



## Short communication

# A low-cost platinum film deposited direct on glass substrate for electrochemical counter electrodes

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## HIGHLIGHTS

- ▶ A low cost metallic platinum film is deposited over common glass.
- ▶ The electrode presents metallic platinum electrochemical fingerprints.
- ▶ Chemical and mechanical stability are adequate to use the electrode for electrochemical devices.

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## ABSTRACT

The preparation and characterization of platinum electrodes on glass substrates obtained by the Pechini method for a potential application as a counter electrode is presented in this paper. This method is based on the dissolution of citric acid (CA) and hexachloride platinum acid ( $\text{H}_2\text{PtCl}_6$ ) in ethylene glycol (EG), and then calcinated in an appropriated temperature to produce the desired metallic film. Characterization was carried out by X-ray diffraction, scanning electron and atomic force microscopy and cyclic voltammetry. X-ray patterns of platinum on glass substrate showed the same features of the platinum bulk metal as well as its voltammetric profile. In order to determine the stability of the electrode, the electrode was subjected to 5000 voltammetric cycles and polarized at constant current of  $100 \text{ mA cm}^{-2}$  for at least 200 h, showing no considerable differences compared with the as synthesized electrode. Moreover, the main advantage of the electrode is the low cost ( $\text{US\$ } 0.03 \text{ cm}^{-2}$ ) of the prepared samples.

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## 1. Introduction

The important properties of noble metals electrodes such as, inertness at high positive overpotential and as electrocatalysts for different processes, make them a powerful tool in different electrochemistry devices [1–4] as well as in fundamental studies on metal surface properties [5].

Since noble metals are expensive, it is important to manufacture these electrodes on a low-cost substrate as long as they retain the same electrochemical and chemical properties observed in the bulk material. Following this idea, in a previous work, our group have demonstrated a facile way to manufacture Pt electrodes on a low-cost substrate, titanium, which presents the electrochemical and chemical fingerprints observed in the bulk material [6]. The method used to synthesize the electrodes was the polymeric precursor method (PPM) (also called Pechini method), in which a metallic salt is dissolved in a mixture of ethylene glycol and citric

acid, giving rise to a polyester network containing the metallic ions homogeneously distributed. The polymeric solution is then applied onto the substrate and the metal oxide (or even metal itself) thin film is obtained by the calcination at adequate temperatures [7,8].

Several methods of producing platinum films are known. In dye-sensitized solar cells (DSSCs), for example, a thin layer of platinum coating on the conducting glass is used as the platinized counter electrode, exhibiting highly electrocatalytic activity for reduction of triiodide [9,10], as well as other kinds of counter electrodes [11–13]. To manufacture these counter electrodes, usually, a few drops of hydrogen hexachloroplatinate (IV) are placed in a conducting substrate, such as ITO and FTO, and them calcined in an appropriated temperature [14–16]. Conductive transparent glass electrodes are less expensive than noble metals one, but their price still affects the final price of the device. In addition, platinum film can be supported onto a substrate by high vacuum techniques, such as, sputtering [17,18] or gas phase reactions of platinum compounds, as chemical vapor deposition (CVD) [19,20]. These high vacuum routes involve more than one step including different materials which are necessary to obtain a mechanically stable electrode.

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The aim of this work is to prepare a metallic platinum thin film obtained by PPM onto common glass substrate. This kind of procedure is a simple and low-cost route to obtain platinum electrodes with controlled apparent thickness and surface areas.

## 2. Experimental

The electrodes were prepared using a glass plate as support. The glass was treated by sandblasting followed by a chemical treatment, immersion in  $\text{KMnO}_4$  1 M solution for 1 h, washed in  $\text{H}_2\text{O}_2$ , followed by immersion in a  $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  solution (1:1:5 M ratio) at  $80^\circ\text{C}$  for 1 h. Finally it was washed with a large amount of distilled water and dried at  $110^\circ\text{C}$  for 30 min.

The precursor solution was prepared dissolving citric acid (SYNTH) in ethylene glycol (MERCK) at  $60^\circ\text{C}$ . Subsequently,  $\text{H}_2\text{PtCl}_6$  (ALDRICH) was added into this solution in a molar ratio of Pt: CA: EG (1:8:32).

