

# Metallic multilayered films electrodeposited over titanium as catalysts for methanol electro-oxidation



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## ABSTRACT

Multilayered Pt/Ir/Pt films were electrodeposited over titanium substrates, controlling the film thickness by the deposition charge. Two probe molecules were used to perform the evaluation of catalytic activity, CH<sub>3</sub>OH and CO. Using a 2<sup>2</sup> factorial design with a central point, optimized intrinsic catalytic activity was obtained over the Ti/Pt<sub>25mC</sub>/Ir<sub>6mC</sub>/Pt electrode. An enhancement of the current density of up to 2.76 times was observed for the methanol oxidation reaction (MOR) compared with the reference sample (Ti/Pt electrodes), even though both samples had the same electroactive area. In addition to the methanol oxidation voltammetry, CO stripping voltammetry suggests that MM-like systems are less susceptible to the catalyst-poisoning phenomenon compared to the Ti/Pt ones. Impedance spectroscopy was mainly used to monitor the charge transference resistance ( $R_{ct}$ ), whose results showed a clear  $R_{ct}$  reduction for the MOR process over MMs compared with Ti/Pt electrodes, corroborating the previous observations regarding the general catalytic improvement.

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## 1. Introduction

With regard to efforts to develop new alternative energy sources, direct methanol fuel cells (DMFCs) have recently been brought to the forefront due to their high applicability in a wide range of portable devices, such as cell phones and laptops [1]. However, current technology is insufficient to support large-scale production of cost-effective and highly efficient DMFCs in which fundamental challenges are mainly related to the sluggish kinetic rates of both the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR) [2]. Particularly in the alcohol oxidation process over pure platinum, the main problem consists in the well-studied poisoning effect caused by CO formation during the multi-step process of MOR [3–6]. To overcome this limitation, a number of works have focused on understanding the surface phenomena associated with the catalysis of organic molecules and, from a more practical point of view, developing new materials to be used as anodes in which the poisoning effect of the adsorbed CO could be lowered. In this sense, among the alternatives described in the literature, the addition of secondary elements to platinum (alloyed or not) such as Ru, Rh, Sn, Mo, W, Os, and Ni [7–15] is often exploited. This effect is usually explained by the combination of two distinct mechanisms: the bi-functional and the electronic mechanisms [16]. More recently a new approach to prepare

electrocatalysts has been proposed, using platinum based nanostructures, as core-shell [17–20] and metallic multilayers (MMs). The great interest in MMs arose with the discovery of the Giant Magnetic Resistance effect by Fert et al. [21] and Grünberg et al. [22]. Thus, these low dimensional systems, such as monolayers and MMs, have been proposed as a new kind of material in which both electronic and structural properties are different from those of the pure metals or their alloys. To the best of our knowledge, our group was pioneer in proposing the implementation of MM-based materials in electrocatalysis [23–30], which exhibit improved properties, referred to by the authors as the Giant Multilayer Effect (GME) [27]. These new materials significantly improve the catalytic activity for the oxidation of small organic molecules, resulting in an increased response of current density as well as a potential onset displacement to more negative potentials [27]. From a practical point of view, those observations allowed the proposition of innumerable other different MM-based materials for use in electrocatalysis. However, as this effect was obtained using high-cost polycrystalline bulk platinum as substrate, the problem remains unsolved from an economic standpoint. In view of the above, the next question was whether the GME effect could be reproduced in other electrode configurations with the aim of reducing the platinum content. To verify this possibility, the present work describes the development of Pt/Ir/Pt MM electrodes over a titanium substrate and its influence on the general catalytic performance.

