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_3OH and CO. Using a 2^2 factorial design with a central point, optimized intrinsic catalytic activity was obtained over the $Ti/Pt_{25mC}/Ir_{6mC}/Pt$ 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.

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 innumerous 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$_2$ 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^2, embedded in epoxy resin. We took special care to inhibit massive growth of TiO$_2$ 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^{-3} mol L^{-1} H$_2$PtCl$_6$ (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^{-3} mol L^{-1} H$_2$PtCl$_6$ (Sigma–Aldrich) and 10^{-4} mol L^{-1} IrCl$_3$ (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^2 Pt plates were used as auxiliary electrodes. All experiments were performed at room temperature (25 °C), using 0.1 mol L^{-1} HClO$_4$ as support electrolyte. The depositions were carried out at constant potential in experiments applying 0.05 V and controlling the charge (Q$_{dep}$). Q$_{dep}$ were used as variables in a 2^2 factorial design with a central point, which was performed to find the catalysts' optimum configuration for the CH$_3$OH oxidation. The voltammetric curves were measured in a potential range between 0.05 and 1.55 V at 50 mV s^{-1}. Prior to the experiments, solutions were deaerated with N$_2$ for 15 min. Methanol oxidation was investigated in a 0.5 mol L^{-1} 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$_4$ 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, platinized 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$_{pc}$) voltammetric fingerprint. The minimum Q$_{dep}$ 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
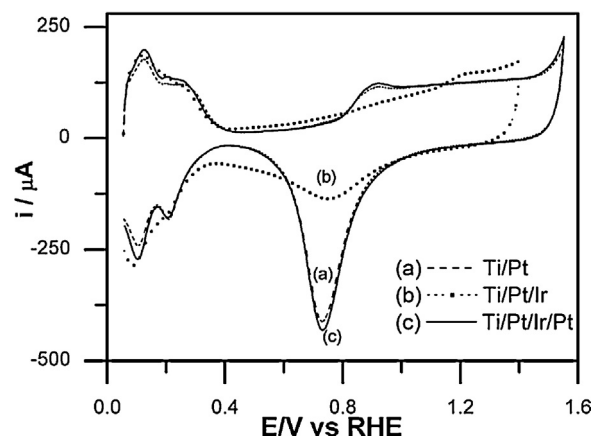

Fig. 1. Typical voltammetric profile obtained for (a) Ti/Pt; (b) Ti/Pt/Ir; (c) Ti/Pt/Ir/Pt.

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 outmost 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^{-1}) 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^{-2} 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$_2$, HCOOH, HCOH, and HCOOCH$_3$ can be formed [3,4,6].