The precursor solutions were painted with a brush onto the support glass and the material was thermally treated at  $130^\circ\text{C}$  for 30 min to eliminate water, then at  $250^\circ\text{C}$  for 30 min to improve film adherence, and finally at  $500^\circ\text{C}$  for 10 min to eliminate the organic portion leading to the formation of the metallic film. This procedure was repeated 5 times. After the fifth thermal cycle, a cooling rate of  $5^\circ\text{C min}^{-1}$  was used. All the materials were obtained in static air atmosphere.

X-ray diffraction (XRD) patterns were obtained using a SIEMENS diffractometer model D-5000 with  $\text{CuK}\alpha$  radiation and  $\lambda = 1.5406 \text{ \AA}$ . Morphology was investigated using a scanning electron microscopy (SEM) (ZEISS microscope, model 105 DSM 940A) and by atomic force microscopy, using a 2100 SPM microscope (Molecular Imaging) model Pico LE™ operated in contact mode at room temperature ( $25^\circ\text{C}$ ). A scanner of  $10 \mu\text{m}$  and silicon probes (NanoSensors™) with spring constant of  $0.12 \text{ N m}^{-1}$  were used. AFM images were recorded over a scan area from  $0.5 \mu\text{m} \times 0.5 \mu\text{m}$  with a scan rate of  $0.5 \text{ line.s}^{-1}$ .

The electrochemical characterization was accomplished using a potentiostat/galvanostat Autolab model PGSTAT302N equipped with scan module. All the electrochemical experiments were carried out at  $25^\circ\text{C}$ . The voltammetric curves were measured in a  $0.1 \text{ M HClO}_4$  solution using a reversible hydrogen electrode (RHE) as a reference electrode and a Pt plate ( $2 \text{ cm}^2$ ) as counter electrode. The sweep potential rate was  $50 \text{ mV s}^{-1}$ . Prior the experiments, the solutions were deaerated with  $\text{N}_2$  for 30 min.

## 3. Results

The platinum load of the electrodes was  $0.6 \text{ mg cm}^{-2}$ , with a thickness of 280 nm. The main advantage of the electrodes prepared here is their low-cost which is about  $\text{US\$ } 0.03 \text{ cm}^{-2}$ . To calculate the electrode cost, we considered the amount of platinum in one square centimeter of the sample and the price platinum metal in the international market. Then, the main purpose of the following experiments is to show that the properties of the electrodes are electrochemically stable and also present the fingerprints of a polycrystalline platinum bulk electrode.

The X-ray diffraction data is shown in Fig. 1. It is possible to observe platinum pattern peaks at  $2\theta = 39.5$  (111),  $45.9$  (200),  $66.9$  (220),  $81.6$  (311),  $85.0$  (222),  $102.5$  (400) and  $117.3$  (331), which are in agreement with (JCPDS 04-0802) file and also with the literature data [6,21–23]. The Pt mean crystallite size were determined from the peak (111) line broadening using the Debye–Scherrer equation [24], and the Pt mean crystallite size observed was 28.5 nm. Jansson et al. [22] studied the deposition of Ti–Pt–C thin films onto Si substrate using DC-Magnetron Sputtering technique, and observed the formation of a polycrystalline film with an average grain size of 10–20 nm. Sen and Sreemany [25] studying sputtered

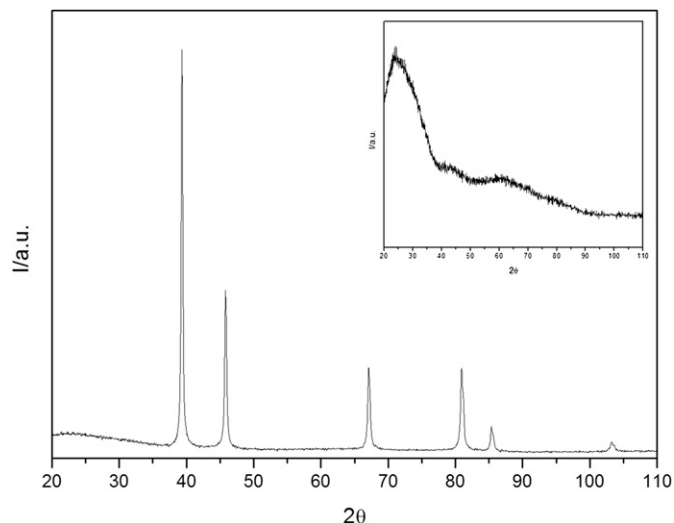


Fig. 1. X-ray diffraction analysis of the platinum thin film (5 painted layers) onto glass substrate. Precursor solution 1:8:32 (Pt:AC:EG) molar ratios, thermally treated at  $500^\circ\text{C}$ . Inset shows the x-ray pattern of the glass substrate.