Herein, the choice of titanium as the substrate was made based on its low cost and high resistance to acid as well as its feasibility for metal electrodeposition. Besides, doping of Ti and

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Ti/TiO<sub>2</sub> electrodes with noble metals has been widely used as an important strategy to improve catalytic activity for a variety of electrochemical reactions, such as oxygen, hydrogen, and chlorine evolution [31–34] and alcohol oxidation [34–39]. Thus, in view of the good properties of titanium as substrate and the good catalytic responses already observed for MM electrodes based on platinum, the preparation and characterization of Ti/Pt/Ir/Pt electrodes of different compositions was performed, focusing first on the influence of the Pt/Ir bilayer thickness on the results for methanol and carbon monoxide electro-oxidation.

## 2. Experimental

Working electrodes were prepared using titanium rods (99.7%, Sigma–Aldrich), with an exposed area of 0.28 cm<sup>2</sup>, embedded in epoxy resin. We took special care to inhibit massive growth of TiO<sub>2</sub> on the Ti substrate, due to the high resistive character of titanium dioxide film. The Ti substrates were mechanically polished down to No. 2000 emery paper and washed several times with reverse membrane purified water. Platinum was electrodeposited on these substrates from a 10<sup>−3</sup> mol L<sup>−1</sup> H<sub>2</sub>PtCl<sub>6</sub> (Sigma–Aldrich) solution, forming the Ti/Pt structures. Then MM structures were prepared by electrodepositing Ir and Pt over the Ti/Pt structures from single baths of 10<sup>−3</sup> mol L<sup>−1</sup> H<sub>2</sub>PtCl<sub>6</sub> (Sigma–Aldrich) and 10<sup>−4</sup> mol L<sup>−1</sup> IrCl<sub>3</sub> (Alfa Aesar), respectively. The electrochemical cell was a three-electrode double-walled thermostated glass cell, and electrochemical characterization was accomplished using an Autolab PGSTAT 30 potentiostat/galvanostat. A hydrogen electrode in the same solution was used as the reference electrode (RHE). Two 4 cm<sup>2</sup> Pt plates were used as auxiliary electrodes. All experiments were performed at room temperature (25 °C), using 0.1 mol L<sup>−1</sup> HClO<sub>4</sub> as support electrolyte. The depositions were carried out at constant potential in experiments applying 0.05 V and controlling the charge ( $Q_{\text{dep}}$ ).  $Q_{\text{dep}}$  were used as variables in a 2<sup>2</sup> factorial design with a central point, which was performed to find the catalysts' optimum configuration for the CH<sub>3</sub>OH oxidation. The voltammetric curves were measured in a potential range between 0.05 and 1.55 V at 50 mV s<sup>−1</sup>. Prior to the experiments, solutions were deaerated with N<sub>2</sub> for 15 min. Methanol oxidation was investigated in a 0.5 mol L<sup>−1</sup> methanol solution. CO stripping measurements were also performed to compare the catalytic properties of Ti/Pt and MM electrodes. CO was adsorbed onto the MM or Ti/Pt electrode by bubbling CO gas (analytical grade) in the 0.1 M HClO<sub>4</sub> solution for 6 min prior to the experiments. The dissolved CO was then removed from the solution by bubbling high purity nitrogen gas for 6 min, maintaining the applied potential at 0.05 V. The electrode surfaces were characterized by atomic force microscopy (AFM) using SPM 5500–Agilent equipment in contact mode. For the impedance spectroscopy (EIS) measurements, the amplitude of AC potential modulation was 10 mV and the frequency was varied from 10 kHz to 0.01 Hz using an Autolab PGSTAT 30 potentiostat/galvanostat with an FRA module. All data were acquired after polarization times of 5 min to achieve the steady state.

