

Formic acid oxidation on Bi covered Pt electrodeposited thin films: influence of the underlying structure



Erwan Bertin, Sébastien Garbarino, Daniel Guay*

INRS-Énergie, Matériaux Télécommunications 1650 Blvd. Lionel-Boulet, C.P. 1020, Varennes, Qc Canada J3X 1S2

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ABSTRACT

Preferentially oriented (100) Pt electrodes, with up to 38% of (100) surface sites, were prepared by potentiostatic deposition. For comparison, disoriented Pt electrodes were obtained from the former electrodes following extensive potential cycling (25 cycles at 50 mV s^{-1} between 0.24 and 1.24 V vs SCE) in 0.5 M H_2SO_4 sulfuric acid. The adsorption of Bi was performed in a saturated bismuth solution for various periods of time resulting in different Bi coverage. The performances of these electrodes for formic acid oxidation were assessed by both cyclic voltammetry (CV) and chronoamperometry (CA) measurements, and compared to that of polycrystalline Pt electrodes. In the absence of Bi, although the three types of Pt electrodes show noticeable difference of activity for HCOOH oxidation during CV measurements, they exhibit the same low level of activity ($ca. 6 \mu\text{A cm}^{-2}_{\text{Pt}}$ at 0.14 V vs SCE) after one hour of electrolysis (CA measurements). In all cases, the adsorption of Bi increases the activity and the stability of the electrodes for HCOOH oxidation. During CV measurements, disoriented Pt shows the highest activity, with a maximum current during the negative-going sweep at optimum Bi coverage reaching 1250, 1400 and $500 \mu\text{A cm}^{-2}_{\text{Pt}}$ for highly oriented (100), disoriented and polycrystalline Pt, respectively. However, after one hour of electrolysis at 0.14 V vs SCE, the preferentially oriented (100) surface displays a higher current ($460 \mu\text{A cm}^{-2}_{\text{Pt}}$ at $\theta_{\text{Bi}} = 88\%$) compared to disoriented and polycrystalline Pt (293 and $214 \mu\text{A cm}^{-2}_{\text{Pt}}$ at θ_{Bi} of 84 and 77%, respectively). This is thought to be due to some inherent instability of the Pt(110) steps that are formed during the disorientation process of the preferentially oriented (100) Pt electrode. Taking into account the roughness factor of the electrodes ($R_f = 32.5$), the actual current of the best electrode after one hour of electrolysis at 0.14 V vs SCE is $ca. 15 \text{ mA cm}^{-2}_{\text{geo}}$.

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1. Introduction

The search for alternative and renewable energy source has attracted considerable interest in the last years. In the area of portable applications, fuel cells have long been considered a promising avenue. The oxidation of several potential fuels, such as hydrogen [1] or organic molecules like formic acid [2], methanol [3], ethanol [4], etc. has been widely studied on a wide spectrum of catalysts. In acidic media, platinum remains the most active catalyst, and was the subject of numerous studies despite its cost and scarcity.

To improve the activity of Pt, several approaches have been proposed, based on increasing the Pt electrochemically active surface area (EASA) and preparing Pt alloys and/or core-shell structure [5,6]. The use of nanoparticles (0D) or nanostructures (1D

nanowires and nanotubes), as well as high surface area supporting materials such as foams and aerogel allowed considerable improvements in the surface to mass ratio [7–10]. Nevertheless, platinum remained highly vulnerable to CO poisoning, a common by-product formed during the oxidation of small organic molecules [8]. The preparation of alloys such as PtCo, PtRu, etc., and the formation of core-shell nanostructure increased the CO tolerance [11], while at the same time allowing a reduction of the amount of Pt involved [4,12]. In some cases, the same strategies also lead to an improvement of the catalytic activity [13,14].