Comparing MM structures deposited on Ti/Pt$_{50 mC}$ with the Ti/Pt$_{50 mC}$ structures, current density increases up to 1.78 times for the main oxidation peak were observed. In the case of the
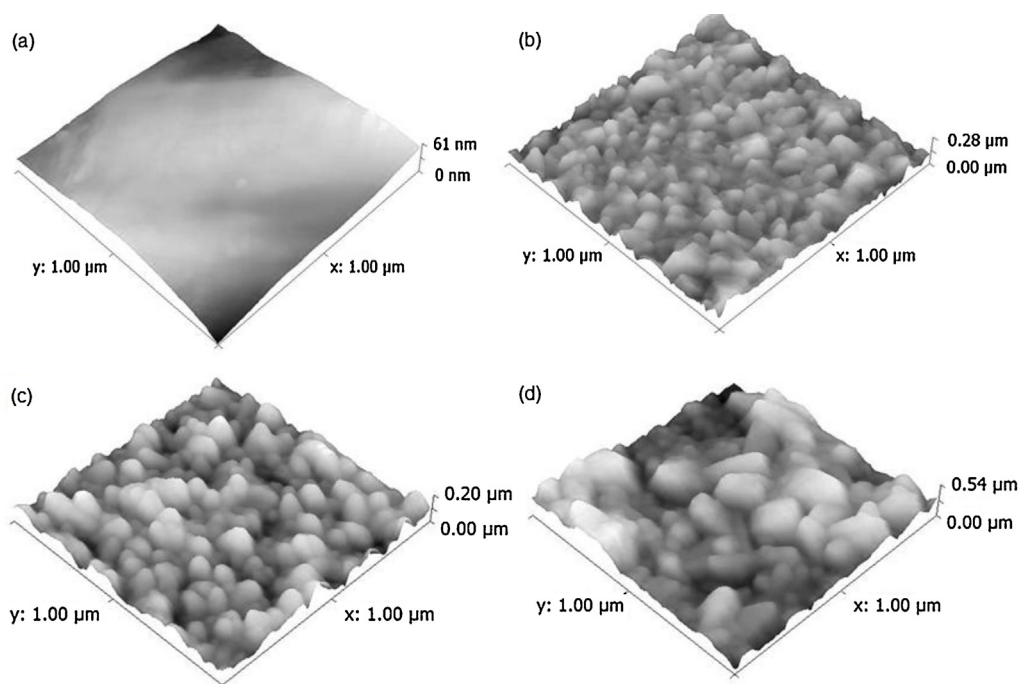
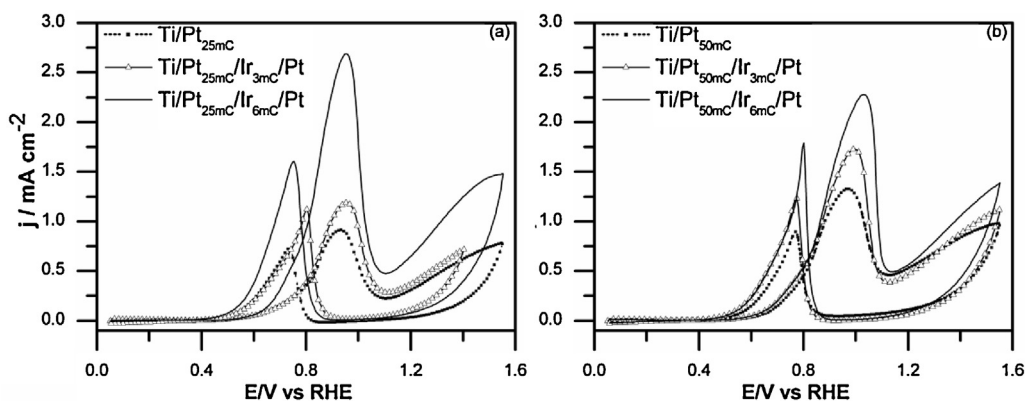**Fig. 2.** AFM images. (a) Fresh titanium used as substrate; (b) Ti/Pt; (c) Ti/Pt/Ir; (d) Ti/Pt/Ir/Pt.

Fig. 3. Oxidation voltammograms of 0.5 mol L^{-1} methanol in 0.1 mol L^{-1} HClO$_4$ support electrolyte over (a) Ti/Pt$_{25\,mC}$ (solid squares), Ti/Pt$_{25\,mC}$/Ir$_{3\,mC}$/Pt (open triangles), Ti/Pt$_{25\,mC}$/Ir$_{6\,mC}$/Pt (solid line); and (b) Ti/Pt$_{50\,mC}$ (solid squares), Ti/Pt$_{50\,mC}$/Ir$_{3\,mC}$/Pt (open triangles), Ti/Pt$_{50\,mC}$/Ir$_{6\,mC}$/Pt (solid line). $T = 25\,°C$; scan rate: 50 mV s^{-1}.

MM structures deposited on the Ti/Pt$_{25\,mC}$ structures, an even higher difference was observed, in which a 2.76-fold increase in current density was well reproduced. To better comprehend the influence of the thickness of the Pt/Ir bilayer on the catalytic activity, relative current density (J_{rel}) was used as the response in a 2^2 factorial design with a central point, which is described in detail in Table 1. Here, J_{rel} is defined as the ratio between the current density observed for MM structures and those on

Ti/Pt electrodes under the same experimental conditions. Effects and interactions between the variables were calculated using a well-established statistical procedure [43]. Considering that the electroactive surface area for Ti/Pt and Ti/Pt/Ir/Pt electrodes was always kept constant, J_{rel} captures the variations in current which are not related to area changes. Therefore, only electronic or mechanistic modifications are discussed using this parameterization.