Pt films deposited onto glass substrate obtained a material with an average crystallite size of 30 nm. Using the Bragg's Law [24], the lattice parameter observed for Pt/Glass was  $a = 3.9308 \text{ \AA}$  considering a cubic  $\text{Fm-3m}$  (225) symmetry, which is a slightly larger than  $a = 3.9231 \text{ \AA}$  observed in the datasheet (JCPDS 04-0802) and  $a = 3.915 \text{ \AA}$  for Pt thin film annealed at  $500^\circ\text{C}$ . Consequently, the unit cells volume observed was  $60.8 \text{ \AA}^3$  and  $60.3 \text{ \AA}^3$  for Glass/Pt and Pt foil respectively. Sen and Sreemany [25] observed that the as-prepared Pt thin films exhibited a compressive lattice strain. However, after the sample annealing at  $500^\circ\text{C}$  for 60 min with a  $3^\circ\text{C min}^{-1}$  cooling rate (similar experimental condition presented in this paper), the lattice strain became tensile and around 0.001%. The lattice strain observed for Pt/Glass electrodes was 0.01%, and, based on the slightly unit cells volume expansion, it is possible to conclude that a tensile strain takes place on the Pt thin film deposited onto glass substrate. The origin of the tensile strain could be related to the lattice mismatch and difference of thermal expansion coefficients between glass and Pt thin film. Finally, a broad peak appearing in the region of  $2\theta = 20$  is related to the glass substrate, as can be observed in the x-ray diffraction (Fig. 1-inset).

Fig. 2 shows the SEM micrographs of the Pt/Glass electrodes. The sandblasting procedure can be well illustrated here, once irregularities were created in the glass surface, which facilitates the anchorage of platinum particles on the substrate (Fig. 2A and B). When the sandblasting procedure was not performed (not shown here), the Pt/Glass adherence was poor and the chemical and electrochemical properties was lost after an initial measurement. The Pt/Glass film obtained using a polymeric precursor solution shows a typical cracked structures of films obtained from this method [26,27] (Fig. 2C and D).

In Fig. 3 are shown the AFM images of the glass sandblasted substrate and the Pt/glass film. One can see that the glass substrate shows a typical globular topography as well for the Pt/Glass film. It is also possible to observe on Fig. 3 that all glass substrate was covered by a Pt film. It is in agreement with the change in the roughness median square (rms) values of 6.06 nm and 2.87 nm for glass substrate and Pt/Glass film, respectively, and with voltammetric profiles data discussed further. The Pt average particle diameter is 24.60 nm and was calculated from Fig. 3b with ImageJ software.

