

Electrocatalysis of methanol, ethanol and formic acid using a Ru/Pt metallic bilayer

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Received 22 July 2006; received in revised form 29 September 2006; accepted 29 September 2006

Available online 17 November 2006

Abstract

This work describes the methanol, ethanol and formic acid oxidation using a metallic bilayer electrodeposited on a platinum substrate. Firstly, one monolayer of ruthenium was deposited on the substrate and over it a 1.1 layer of metallic platinum. In the blank solution it was observed that the electrochemical behavior of both the Pt/Ru/Pt and bulk Pt were very similar, except in the oxygen evolution potential region. Using X-ray photoelectronic spectroscopy (XPS) it was not possible to identify the presence of Ru atoms on the bilayer surface. The electroactive area and the RMS roughness factor measured with atomic force microscopy (AFM) for both materials are the same. A CO monolayer oxidation procedure confirmed that the systems have the same real surface area and also showed a shift in the negative direction for 54 mV on the CO peak potential for the bilayer. For the voltammetric organic molecules oxidation, an enhancement in the current densities of 350, 390 and 420% was observed for ethanol, methanol and formic acid, respectively, for the bilayer system compared to the bulk Pt electrodes. Also, a decrease of 110 mV in the beginning of the ethanol oxidation process was observed over the bilayer system compared to bulk Pt.

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Keywords: Ruthenium; Platinum; Small organic molecules; Oxidation; Nanotechnology

1. Introduction

Nowadays, the search for new sources of energy is important due to finite availability of fossil fuel reserves and also due to environmental concerns. In this context, fuel cells are a valuable option since they have high energy efficiency and low pollutant emission [1–5]. Different kinds of small organic molecules, such as methanol, and ethanol can be used as fuel. The main problem concerning the use of small organic molecules as fuel is that CO is an intermediate in the oxidation pathway [6–10]. This species adsorbs strongly on the platinum surface. Therefore, different authors have investigated the reaction mechanism and also the development of new electrode materials aiming at the identification of the intermediate species, the reaction byproducts and the displacement of the processes towards more negative potentials

[11]. In this sense, most of the papers in the literature describe the methanol oxidation [12–19]. During the oxidation process, the electrocatalyst must break the C–H bond enabling the reaction of the intermediate products (CO, H₂CO and HCOOH) with an O containing species leading to CO₂ at low potentials [7]. In the case of ethanol oxidation the catalyst must also break the C–C bond [20–22].

A simple and successful alternative to decrease the CO poisoning effect is the addition of supporting elements to Pt, ruthenium being employed most frequently. Other elements such as Sn and Rh have also been studied [23,24]. These elements provide the generation of O containing species at low potentials compared to pure Pt. This phenomenon is the well-known bifunctional mechanism, where the intermediate adsorbed products (CO_{ads}, as an example) react with hydroxylated species [25].

Recently, a new approach to the development of electrocatalysts has been proposed by our group [26,27]. We prepared multilayers of noble metals which have enhanced properties compared to pure metals or alloys [26,27]. The magnetic and

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electronic properties of multilayers have been widely studied in the literature and new attributes have been observed which are generically described as spintronic behavior [28]. From a theoretical point of view, Norskov and co-workers have investigated several aspects of the properties of metals and alloys [29–34]. These authors show that the CO adsorption energy is related to the substrate d-energy level. Recently, a paper was published that describes the effect of a platinum monolayer over different single crystals materials for the oxygen reduction reaction [35]. There, the electrocatalytical effect observed was also discussed based on d-orbitals level energy.

Our results for the bilayers show an improvement for the current density voltammetric peaks for small organic molecules oxidation up to 380% compared to flat polycrystalline Pt [26,27]. The same behavior was observed for the chronoamperometric measurements. These results indicate a decrease of the surface poisoning related to strongly bonded adsorbates. In the present paper, we prepared a new bilayer system based on a Ru/Pt deposited over a polycrystalline Pt substrate. The Pt layer was the metal exposed to the solution. We chose ruthenium due to the important literature results using this element alloyed to Pt as an electrocatalyst for small organic molecules oxidation. The bilayer system was characterized using X-ray photoelectronic spectroscopy (XPS), atomic force microscopy (AFM) and electrochemical techniques.

