

Synthesis and Stability of Pt_3Co and $\text{Pt}_{0.7 \leq x \leq 1}\text{Co}$ Films Voltammetrically Activated in Acidic Medium for Methanol Fuel Cell Application

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Abstract. Pt-Co thin films have been prepared by means of electrodeposition method, due to the interest of this alloy as catalyst in acid fuel cells. As the stability of the catalyst is fundamental to consider its applicability, the behavior of the films as a function of the composition during voltammetry activation in acidic medium has been studied. The Pt_3Co films show high stability, maintaining their morphology, X-ray diffraction profile, composition and high surface area, and show good catalytic behaviour for methanol electro-oxidation in acidic medium. However, the $\text{Pt}_{0.7 \leq x \leq 1}\text{Co}$ films present low stability and evolve during the test to flatter films of lower effective area and Pt_3Co stoichiometry, by losing cobalt. Only Pt-Co electrodeposited films of defined compositions show the enough stability and properties to be used as good materials for electro-oxidation processes in acidic media.

Keywords: PtCo films, electrodeposition, catalyst for acid fuel cells, voltammetry, electro-oxidation processes.

1 Introduction

Direct methanol fuel cells (DMFCs) have attracted great attention as power sources for portable devices because of their high energy density, easy handling of methanol and low operation temperature [1-5]. Nevertheless, the performance of these devices is limited by several drawbacks, such as kinetics constraints and catalysts poisoning [6]. Methanol oxidation is a slow reaction that requires active sites on the electrodes for the adsorption of methanol and the presence of adsorbed OH species for the oxidation of the by-products [7]. Platinum-based catalysts are the most popular and effective anodes for methanol oxidation. However, CO tolerance and metallic loadings need be enhanced to achieve the common application in DMFCs. Bimetallic catalysts such as Pt-Ru, Pt-Sn, Pt-Ni or Pt-Co are more tolerant to CO poisoning than bare Pt, due to their greater ability to adsorb suitable oxygen-containing species in potential region for methanol oxidation [6-15]. In this sense, some authors have found that the presence of cobalt could favour the oxidation of methanol at lower potentials than pure Pt, likely owed to the formation of Co oxidized species [7].

Pt-Co alloys have been tested as catalysts for oxygen reduction reaction and alcohol oxidation reactions [16, 17]. However, when successive voltammetry cycles are performed in order to activate the catalysts surface, the electrochemically active surface area (ECSA) values can decrease in some cases, which can inform about the durability and usefulness of the catalyst. For this reason, the morphological and structural changes of Pt-Co films should be studied after the samples are subjected to successive voltammetry cycles in H_2SO_4 medium in the absence or presence of methanol. Thus, in this work two types of Pt-Co films with different platinum content ($\text{Pt}_{0.7 \leq x \leq 1}\text{Co}$ and Pt_3Co) are selected to study their performance as methanol oxidation catalysts and their evolution after the electrochemical activation. High percentages (in weight) of Pt were tested to confer stability and enhance the catalytic response. The possible variation of ECSA value, composition, morphology and crystalline structure are studied, and the best conditions for the methanol oxidation are selected. To this end, several samples of bimetallic Pt-Co alloys are prepared by electrodeposition on Si/Ti/Au pieces. The Pt-Co samples are

subjected to oxidation/reduction cycles until stable voltammograms are obtained. They are studied structurally and morphologically before and after the electrochemical treatment by X-ray diffraction (XRD), X-ray fluorescence (XRF), energy dispersive X-ray spectroscopy (EDS), and scanning electron microscopy (SEM). The effect of the catalysts variations in performance of methanol oxidation is also studied. Therefore, here we report a comparative study of the changes observed for Pt-Co films during cyclic voltammetry activation in acid medium in order to detect possible variations that affect the catalysts behaviour and to select the better composition of the Pt-Co films.

