

Short communication

Ethanol oxidation using a metallic bilayer Rh/Pt deposited over Pt as electrocatalyst

R.T.S. Oliveira^a, M.C. Santos^a, B.G. Marcussi^a, S.T. Tanimoto^b,
L.O.S. Bulhões^{a,c}, E.C. Pereira^{a,*}

^a Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Centro Multidisciplinar para o Desenvolvimento de Materiais Cerâmicos, Departamento de Química, Universidade Federal de São Carlos, C.P. 676, CEP 13565-905 São Carlos, SP, Brazil

^b GME, Departamento de Físico-Química, Instituto de Química de São Carlos, USP, Avenida do Trabalhador Sancarlense 400, CEP 13560-970 Centro, São Carlos, SP, Brazil

^c CENIP, Centro Universitário Central Paulista, UNICEP, Rua Miguel Petroni 5111, CEP 13563-470 São Carlos, SP, Brazil

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Abstract

This paper presents the preparation and characterization of a Rh/Pt bilayer electrodeposited on Pt and its behavior for ethanol oxidation in perchloric acid solution. The electrodes were characterized by atomic force microscopy (AFM) and cyclic voltammetry. The ethanol oxidation was studied on a Pt/Rh/Pt bilayer using cyclic voltammetry and chronoamperometry techniques. In this study, an increase of 268% in the current density peak for the ethanol oxidation and a displacement of 100 mV towards more negative values in the beginning of this process on the Pt/Rh/Pt are observed. The ethanol oxidation at constant potential ($E=0.5$ V versus reversible hydrogen electrode (RHE)) showed an increase of 10 times in the current density compared to polycrystalline platinum.

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1. Introduction

The electrocatalytic oxidation of small organic molecules such as methanol and ethanol has been the subject of a large number of recent investigations [1–9], due to their possibilities to convert chemical energy directly into electrical energy from a high energy density liquid fuel.

Most of the studies about ethanol electrooxidation have been devoted to study the reaction mechanism [6,8–10]. In these studies it has been established by spectroscopic methods or differential electrochemical mass spectrometry that acetaldehyde, acetic acid and carbon dioxide are the major products during the oxidation on Pt surfaces. Methane and ethane have also been detected [10]. One of the problems of the ethanol oxidation reaction is the poisoning of the

electrocatalyst surface with CO molecules [6–10]. Besides this problem, the break of the C–C bond, which is necessary to complete the oxidation of the molecule to CO₂, is another central problem of this process. The limited extension to which this reaction pathway occurs difficult the direct application of ethanol for energy conversion. Thus, a good electrocatalyst for the complete oxidation of ethanol to CO₂ must activate the C–C bond breaking while avoiding the poisoning of the catalytic surface by CO species.

Previous studies on ethanol electro-oxidation showed that Pt–Ru [9,11], Pt–Rh [8], Pt–Sn [6,12] alloys catalysts lower the onset potential of oxidation and increase the current density compared to Pt electrodes due to a decrease in the CO poisoning. This is a synergistic effect that can be interpreted in terms of the capability of Ru, Rh and Sn as an oxygen supplier at low potentials, which inhibits the adsorption of strongly bounded species generated from the oxidation.

* Corresponding author. Tel.: +55 16 3351 8214; fax: +55 16 3351 8214.
E-mail address: decp@power.ufscar.br (E.C. Pereira).

From a theoretical point of view, Norskov et al. [13,14] investigated the effect of a monolayer over pure metals, or even alloys, on its electrocatalytical properties. In these papers, the authors proposed that the most important parameter is the mean energy value of the “d” band level. Although there are papers concerning the experimental and theoretical behavior of the electrocatalytical properties of metals and alloys, only one paper was published considering the use of bilayers or multilayers for electrocatalysis purpose [1], where the authors studied the methanol electrooxidation on Pt/Rh/Pt bilayer in HClO₄ medium. The results observed in that paper showed an increase of 295% in the voltammetric current density peak for methanol oxidation over the Pt/Rh/Pt bilayers compared to Pt. The same behavior was also evident during constant-polarization studies.

Considering the results observed for methanol electrooxidation using Pt/Rh/Pt bilayer as electrocatalysts, in this paper it is proposed to investigate the electrocatalytical properties of Rh/Pt bilayers electrodeposited over platinum substrate for ethanol oxidation.