More recently, a different approach has started to emerge as a new way to prepare electrocatalysts, involving the formation of well defined crystalline surfaces. This approach originates from studies of single crystal surfaces which demonstrated that most electrochemical reactions are structure sensitive [15]. For example, the oxidation of ammonia [16] and hydrazine [17] on platinum in alkaline media occurs mainly on (100) surfaces. In acid media, platinum (100) surfaces have higher activity for formic acid and methanol oxidation, even though the poisoning tolerance of this

* Corresponding author.

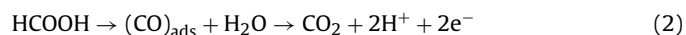
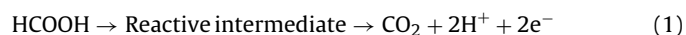
E-mail address: guay@emt.inrs.ca (D. Guay).

specific surface is lower than on the (111) surfaces [18]. So, from a conceptual viewpoint, it would be highly desirable to prepare electrodes with both a high electrochemically active surface area and a specific surface orientation to increase the electrocatalytic activity. However, up to now, it has been difficult to prepare electrodes with high electrochemically active surface area AND specific surface orientation. Indeed, in some cases, even if it was possible to drastically increase the electrocatalytic activity of the material, expressed in terms of current per Pt surface atom, the rugosity of the electrode remained low and the resulting activity, in terms of current per geometric surface area, was not very large [19].

At the end of the 1990th, the successful synthesis of platinum nanoparticles with a preferential orientation circumvented that issue, allowing the preparation of nanoparticles with both a specific crystalline surface structure and a high surface to mass ratio [20]. However, the method used organic ligand stabilizers, which can be challenging to remove without altering the surface structure. Only recently methods were developed to allow the preparation of macroscopic surfaces with preferential orientation without the use of any organic surfactants [21–26]. Among them, electrodeposition, under a careful set of conditions, appears a simple and versatile method to prepare these surfaces [22]. It also allows the formation of 3D nanostructured electrodes, e.g. nanowires and nanotubes, through a template assisted method that displayed the same preferential (100) surface orientation [22].

Although these methods lead to catalysts with a specific crystalline surface structure and a high electrochemically active surface area, they do not solve the issues caused by platinum sensibility to CO, a poisoning surface species. However, the addition of an element, such as Bi [27], Pb [28] or Sb [29] at the surface of the catalyst is known to increase the CO poisoning tolerance, and sometimes the electrocatalytic activity. The results were shown to depend not only on the nature of the adatom, but also on the geometry of the underlying platinum surface [27]. Most of these studies were performed for formic acid oxidation.

Direct formic acid fuel cells are nowadays an attractive power source for portable application [30] due to a higher open circuit voltage and lower fuel crossover compared to methanol. From a fundamental viewpoint, formic acid oxidation is also an ideal test reaction due to its well known dual path mechanism [31,32].



The species implied in the dehydrogenation process (Eq. 1) are not well established, as some studies suggest it does not exist [33], whereas other identify it as formate [34]. However it is well known that the dehydration path (Eq. 2) is occurring on bare platinum [35], which results in fast poisoning of the catalyst, especially on (100) and (110) surfaces [36].

In this study, electrodeposited platinum thin films were prepared by potentiostatic deposition. Polycrystalline and preferentially (100) thin films were prepared and characterized, both before and after surface reconstruction by cyclic voltammetry. The fraction of (100) and (111) surface sites was determined by deconvolution of the hydrogen desorption region and bismuth irreversible adsorption, respectively. The electrocatalytic performances for adsorbed CO and formic acid oxidation were then determined. The results show that all three types of Pt surfaces benefit from the adsorption of bismuth, although not equally. The maximum activity is observed for preferentially oriented (100) Pt partially covered with Bi ($\theta_{\text{Bi}} = 0.84$), which gives $460 \mu\text{A cm}^{-2}_{\text{Pt}}$ after 1 hour of electrolysis at +0.14 V vs SCE, which corresponds to an enhancement factor of 75 as compared to bare Pt surfaces. Taking into account the roughness factor of the electrode ($R_f = 32.5$), this corresponds to a current of *ca.* $15 \text{ mA cm}^{-2}_{\text{geo}}$.