Table 1
Electrodes description, relative current density responses used in the 2^2 factorial design, and current gains for the MOR at 25 °C in 0.1 mol L^{-1} HClO$_4$.

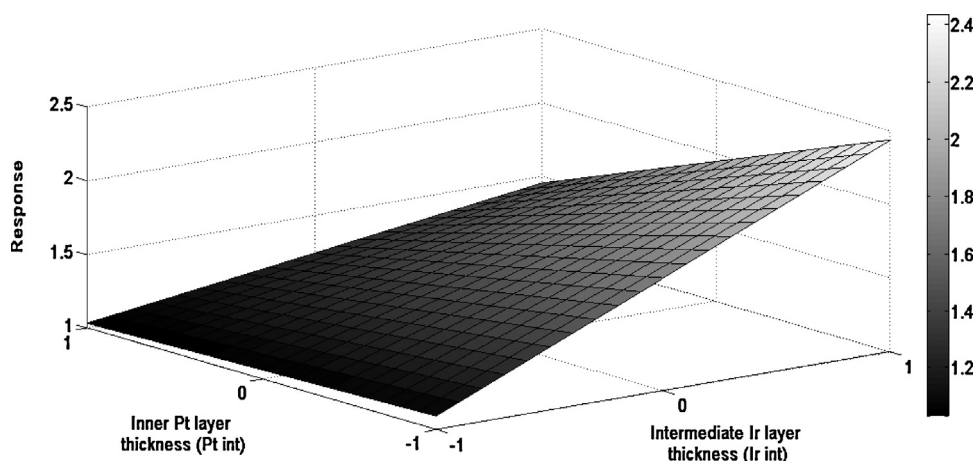| Electrode description	Q$_{dep}$ (mC)		Coded values		Electroactive area (cm^2)	J_{rel}	Current gain (%)
	Pt$_{int}$ (x_1)	Ir$_{int}$ (x_2)	x_1	x_2			
Ti/Pt$_{25\,mC}$/Ir$_{3\,mC}$/Pt	25.0	3.0	−1	−1	1.77	1.42	42
Ti/Pt$_{25\,mC}$/Ir$_{6\,mC}$/Pt	25.0	6.0	−1	+1	1.91	2.76	176
Ti/Pt$_{37.5\,mC}$/Ir$_{4.5\,mC}$/Pt[a]	37.5	4.5	0	0	2.13	1.15	15
Ti/Pt$_{50\,mC}$/Ir$_{3\,mC}$/Pt	50.0	3.0	+1	−1	2.91	1.36	36
Ti/Pt$_{50\,mC}$/Ir$_{6\,mC}$/Pt	50.0	6.0	+1	+1	2.99	1.78	78

[a] Central point.

Fig. 4. Surface response obtained from the adjusted model equation for the 22 factorial design with a central point.

Two variables – the inner platinum layer (Pt_{int}) and the intermediate iridium layer (Ir_{int}) thickness (charges) – were studied for two different values (levels) of deposition charge plus a central point, and its codification was used to model a response surface, considering it as a linear function. The resultant surface response is shown in Fig. 4. The optimum conditions are clearly visualized in the region where higher values of iridium content and lower values of platinum content are localized.

It is important to stress that all the values are averages of at least three experiments. In Table 2, the data are not the responses themselves but instead the effect of the changes in variables on their values. Therefore, a negative effect like the one obtained for the Pt_{int} variable means that an increase in the layer thickness is accompanied by a decrease in the response J_{rel}.

On the other hand, a positive effect like that obtained for the Ir_{int} variable suggests that a larger layer thickness of iridium favors an increase in J_{rel} values. Regarding the interaction between the variables, a negative value was found, which means that increasing the thickness of both layers simultaneously is not favorable for the enhancement of the response.