## 3. Results and discussion

First of all, platinumized titanium electrodes (Ti/Pt) were prepared by reducing Pt ions over titanium substrate, applying 0.05 V versus the RHE and controlling the deposition charge. The charge of the platinum deposition was high enough to guarantee the well known polycrystalline platinum (Pt<sub>pc</sub>) voltammetric fingerprint. The minimum  $Q_{\text{dep}}$  necessary to obtain such a reproducible Ti/Pt profile was 25 mC. To study the optimization of the catalytic properties of MM electrodes, two levels of platinum internal layer thicknesses were chosen, named 25 mC and 50 mC, which stand for the deposition

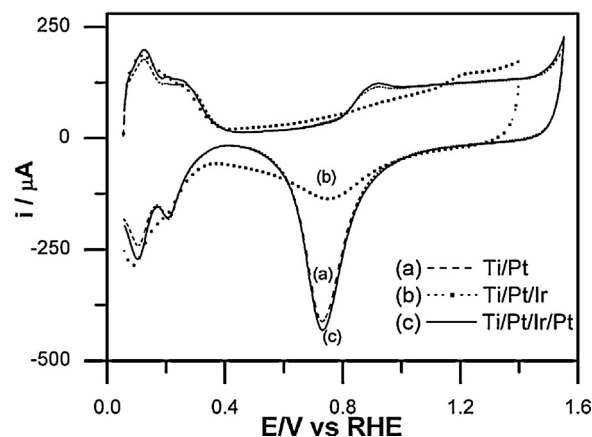


Fig. 1. Typical voltammetric profile obtained for (a) Ti/Pt; (b) Ti/Pt/Ir; (c) Ti/Pt/Ir/Pt.

charges. On these Ti/Pt substrates, Ir layers were electrochemically deposited using 3 or 6 mC charges. Finally, Ti/Pt/Ir structures were submitted to another electrodeposition to form an external platinum layer. The outermost platinum layer was deposited taking into account an electroactive area criterion; that is, the outer layer deposition charge was chosen to match the electroactive area of the Ti/Pt electrode. Fig. 1 presents a typical voltammetric profile of the MM structures obtained after each step of preparation described above. We emphasize that these voltammograms (Fig. 1) are not normalized by any parameter such as area or electroactive area. As can be visualized in Fig. 1, the voltammograms are in agreement with the classical works of Conway et al. for these metals in acidic medium [40,41]. Even after a large number of cycles using a high scan rate (2000 cycles in 1 V s<sup>−1</sup>) the voltammetric response remained the same, revealing good adherence and chemical stability of the deposited layers.

The hydrogen under potential deposition (UPD) region was employed to calculate the electroactive area using 210 μC cm<sup>−2</sup> as the standard charge density for the adsorption of one hydrogen monolayer [42], and these values were then used to normalize the electrochemical data. AFM images helped to confirm the full and regular platinum surface covering (Fig. 2). It is possible to verify that in the first deposited layer the coalescence process resulted in well distributed nanometric platinum grains. It is important to point out that the electroactive area obtained by the hydrogen UPD region does not differ significantly between the two samples (presented in Fig. 2b and d).

Multilayered electrodes (Ti/Pt/Ir/Pt) with different platinum and iridium contents were tested for methanol oxidation using cyclic voltammetry. These results were compared with Ti/Pt electrodes. Typical platinum responses for methanol oxidation in acidic media were observed in all the electrocatalysts: two oxidation peaks centered in the positive sweep and a reactivation process indicated by a third anodic peak in the negative one [1]. As can be observed in Fig. 3a and b, comparing Ti/Pt electrodes with MM structures, no significant difference can be observed for the onset potential, which remained around 0.6 V in all cases. Nevertheless, the first oxidation peak in the positive sweep revealed an important increase in current density. This first anodic step is attributed to the removal of dehydrogenated/adsorbed species (e.g., adsorbed CO) from the platinum surface by the oxygenated ones such as PtOH [3]. During this process centered at 0.9 V (main oxidation peak), chemical species such as CO, CO<sub>2</sub>, HCOOH, HCOH, and HCOOCH<sub>3</sub> can be formed [3,4,6].

Comparing MM structures deposited on Ti/Pt<sub>50mC</sub> with the Ti/Pt<sub>50mC</sub> structures, current density increases up to 1.78 times for the main oxidation peak were observed. In the case of the

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