2. Experimental

Initially, the Pt electrodes were mechanically polished down to 1 μm with diamond paste and rinsed with acetone and a large amount of purified water (Milli-Q[®] system). Subsequently, one Ru monolayer was electrodeposited on the polycrystalline Pt substrate (geometric area = 0.2 cm^2) at 0.05 V versus hydrogen electrode in the same solution (HESS) during 300 s using a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ solution in 0.1 mol L^{-1} H_2SO_4 . After Ru deposition the electrode was rinsed prior to Pt deposition and placed in the Pt solution on an open circuit potential (ocp). Even at ocp it was not observed Ru dissolution prior Pt deposition. A 1.1 Pt monolayer was obtained over the Ru layer using a $5.0 \times 10^{-4} \text{ mol L}^{-1}$ H_2PtCl_6 in 0.1 mol L^{-1} HClO_4 solution. This electrodeposition was carried out at 0.05 V for 20 s. The thickness of the metal layers was calculated by the integration of the charge passed during the electrodeposition. Two Pt sheets with 2 cm^2 each were used as auxiliary electrodes. The small organic molecules oxidation was investigated in a 0.1 mol L^{-1} perchloric and 0.1 mol L^{-1} sulphuric media, using cyclic voltammetry and chronoamperometry. All the current densities are referred to electroactive area, which was calculated using the well-known procedure (hydrogen UPD desorption charges), obtaining a value of 0.38 cm^2 . Also, CO oxidation was performed to compare the catalytic properties of the two systems and verify their real surface areas. CO was adsorbed onto the polycrystalline Pt electrode by bubbling CO gas in a 0.1 mol L^{-1} perchloric acid solution for 30 min. Solution CO was subsequently removed by bubbling high purity nitrogen gas for 30 min holding the potential at 0.05 V. The potential was then cycled starting at 0.05 V for one complete oxida-

tion/reduction cycle. To check the reproducibility, the electrodes preparation and electrochemical experiments were performed twice at room temperature. The chronoamperometric oxidation data were measured at 0.5 V for ethanol and formic acid, and 0.6 V for methanol. The organic concentrations in the solutions were 0.5 mol L^{-1} for ethanol and methanol, and 1.0 mol L^{-1} for formic acid. All the solutions were prepared using analytical grade reagents and Milli-Q[®] system purified water.

An EG&G PARC 263 potentiostat was used in the electrochemical measurements. The monolayers were characterized by X-ray photoelectron spectroscopy and atomic force microscopy. XPS measurements were performed on freshly prepared Pt/Ru/Pt surfaces in ultra-high vacuum (low 10^{-7} Pa range) using a Kratos XSAM HS spectrometer. Non-monochromatic Al K α ($h\nu = 1486.6 \text{ eV}$) radiation was used as X-ray source, emission current of 12 mA at a voltage of 14 kV. High-resolution spectra were obtained with analyser energy of 20 eV. Shirley background, mixed Gaussian/Lorentzian functions and a least-square routine were used for the fitting to the peaks. AFM images and the roughness measurements were performed using a scanning tunneling microscope Digital Instruments (DI) Multimode AFM/STM controlled by Nanoscope III system (DI).

3. Results and discussion

3.1. Preparation and characterization of the Ru/Pt bilayer over Pt substrate

Fig. 1 shows the AFM micrographs for both Pt substrate (Fig. 1a) and Ru/Pt bilayer (Fig. 1b). To calculate the roughness mean square, five regions were measured on the surfaces

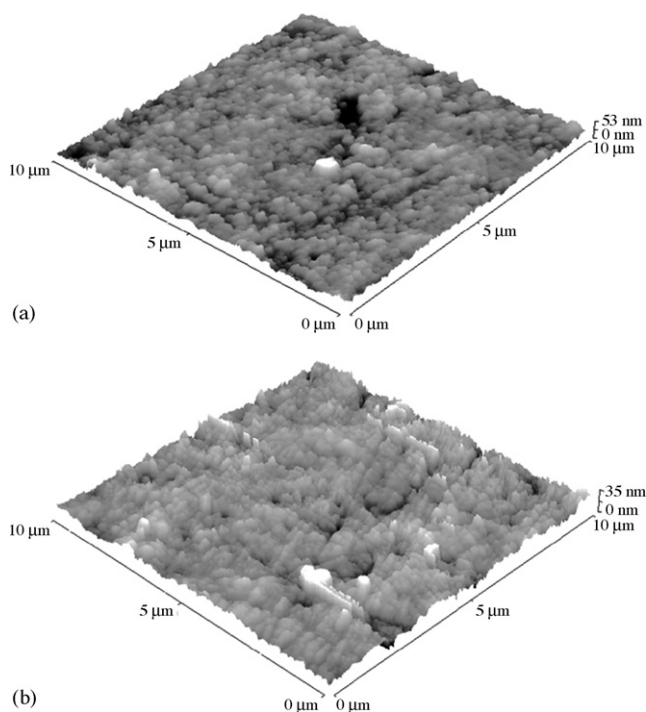


Fig. 1. AFM images for: (a) Pt substrate and (b) Ru/Pt bilayer electrodeposited over Pt.

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