2. Experimental

Initially, the Pt electrode was mechanically polished down to 1 μm with diamond paste, washed with acetone and a large amount of water purified by the Milli-Q system. Rhodium was electrodeposited on the Pt polycrystalline substrate from a $2.0 \times 10^{-5} \text{ mol L}^{-1}$ RhCl₃·2H₂O solution in 0.1 mol L⁻¹ HClO₄ medium at $E = 0.05 \text{ V}$ (versus reversible hydrogen electrode, RHE) for 1800 s [15]. The Pt layer over the Rh layer was electrodeposited from a $5.0 \times 10^{-4} \text{ mol L}^{-1}$ H₂PtCl₆ in 0.1 mol L⁻¹ HClO₄ medium at $E = 0.05 \text{ V}$ for 20 s [1]. The thickness of the metals layers 2.3 and 1.7 monolayers for Rh and Pt, respectively, were calculated from the integrated charge during the electrodeposition. As reference and auxiliary electrodes, a RHE and a Pt plate with 2 cm² were used, respectively.

The ethanol oxidation was investigated in 0.1 mol L⁻¹ HClO₄ solution with different ethanol concentrations using cyclic voltammetry and chronoamperometry. All the electrochemical experiments were carried out at 25 °C. An EG&G PARC 263 potentiostat was used in the electrochemical measurements.

The 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

Fig. 1 presents the voltammetric characterization of the samples in 0.1 mol L⁻¹ HClO₄. In order to obtain a reproducible surface, prior to the experiments, all the electrodes were cycled between 0.05 and 1.55 V at 1 V s⁻¹ for 300

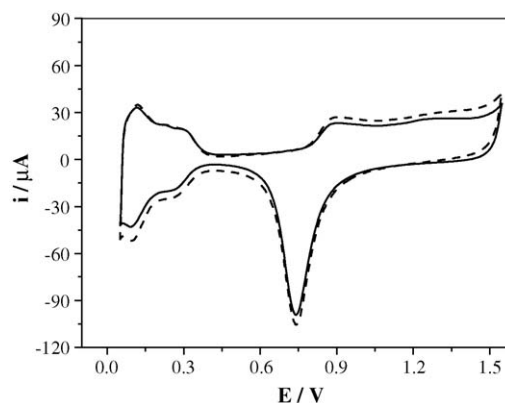


Fig. 1. Cyclic voltammograms of Pt electrode (dashed line) and Pt/Rh/Pt bilayer (solid line). The electrolyte was 0.1 mol L⁻¹ HClO₄ and $v = 0.1 \text{ V s}^{-1}$. $T = 25 \text{ °C}$.

cycles. For the polycrystalline platinum electrode (Fig. 1, dashed line), the voltammogram is well characterized [16], in the more positive potential direction, by the adsorbed H oxidation (0.05–0.40 V), followed by the double layer region (0.40–0.80 V), and finally, at higher potentials, by the PtO formation (0.80–1.55 V). In the scan toward negative potentials the reverse process occurs.

The solid line in Fig. 1 presents the electrochemical behavior of Pt/Rh/Pt bilayer, and it is similar to that of Pt polycrystalline electrode [1]. To determine the surface area of the Pt, and Pt/Rh/Pt bilayer, it was used the UPD of hydrogen desorption [17]. In the present paper, the currents presented in the figures were divided by the electrochemical active area ($A = 0.38 \text{ cm}^2$), considering $210 \mu\text{C cm}^{-2}$ as the desorption charge for hydrogen (UPD) on Pt.

The Pt voltammetric curve shape is completely recovered when the bilayer structure is formed, i.e., a Pt layer (1.7 monolayers) is deposited on top of the Rh layer (2.3 monolayers) (Fig. 1, solid line). Even the current density, which is related with the surface area, was recovered, indicating that the roughness factor did not change. Therefore, it is expected that no Rh sites exist on the bilayer surface because the voltammetric profile for rhodium [15] is totally different from that one here obtained at (Fig. 1, solid line). The voltammetric data is in agreement with XPS measurements previously published [1].

AFM images obtained for Pt electrode and Pt/Rh/Pt bilayer are presented in Fig. 2. The roughness mean square (RMS) for the Pt and Pt/Rh/Pt (bilayer) was calculated using the AFM measurements. The RMS data showed no significant changes between Pt electrode and the bilayer Pt/Rh/Pt system as can be seen in Table 1.

