



Formic acid oxidation on antimony-covered platinum films with a preferential (100) orientation



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HIGHLIGHTS

- Sb submonolayers/Pt_{100 pref} electrodes were studied for the oxidation of HCOOH.
- Only a fraction of as-adsorbed Sb adatoms were in a metallic state.
- After potential cycling, all Sb adatoms were in a metallic state.
- Maximum activity was observed on disoriented Pt_{100 pref} with $\theta_{Sb} = 75\%$.
- After 1 h of electrolysis, currents as high as $15 \text{ mA cm}^{-2}_{\text{geometric}}$ were recorded.

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ABSTRACT

The spontaneous adsorption of Sb onto nanostructured platinum electrodeposited films with a preferential (100) surface orientation, hereafter denoted Pt_{100 pref}, was studied by means of electrochemical quartz microbalance (EQCM) and X-ray photoelectron spectroscopy. EQCM results indicated the formation of a Sb monolayer, while XPS analyses confirmed that a fraction of the as-adsorbed Sb adatoms were in a metallic state, while the others were in an oxidized state. After cycling, all of the Sb adatoms were in a metallic state. The electrocatalytic performances towards formic acid oxidation were assessed through cyclic voltammetry and chronoamperometry. On Pt_{100 pref}, the presence of Sb markedly increased the current on the forward scan up to the potential value (typically 0.20 V) corresponding to a redox reaction occurring on the adatom. After one hour of electrolysis, the current on the Pt_{100 pref} electrode covered with 75% Sb was ca. $15 \text{ mA cm}^{-2}_{\text{geometric}}$ at 0.14 V vs SCE, which is 100 times higher than on the bare Pt_{100 pref} electrode. The short- and long-term activities of the Pt_{100 pref} electrode were maintained even when the electrode was disoriented through potential cycling in the Pt oxide formation and reduction region.

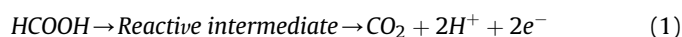
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1. Introduction

The search for alternative and renewable energy sources has attracted considerable attention in recent years. In that respect, the Polymer Electrolyte Membrane Fuel Cell (PEMFC) offers several advantages in converting the chemical energy of fuels into electrical energy. To overcome the challenges facing H₂-fed anode PEMFCs, the direct oxidation of liquid fuels is now viewed as an interesting alternative. Among the small organic molecules available as liquid fuels, formic acid (HCOOH) differentiates itself

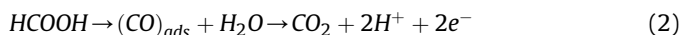
through its high theoretical electromotive force and lower permeation properties in Nafion® membranes, which leads to less crossover between the anode and cathode compartments and allow the use of higher-concentration solutions.

The HCOOH oxidation mechanism has been widely explored [1,2]. The oxidation of HCOOH is known to occur through either a direct pathway (full dehydrogenation of the HCOOH molecule; see Equation (1)) without any build-up of surface poisoning intermediates, or an indirect pathway (dehydration of the HCOOH molecule; see Equation (2)) leading to the formation of adsorbed CO and poisoning of the electrode surface.



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The species implied in the dehydrogenation process (Equation (1)) are not well-established, as some studies suggest that adsorbed formate decomposition is not rate-limiting [3], whereas others identify adsorbed formate (HCOO_{ads}) as a reactive intermediate in the main pathway and its decomposition to CO_2 as the rate-determining step [4–6].

Pt's properties for the dehydrogenation reaction make it the best choice for the electrooxidation of HCOOH. However, it is well-known that the dehydration path (Eq. (2)) is occurring on bare platinum [7], which results in rapid poisoning of the catalyst, particularly on (100) and (110) surfaces [8]. Accordingly, as the reaction proceeds, a growing proportion of the Pt surface is continuously poisoned by adsorbed CO, which eventually leads to a decrease in the overall reaction rate.

From single-crystal studies, it is now well-recognized that Pt(100) surface planes are the most active towards formic acid oxidation among the low index Miller indices [8–10]. Based on these model catalytic surfaces, studies performed on shape-controlled nanoparticles (e.g., cubic Pt nanoparticles enclosed with (100) faces [8] and preferentially (100)-oriented Pt thin films with high surface [11]) have confirmed the enhanced HCOOH activity at Pt(100) surface atoms. However, as shown by Grozovski et al., although Pt(100) surface atoms can achieve a maximum intrinsic activity 2.8 times higher than other Pt polycrystalline surfaces, they are also more prone to poisoning, and their poisoning resistance is 2.5 times lower than that of polycrystalline Pt [12].

To overcome the poisoning issue (by favoring the dehydrogenation pathway) while maintaining optimal HCOOH activity (exposure of (100) surface atoms), surface decoration by monolayer or sub-monolayer deposition of different adatoms onto Pt(100) surfaces was investigated. This strategy was determined to result in increased resistance to poisoning, as the overall HCOOH electrooxidation mechanism is modified by the presence of these adatoms. Among them, Pb, Pd, Bi, Te and Sb display both enhanced activity and long-term stability when deposited at monolayer or sub-monolayer coverages on Pt(100) single crystals (Bi [13], Sb [14], Te [15] and Pd [16]), on polycrystalline platinum electrodes (Pb [17]), on cubic nanoparticles (Pd [18]) and on poly-oriented nanoparticles (Bi [19]). Significant improvements were also observed on Pt(111) single crystals decorated with Bi [20], as well as on Bi-modified preferentially (111)-oriented Pt nanoparticles [19]. In a more recent study, the effect of Bi on the activity and stability of preferentially (100)-oriented Pt thin films with high surface area was investigated. Both the activity and stability of the electrode were shown to improve as a result of Bi adsorption [21,22].

