 0.56 V, in the double layer region) with the horizontal axis.

3. Results and discussion

3.1. Electrochemical characterization of the deposits

The experimental conditions required to prepare electro-deposited Pt thin films that are both highly porous and with a preferential {100} orientation are now well established [31]. The cyclic voltammogram (CV) in 0.5 M H_2SO_4 of a few typical examples are shown in Fig. 1 for Pt thin films prepared at a deposition potential, $E_d = -0.10$ V and low (0.5 mM) platinum salt concentration but variable deposition charges, Q_d , together with the electrochemical response of a polyoriented Pt thin film prepared at $E_d = +0.10$ V. In the lower potential range, the hydrogen desorption region displays three characteristic peaks (h_1 – h_3) located at 0.13, 0.26 and 0.35 V that are associated with (110) sites, (100) steps, and (100) terraces, respectively [31]. A fourth additional peak, h_4 , is observed at 0.48 V and is related to sulfate adsorption on wide (111) domains.

A qualitative assessment of preferential orientation in Pt thin films can be reached by looking at the relative intensity of h_1 – h_3 , and calculating the peak current ratio h_2/h_1 . Thus, it was

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