The ethanol electrooxidation process was investigated on Pt (polycrystalline) electrode (dashed line) and Pt/Rh/Pt bilayer system (solid line) in 0.1 mol L⁻¹ HClO₄ at 100 mV s⁻¹ (Fig. 3a) and 5 mV s⁻¹ (Fig. 3b). The general features of both voltammograms are the same. Two anodic peaks can be observed in the positive potential sweep from 0.05 up to 1.55 V versus RHE on both electrocatalysts, Pt/Rh/Pt and

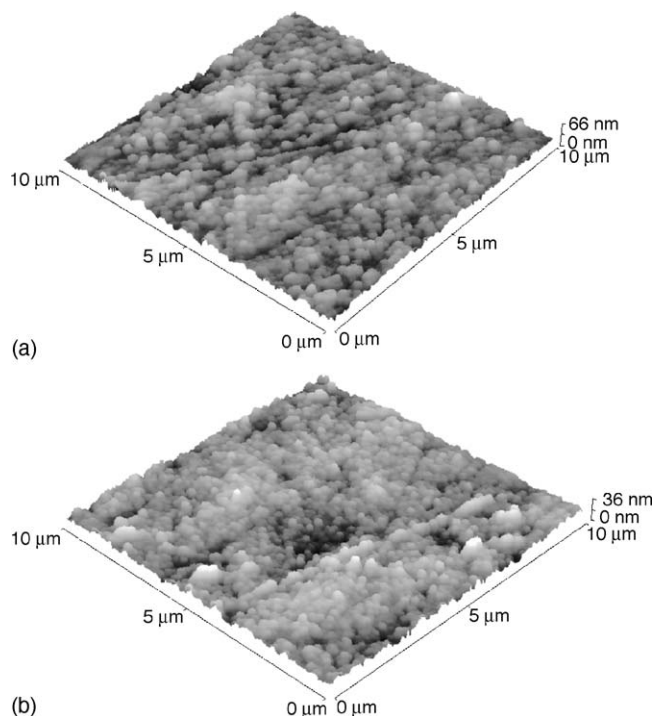


Fig. 2. AFM images of (a) Pt electrode and (b) Pt/Rh/Pt bilayer.

Pt. During the sweep toward negative potentials, from 1.55 to 0.05 V, one peak was observed related with ethanol adsorbates re-oxidation. The first peak in the cyclic voltammogram for ethanol oxidation on Pt is explained by a two-path mechanism, with the formation of CO_{ads} strongly bonded to the Pt substrate and also bulk oxidation [18]. The peaks in the oxide region of the CVs for Pt in acid solution are caused by production of CO_2 and carboxylic acid [18]. The main products of ethanol oxidation are adsorbed CO, adsorbed CH_3CO , CH_3CHO , CH_3COOH and CO_2 , which were detected by in situ reflectance spectroscopy and chromatography techniques [6]. Similar species have already been described in previous papers [8,9].

In this case the ethanol electrooxidation process onto bilayer Pt/Rh/Pt system (solid line) showed 268% increase of current density (0.85 V versus RHE), compared with Pt (polycrystalline) electrode (dashed line). The second anodic peak (1.23 V versus RHE) also presented a similar behavior, where an increase of 240% in the current density was observed. No

Table 1

Roughness mean square (RMS, nm) of Pt and Pt/Rh/Pt bilayer measured from AFM images in different regions of the electrodes

Region	Pt	Pt/Rh/Pt
1	4.9161	4.7415
2	6.7227	5.6331
3	6.2430	7.6844
4	7.4414	5.0037
5 ^a	7.2273	8.8699
Mean	6.5192 ± 1.0048	6.3867 ± 1.8005

^a Measured in the center of the sample.