Extending the systematic study of the catalyst performance, another important parameter to be probed is the CO anodic oxidation. The purpose of this part of the work is to better understand the fundamental aspects of the oxidation reaction of a simple intermediate species over the material surfaces developed here. In Fig. 5 the results for the adsorbed CO stripping voltammetry are presented. Important features were observed: (a) differences in the onset potential; (b) differences in the current density and charge of the oxidation peak; (c) changes in the general voltammetric shape. Comparing the MM electrode ($Ti/Pt_{25\,mC}/Ir_{6\,mC}/Pt$) with the Ti/Pt ($Ti/Pt_{25\,mC}$) one, it is possible to note a sharper oxidation peak with a 2.5-fold current density increase and an onset potential shift of 70 mV to more negative potentials. Besides, the peak charge for the MM electrode is smaller than that for the Ti/Pt, which could be related to a weaker CO adsorption on MM-type electrodes [44]. Broader peaks could suggest that several coupled processes are

occurring but appear as a single response at this scan rate. One possible explanation for the observed effects could be the one proposed by Gutiérrez et al. [45]. The authors studied CO stripping profiles over Pt deposited on Au substrates, and reported an increase in current density values along with shifts in the onset potential to more negative values as the thickness of the metallic layers increased. The authors suggest that the electrocatalytic changes are due to two main factors: (1) the different lattice parameters of Pt and Au, which would cause tension in the structure (thereby weakening the Pt-CO bonds) and (2) the increased density of active sites (steps and kinks) on the Pt surface.

Besides, regarding the possible weakening of CO adsorption over Pt modified structures, Hoster et al. [46] reported changes of adsorption energies and showed vertical ligand effects in systems with mono- and multi-layers of platinum on ruthenium. Correlating voltammetric data and studies by DFT (density functional theory) and STM (scanning tunneling microscopy), the authors demonstrated the presence of lateral atomic strains compared to similar bulk structures, for example Pt (1 1 1). Other authors propose that the characteristics of the surface metal d-bands, particularly the weighted center of the d-band (ε_d), play a decisive role in determining surface reactivity [47–49]. Compressive strain tends to downshift ε_d in energy, causing adsorbates to bind less strongly, whereas the tensile strain has the opposite effect. From this point of view, it is plausible to consider that the position of ε_d for Pt in the studied structures is affected by the strain (geometric effects)

Table 2
Calculated effects and interaction between variables of the 2^2 factorial design with a central point.

	Effects		Errors
Mean value	1.85	±	0.02
Pt_{int}	−0.54	±	0.04
Ir_{int}	0.89	±	0.04
$Pt_{int} \times Ir_{int}$	−0.50	±	0.04

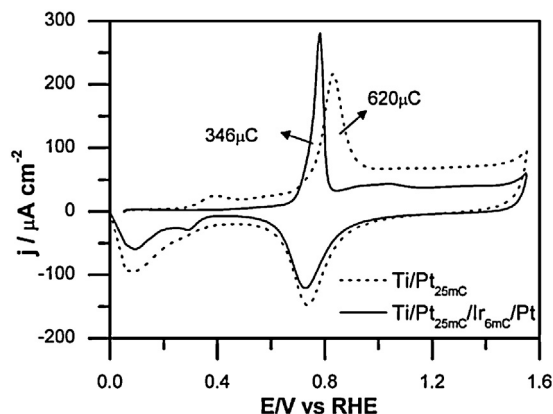**Fig. 5.** CO stripping voltammograms over Ti/Pt (dotted line) in comparison with MM electrode (solid line). $T = 25\,°C$; $\nu = 50\,mV\,s^{-1}$. Peak charges are indicated by arrows.
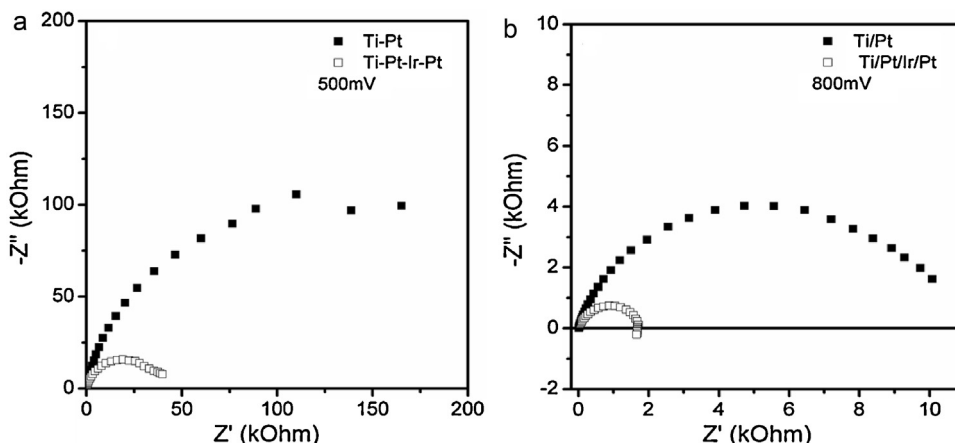
Fig. 6. Nyquist plots for MOR process at steady state over MM electrode (empty squares) and Ti/Pt electrode (full black squares) at (a) 500 mV and (b) 800 mV DC bias potential.