Until recently, platinum single crystals were employed to study the effect of the decoration by adatoms on the electrooxidation of formic acid. However, because of the low roughness factor, even if high electrocatalytic activities were reported, the resulting current, normalized to the geometrical surface area, was low [23]. New synthesis methods allowed the preparation of shape-controlled platinum nanoparticles with a preferential surface orientation [24]. However, these methods rely on the use of capping agents, which are challenging to remove without altering the platinum structure. In the following work, high specific surface area platinum films with a preferential (100) surface orientation will be obtained in absence of any capping agents through a straightforward potentiostatic deposition [25], which allows the formation of preferentially (100) oriented films on a variety of substrates (such as Ti or carbon cloth), and decorated with Sb. The irreversible adsorption of Sb on well characterized platinum surfaces has been far less studied than Bi [26–28], and up to now the ratio Pt:Sb has

only been obtained through calculation performed using the oxidation charge and assuming that SbO was initially formed, although no experimental evidence of the formation of that compound was presented. In this work, the spontaneous deposition of Sb will be studied by electrochemical quartz crystal microbalance measurements and the chemical state of adsorbed Sb will be probed by X-ray photoelectron spectroscopy. The influence of Sb coverage onto both HCOOH activity and long-term stability will then be assessed. Finally, a reorganization of the Pt surface atoms will be performed via potential cycling, and the impact on Sb deposition and the electrooxidation of HCOOH will also be discussed in the light of recent density functional theory calculation, suggesting that Sb does not have only a third body effect on Pt(100) [29].

2. Experimental

Preferentially (100)-oriented platinum thin films, hereafter denoted Pt_{100 pref}, were electrodeposited on Ti substrates (1 cm², square, Alfa Aesar, 99%, 0.2 mm thickness) pretreated according to the procedure described previously [30]. The electroplating solution consisted of HCl 10 mM (Fisher Scientific, ACS) and Na₂PtCl₆·6H₂O 0.5 mM (Alfa Aesar) [11,25,31]. All depositions were achieved under potentiostatic conditions using a Versa Stat 3 potentiostat (Princeton Applied Research), with the deposition potential ($E_d = -0.35$ V) referred to the standard calomel electrode (SCE). In the following, all potentials are quoted with respect to the SCE. After deposition, the samples were rinsed with deionized water (Millipore, specific resistivity > 18.2 MΩ cm) and the electrochemical features were assessed in 0.5 M H₂SO₄ to probe the quality of the Pt crystallographic surface orientations and measure the electrochemical surface area (ECSA) [11,32]. Typically, deposits of 2C cm⁻²_{geometric} were performed, which results in films with an ECSA of 29 ± 3 cm⁻²_{Pt} or a roughness factor (R_f) of 29 ± 3. The roughness factor, R_f , is defined as the ratio between the ECSA (expressed in cm²_{Pt}) and the geometrical surface area (in cm²). Analysis of this electrode by bismuth irreversible adsorption and deconvolution of the hydrogen desorption region revealed that the surface is composed of 38 ± 3% and 19 ± 3% of (100) and (111) sites, respectively [21]. The disoriented Pt surfaces were obtained from Pt_{100 pref} films subjected to a potential cycling procedure consisting of 25 cycles at 50 mV s⁻¹ between -0.24 V and 1.24 V in 0.5 M H₂SO₄ [25,31]. After this procedure, surface analysis shows that only 18 ± 3% of (100) sites remains, and 14 ± 3% of (111) sites [21]. Finally, Sb deposition onto the different Pt thin films was carried out by irreversible adsorption by soaking them in a Sb saturated (Sb₂O₃, Alfa Aesar) solution of 0.5 M H₂SO₄ for various durations to obtain different coverages.

Electrochemical quartz crystal microbalance (EQCM) experiments were performed on gold-plated crystals (QCM 922, Princeton Applied Research, 9 MHz AT-cut, 0.2 cm²). Platinum thin films were electrodeposited from the same plating bath as noted above, but for shorter time periods (0.3C cm⁻²_{geometric}) to avoid saturation of the quartz crystal. The calibration constant (1.15 ng Hz⁻¹) was determined by lead deposition.

X-ray photoelectron spectroscopy (XPS) studies were performed on a VG Escalab 220i-XL using an Al K_α monochromatic source and a hemispherical analyzer with a multichannel detector. The baseline was established using a Shirley function. The O 1s core level was fitted using a mixed Gaussian–Lorentzian function, whereas the Sb 3d and Pt 4f core level regions were fitted using an asymmetric function (GL(90)T(1)).

Electrochemical characterization was carried out in a standard three-compartment cell at room temperature using Pt gauze as a counter electrode and SCE as a reference. The electrochemically

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