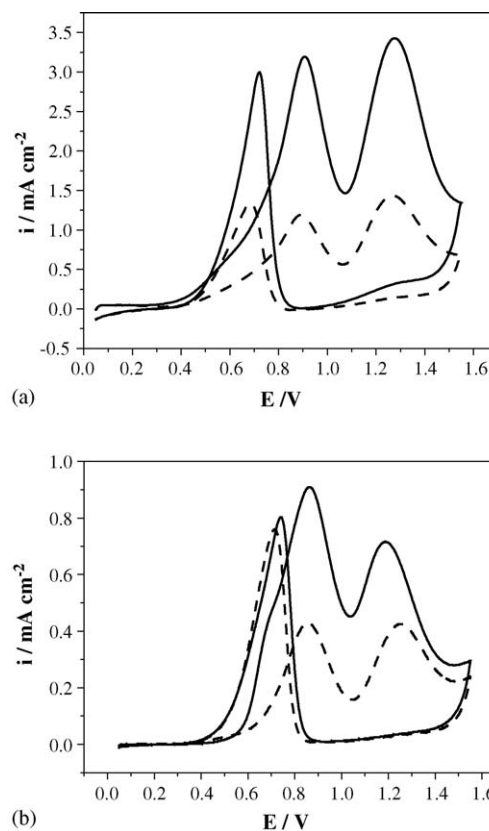


Fig. 3. Cyclic voltammograms for 0.5 mol L^{-1} ethanol oxidation in 0.1 mol L^{-1} HClO_4 solution on Pt electrode (dashed line) and Pt/Rh/Pt bilayer (solid line): (a) $v = 100 \text{ mV s}^{-1}$ and (b) $v = 5 \text{ mV s}^{-1}$. $T = 25^\circ\text{C}$.

changes of peak potentials were presented during positive sweep when we compared the Pt (polycrystalline) electrode and Pt/Rh/Pt bilayer. During reverse sweep, different potentials related to ethanol re-oxidation were observed on both electrocatalysts: on Pt (polycrystalline) electrode the current density peak is located at 0.68 V and on Pt/Rh/Pt bilayer at 0.72 V versus RHE, respectively. The increase of current density observed for the ethanol re-oxidation process was 222% higher on the bilayer than on Pt electrode. Although the general features of the ethanol oxidation were observed in both sweep rates investigated, there are differences between them: (a) for the measurement at 5 mV s^{-1} , the oxidation current density peaks do not have the same values; (b) the second oxidation peak potential, in the 1.2 V region, is displaced 70 mV towards more negative values; (c) during the sweep towards more negative potentials, the re-oxidation peak is not higher than those observed for Pt, although it is 40 mV more positive; (d) finally, at Pt/Rh/Pt it is observed a shoulder at 0.7 V.

Another important effect observed in the voltammogram measured using 100 mV s^{-1} is that the ethanol electrooxidation on Pt/Rh/Pt bilayer started in a less positive potential (100 mV) compared to Pt electrode as shown in Fig. 4. At 5 mV s^{-1} , it is not possible to detect accurately the potential where the oxidation process starts once there is a

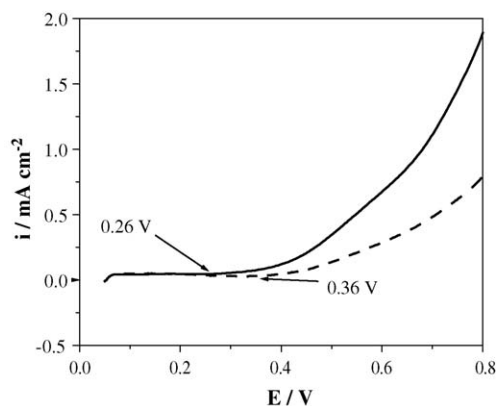


Fig. 4. Cyclic voltammograms presenting the beginning of the oxidation reaction. Solution: 0.5 mol L^{-1} ethanol in 0.1 mol L^{-1} HClO_4 . Pt (dashed line) and Pt/Rh/Pt bilayer (solid line). $v = 100 \text{ mV s}^{-1}$; $T = 25^\circ\text{C}$.

small shoulder observed in this potential region over the Pt electrodes.

Fig. 5 shows that, at different ethanol concentrations, both characteristics: the enhancement of current density for ethanol oxidation and the displacement of the potential towards negative values for the beginning of this process were observed on Pt/Rh/Pt, as previously pointed out. The propor-