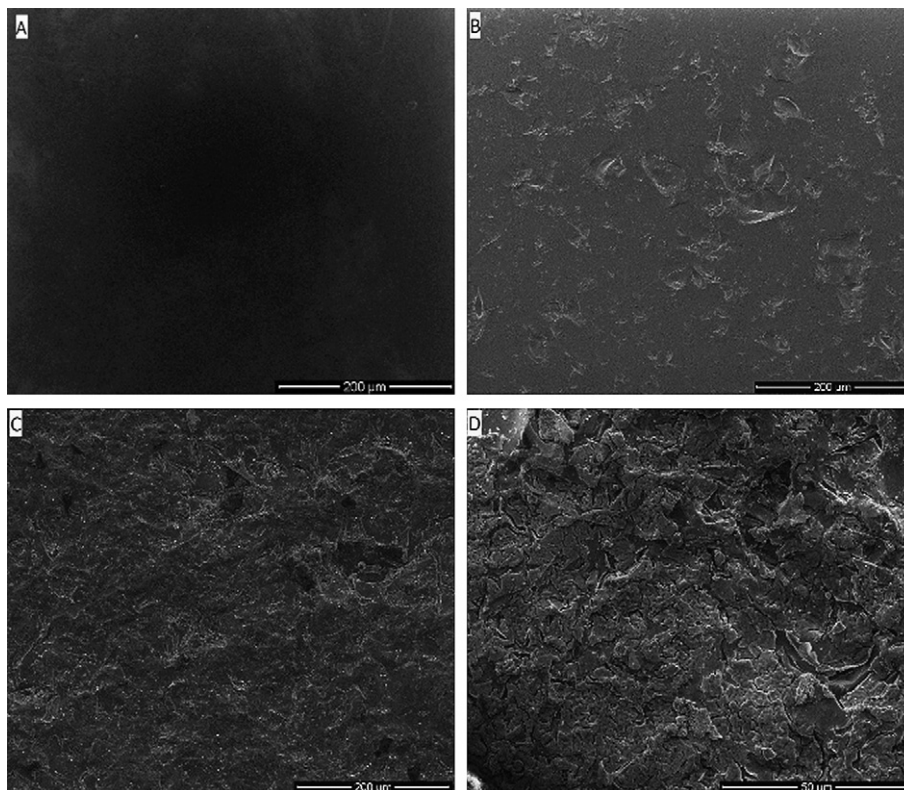


Fig. 2. SEM micrographs of A) glass, B) glass sandblasted, C) and D) Pt/Glass. The magnification was 500 $\times$  for micrographs A), B) and C), and 2500 $\times$  for D).

The electrochemical measurements are shown in Fig. 4. Prior the registration of the voltammogram at 50  $\text{mV s}^{-1}$  in 0.1  $\text{HClO}_4$ , the electrode was cycled at 500  $\text{mV s}^{-1}$  to clear and ensure a reproducible surface. The feature of this voltammetric profile is similar to those related in the literature where a platinum film was deposited by the polymeric precursor method as well the process related [6,28]. The processes can be associated to: *i*) hydrogen adsorption and desorption between 0.05 and 0.4 V, *ii*) double layer region between 0.4 and 0.8 V and *iii*) formation and reduction of PtO, between 0.8 and 1.55 V and 1.55 V and 0.4 V, respectively. The surface areas of the electrodes were calculated using the procedure well established in the literature [29] which considers a charge density of 210  $\mu\text{C cm}^{-2}$  as being equivalent to the desorption of one hydrogen monolayer on polycrystalline Pt, and the relation between the electrochemical area ( $A_e$ ) and the geometric area ( $A_g$ ) was 60.

In order to investigate the electrode stability, two measurements were performed. In the first one, a voltammetric cycle was measured immediately as synthesized and then after 5000 cycles

(Fig. 4). One can see that the behavior has not suffered a significant change after five thousand cycles, showing a good stability of this film. The other stability test was made applying a constant current of 100  $\text{mA cm}^{-2}$  over than 200 h. The result is shown in Fig. 4 and one can see that after 200 h applying 100  $\text{mA cm}^{-2}$ , the electrode behavior changed toward polycrystalline platinum and a little loss of surface area occurred, once we can see a decrease in the cathodic and anodic response. In general, all Pt/Glass electrodes remain similar polycrystalline profile as described previously for both stability tests, and slightly differences can be observed, e.g. the reduction of PtO, between 0.6 and 0.8 V.

These differences have been assigned to the reduced adsorption strength of oxygenated species on these prepared electrodes, and according to Norskov et al. [30], due to the downshift of the surface *d*-band center.

Markovic et al. [31] also observed similar shift in the oxide reduction peak obtained in the cathodic sweep during the cyclic voltammograms for Pt-skeleton, Pt-skin and polycrystalline Pt and correlated with *d*-band center values. According to the authors,

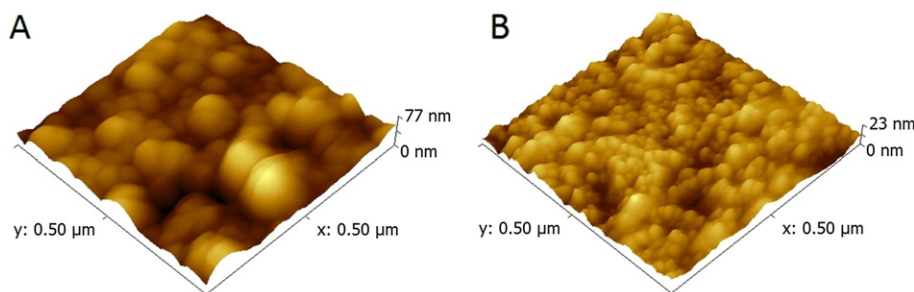
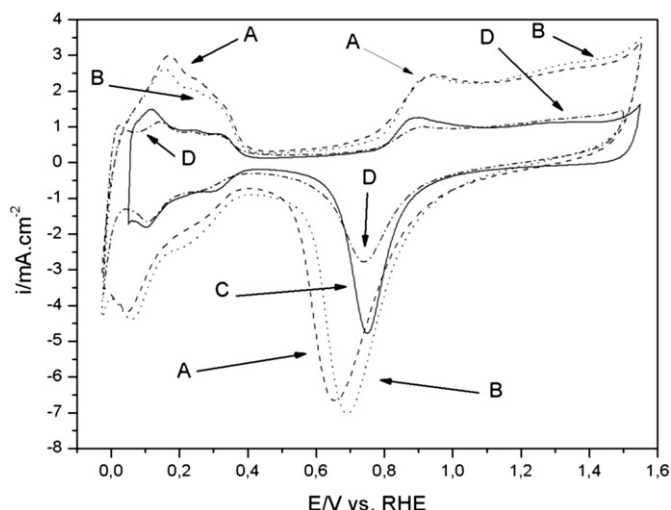