2. Experimental

Platinum thin films were electrodeposited on Ti substrate (Alfa Aesar, 99%, 0.2 mm thickness), pretreated according to the procedure described elsewhere [37]. The electroplating solution consisted of HCl 10 mM (Fisher Scientific, ACS) and $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar) 0.5 mM for the preferentially oriented (100) electrode and the disoriented electrode. Both electrodes were prepared at the same deposition potential, $E_d = -0.35 \text{ V}$. The disoriented electrodes were obtained from preferentially oriented (100) Pt electrode through a potential cycling program consisting of 25 cycles at 50 mV s^{-1} between -0.24 V and 1.24 V in $0.5 \text{ M H}_2\text{SO}_4$ [21]. Platinum polycrystalline electrodes were prepared using an electroplating solution consisting of HCl 10 mM (Fisher Scientific, ACS) and $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar) 5.0 mM. In that case, $E_d = -0.15 \text{ V}$ was used. These conditions were chosen after a recent study describing the conditions needed to obtain a preferential (100) orientation during the electrodeposition of platinum [22]. All depositions were achieved under potentiostatic conditions using a Si 1287 potentiostat-galvanostat (Solartron), with the deposition potential referred to a standard calomel electrode (SCE). After deposition, the samples were rinsed with de-ionized water (Millipore, specific resistivity $> 18.2 \text{ M}\Omega \text{ cm}^{-1}$). Scanning electron microscopy measurements (not shown) reveals that all films have the approximately the same thickness (*ca.* $1 \mu\text{m}$ thick, corresponding to an electrodeposited charge of 2 C cm^{-2}).

Electrochemical characterisation was performed in a standard three-compartment cell using the SCE as reference electrode and platinum gauze as a counter electrode. A Luggin capillary was used to minimize the iR drop. All solutions used were de-aerated using argon (N5.0, Praxair). 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 Ar saturated H_2SO_4 0.5 M (Fisher Scientific, Trace Metals Grade), considering a charge associated with one monolayer of hydrogen adsorbed on platinum of $230 \mu\text{C cm}^{-2}_{\text{Pt}}$ [38]. During all measurements, an argon blanket was maintained above the solutions. For all the electrodes investigated in the present study, the roughness factor, R_f , which is the ratio between the EASA (as determined above) and the geometric surface area of the electrode, was 32.5 ± 2.5 . Also, in the present study, all currents were normalised to the initial surface area to reflect the overall performances of the electrodes.

The quantification of the (100) and (111) surfaces was achieved by bismuth adsorption and by deconvolution of the hydrogen desorption region according to the procedure described elsewhere [18]. Bismuth irreversible adsorption was performed in a saturated bismuth solution (Bi_2O_3 , Sigma Aldrich, 99.999%) in sulphuric acid 0.5 M. The subsequent deconvolution of the hydrogen desorption region was performed with MagicPlot Student 2.0 using Lorentzian peak profile.

Carbon monoxide (N2.5, Praxair) adsorption was performed by bubbling CO gas in the electrolyte at -0.16 V . After 3 minutes, the excess of dissolved CO was removed by bubbling Ar in the electrolyte for 30 min while holding the potential at -0.16 V . Following that, three successive CO stripping voltammograms were recorded at 5 mV s^{-1} between -0.24 and 0.54 V .

Formic acid (Fluka 98–100%, Trace Metal Grade) oxidation reaction was performed in $\text{HCOOH } 0.5 \text{ M} + \text{H}_2\text{SO}_4 \text{ } 0.5 \text{ M}$. Before the chronoamperometric (CA, performed at 0.14 V) and the cyclic voltammetry (CV, performed at 5 mV s^{-1}) measurements, a potential of 0.64 V was applied to remove any CO species at the surface and ensure that the electrodes were in similar conditions at the beginning of each experiment.

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