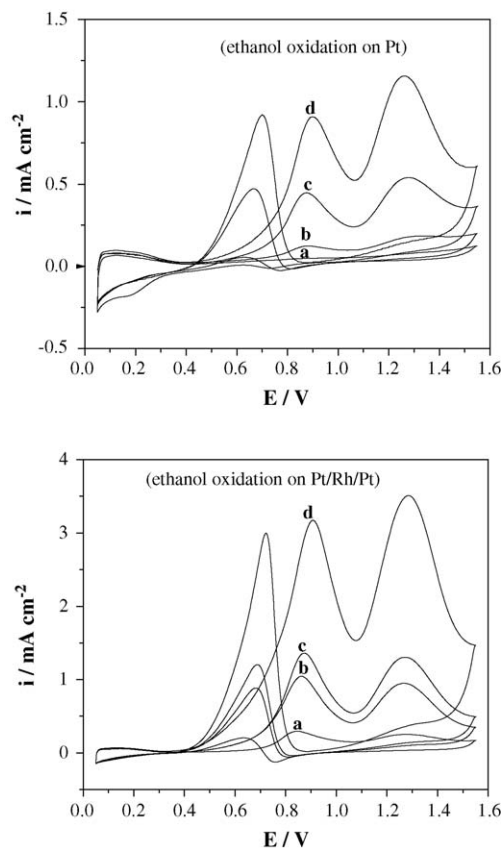


Fig. 5. Cyclic voltammograms of ethanol oxidation at different concentrations in 0.1 mol L^{-1} of HClO_4 solutions: (a) $10 \times 10^{-3} \text{ mol L}^{-1}$; (b) $50 \times 10^{-3} \text{ mol L}^{-1}$; (c) 100×10^{-3} and (d) $500 \times 10^{-3} \text{ mol L}^{-1}$ of ethanol. $v = 100 \text{ mV s}^{-1}$; $T = 25^\circ\text{C}$.

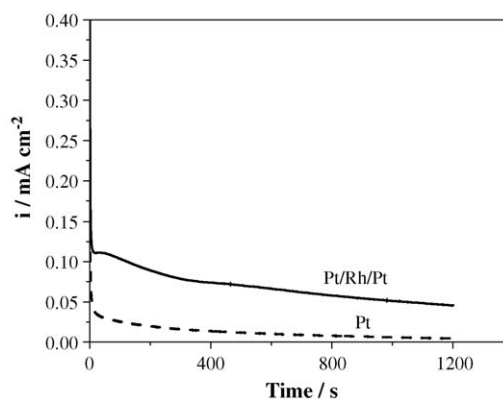


Fig. 6. Chronoamperograms measurements of the 0.5 mol L^{-1} ethanol oxidation in 0.1 mol L^{-1} HClO_4 at Pt (dashed line) and Pt/Rh/Pt bilayer (solid line) at $E_{\text{ox}} = 0.5 \text{ V}$. $T = 25^\circ\text{C}$.

tions of density current values for ethanol oxidation peaks remained constant as the ethanol concentration increased.

Fig. 6 presents the chronoamperograms at 0.5 V versus RHE obtained for 0.5 mol L^{-1} ethanol in 0.1 mol L^{-1} HClO_4 electrolyte. It is important to notice that the current densities observed in the chronoamperograms at 0.5 V versus RHE for the ethanol electrooxidation on Pt/Rh/Pt bilayer are 10 times higher than those observed on Pt electrode. The current densities measured for ethanol oxidation on Pt/Rh/Pt bilayer indicates that the bilayer structure decreases the poisoning effect of the strongly adsorbed species (e.g., CO) generated during ethanol oxidation.

The results here presented show clearly that the electrochemical oxidation of ethanol on the bilayer has an important catalytic effect in comparison with Pt electrode. Further experiments will be necessary to clarify the mechanism of this effect and to elucidate the electrochemical ethanol oxidation reaction mechanism.

4. Conclusions

An increase in the oxidation current density peak of 268% was observed for ethanol oxidation on Pt/Rh/Pt compared to Pt. Besides the ethanol electrooxidation on Pt/Rh/Pt bilayer started in a less positive potential (100 mV) compared to Pt electrode. For the voltammetric curves measured using 5 mV s^{-1} it was observed a shoulder in the 0.7 V region. Also there are difference in the ratio between the first and the second oxidation current density peaks compared to the data measured at 100 mV s^{-1} . The current densities observed in the chronoamperograms at 0.5 V versus RHE for this reaction on Pt/Rh/Pt bilayer are 10 times higher than those observed on Pt electrode. These results indicate that a decrease in the poisoning caused by strongly adsorbed intermediates (e.g., CO_{ads}) occurs. The observed current increase is not due to an increase in the surface area, which was the same value for both the bilayer and the Pt electrodes. On the basis of the results presented here, the Pt/Rh/Pt bilayer

appears as an improved electrocatalytical material for ethanol oxidation.

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