and by the electronic interaction between the Pt and the substrate (the ligand effect).

Another important parameter in catalysis, the apparent activation energy of the process, was calculated for the Ti/Pt$_{25 mC}$/Ir$_{6 mC}$/Pt sample. Voltammetric experiments at different temperatures were performed under the same conditions in order to calculate the activation energy by means of an Arrhenius plot. The apparent activation energy was calculated as 39.8 kJ mol^{-1}, a slightly lower value than the 43.5 kJ mol^{-1} reported for polycrystalline platinum in a very similar experiment using basically the same conditions as the present work [29]. The decrease in the apparent activation energy also supports the enhancement of J_{rel} as well as absolute current, J, observed in the present work.

Using the EIS technique it was possible to monitor the differences regarding the electrical characteristics of the electrode/solution interface of the systems under study, i.e. the charge transfer resistance for the MOR process. The investigation at steady state was carried out by the application of DC potentials (50 mV to 1.55 V) in a 0.5 M methanol solution over Ti/Pt$_{25 mC}$ and Ti/Pt$_{25 mC}$/Ir$_{6 mC}$/Pt. Fig. 6 presents Nyquist plots recorded at 500 mV (Fig. 6a) and at 800 mV (Fig. 6b) for the two different electrodes, where Z'' and Z' stands for the imaginary and real components of the impedance, respectively. It can be seen that on both axes the impedance is much lower in the case of Ti/Pt$_{25 mC}$/Ir$_{6 mC}$/Pt than in the case of Ti/Pt$_{25 mC}$. In the low frequency region – which is associated with charge transfer processes [50] – much lower charge transfer resistance values obtained on MM electrodes clearly indicate that MOR is being facilitated on those catalysts compared to Ti/Pt ones.

Besides, it is possible to verify the appearance of a pseudo-inductive behavior in Fig. 6b for the MM electrode, represented by the arc intersection on the Z' axis, producing positive impedance regions. At the same potential the Ti/Pt electrode does not exhibit the same features. This kind of observation is often associated with an inductive component created by adsorbed species at the electrode surface, which may induce an electric field perpendicular to the electrode [51–53]. Thus, one can say that the reaction rates on Ti/Pt electrodes at 0.8 V are not high enough to produce intermediates that could be detected by EIS, whilst on the other hand MM electrodes can catalyze the reaction, as attested by the intermediate species present at the same potential [53]. In view of that, it is reasonable to infer that MOR occurs with a favored kinetics at MM electrodes compared to Ti/Pt ones. Moreover, the hypothesis that a catalytic promoter effect of electronic nature is taking over is strengthened by the impedance data obtained.

4. Conclusions

This work brings a new approach for the preparation of Pt/Ir/Pt multilayered structures electrodeposited over a low cost titanium substrate and their catalytic activity toward methanol and CO oxidation. All data obtained revealed improved properties for the MM-like structures compared with Ti/Pt electrodes, with increases of up to 2.7 times in current density. Using a 2^2 factorial design, it was possible to infer that an increase in the iridium thickness (intermediate layer) and a decrease in the platinum thickness (internal layer) lead to an increase in the current density observed by voltammetry. For the oxidation of CO, a decrease in the charge was observed as well as a displacement of the onset potential toward more negative values, which likely indicates weaker adsorption energy for this molecule over the MM surface. Finally, a decrease in the calculated apparent activation energy and much lower R_{ct} for MOR obtained through EIS were observed, agreeing with the catalytic enhancement already described for MM electrodes. Besides, we emphasize that the use of titanium as a substrate also meets the requirement for the catalyst to have a low cost, a strategic point to be considered for both industrial and academic purposes.

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