Fig. 3. AFM images of the glass sandblasted substrate A) and Pt/Glass film electrode B).





**Fig. 4.** Voltammetric profile for Pt/glass electrodes in 0.1 M HClO<sub>4</sub> solution, sweep rate of 50 mV s<sup>-1</sup> (A-dash) Pt/Glass as synthesized, (B-dot) Pt/Glass after five thousands cycles, (C-solid) platinum bulk electrode ( $\times 40$ ) and (D-dash dot) Pt/Glass after 200 h applying a constant current of 100 mA cm<sup>-2</sup>. Normalized by geometric area.

OH<sub>ads</sub> chemisorption energy increases as the *d*-band center moves close to Fermi level [30], that is, in the present case:  $\theta_{\text{OH}}$  Polycrystalline Pt <  $\theta_{\text{OH}}$  Pt (2 h at 100 mA cm<sup>-2</sup>) <  $\theta_{\text{OH}}$  Pt (after 5000 cycles) <  $\theta_{\text{OH}}$  Pt (as-prepared), respectively. According to Markovic et al. [32], the positive shift of the Pt-OH<sub>ads</sub> peak for polycrystalline Pt indicates smoother and less oxophilic surface with significantly reduced number of low coordination surface atoms [32,33]. The smoother characteristic of polycrystalline Pt compared to Pt thin film obtained by precursor polymeric method, as presented herein, are in agreement with literature [6].

Finally, Ciapina and Ticianelli [34] studied the effects of acid cycling and CO annealing on PtCo nanoparticles as prepared, and compared to Pt/C. The authors also observed shifted in the PtO reduction peak during negative-going sweep, and correlated the strength of Pt-OH<sub>ads</sub> interaction to differences in the surface structure.

Although there are slightly differences in the voltammograms, it does not affect the function of such electrodes as counter electrode. Pereira et al. [6] studied Pt thin film obtained by precursor polymeric method, as presented herein with electrochemical surface area varying from 6.2 to 30.3 cm<sup>2</sup>. According to the authors, the Pt thin films electrodes exhibited higher stability even in H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> acid medium.

#### 4. Conclusions

In this paper we have shown a low-cost and facile way to manufacture a platinum film on glass substrates electrode for electrochemical applications. In order to obtain a good adherence between the platinum film and the glass substrate, the sandblasting pre-treatment was crucial. This treatment generated irregularities in the glass where the film could be mechanical anchored and so, increasing film adherence.

X-ray diffractions showed the characteristic behavior of the platinum metallic bulk as well the electrochemical behavior, showing that this electrode is a good alternative for platinum bulk electrodes. SEM micrographs showed a typical cracked structured film synthesized by Pechini method and AFM images showed a homogeneous distribution of platinum particles sizes. Furthermore, the smallest rms value

obtained for Pt/Glass film are related to a flatted and compact film compared to the glass sandblasted substrate.

The effects of stability test affect the Pt structural surface in different ways. The positive shift of the Pt-OH<sub>ads</sub> peak for polycrystalline Pt electrodes indicates smoother and less oxophilic surface, compared to Pt/Glass as prepared and submitted to 5000 voltammetric cycles and 100 mA cm<sup>-2</sup> up to 200 h.

Finally, as highlighted before, one of the main advantage of this electrode is its low-cost (US\$ 0.03 cm<sup>-2</sup>).

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