2 Experimental

A conventional three-electrode glass cell and a temperature of 25 °C were used for all the electrochemical experiments. An Ag/AgCl, KCl 3 M and a platinum spiral were used as reference and counter electrodes, respectively. The reagents used for preparing the different solutions were of analytical grade and the solutions were prepared with distilled water treated with a Millipore Milli Q system. Electrodeposition and electrochemical measurements were carried out using a microcomputer-controlled potentiostat/galvanostat Autolab PGSTAT30 with GPES software.

Pt-Co films were prepared by means of potentiostatic electrodeposition on Si/Ti(10nm)/Au(100nm) pieces, supplied by IMB-CNM.CSIC (Centro Nacional de Microelectrónica), using electrolytic solutions containing 2.5 mM CoCl_2 + 0.1 M NH_4Cl + 10 g/L H_3BO_3 and concentrations of Na_2PtCl_6 between 2 and 4 mM, to obtain different compositions of the Pt-Co films (from 70 to 91 wt. % of Pt). The pH value was maintained at 4.5. The exposed area of the Si/Ti/Au pieces, after washing them with ethanol and Milli-Q water, was between 0.20 and 0.25 cm^2 . The solution was de-aerated by argon bubbling before each experiment and maintained under argon atmosphere during it. Stirring of the solution (magnetic stirrer, 100 r.p.m.) was maintained during the electrodeposition to assure a constant composition throughout the deposits.

The electrochemically active surface area of each prepared Pt-Co film was calculated after the electrodes were subjected to 40 scans of cyclic voltammetry (CV) in 0.5 M H_2SO_4 at 100 mV s^{-1} between -0.2 and 1.2 V, a typical procedure to clean and activate the electrode surface. The ECSA of electrodes was calculated by using the charge associated to the hydrogen adsorption/desorption region from the stationary CV profiles as follows (Equation 1):

$$ECSA = \frac{q_H}{q_{H/Pt}} \quad (1)$$

where q_H is the charge density corresponding to the hydrogen adsorption/desorption, and $q_{H/Pt}$ represents the charge density required for the adsorption of a monolayer of hydrogen atoms on a Pt surface (210 $\mu\text{C cm}^{-2} \text{Pt}$). The catalytic performance of the Pt-Co films after the activation process in 0.5M H_2SO_4 was tested in a solution containing 0.5 M H_2SO_4 and 1 M methanol by CV at 100 mV s^{-1} between -0.2 and 1.2 V.

The possible variation of the morphology, composition and crystalline structure of the Pt-Co prepared films of different composition during the voltammetry cycling was studied. The composition of the deposits, as-prepared and after the activation in sulfuric medium, was analyzed by means of both a Leica Stereoscan S-360 equipped with energy dispersive X-ray analysis and an X-ray Fluorescence Fischerscope® X-RAY XDAL®. A good concordance has been observed between the two determinations. Field-Emission Scanning Electron Microscopy (FE-SEM) (Hitachi 800 MT) was used for the observation of the different samples. The crystalline structure of the deposits was studied by means of a PANalytical X'Pert-PRO MRD diffractometer with parallel optical geometry and using Cu $K\alpha$ radiation ($\lambda = 0.1542$ nm) and incident angle of 1° to avoid the response of the seed-layer. A 2θ scan between 10 and 120° was used, with a step size of 0.033° and a measuring time of 300 s per step.

3 Results and Discussion

Potentiostatic electrodeposition was used to prepare Pt-Co films in order to study the catalytic behaviours of these materials for methanol oxidation in acidic medium. The deposition potential and the concentration of the Pt and Co precursors were adjusted to obtain Pt-Co films with two different

platinum percentages: around 70-77% (corresponding to $\text{Pt}_{0.7 \leq x \leq 1}\text{Co}$ alloys) and around 91 wt. % (corresponding to Pt_3Co) (Table 1). The electrodeposition was performed at two different deposition charges (7 and 11 C cm^{-2}) in order to ensure the constancy of the composition with the thickness of the films. Results show that the deposits' composition remains constant with the transferred charge when stirring conditions was maintained during the electrodeposition. Figure 1 shows the potentiostatic curves corresponding to the preparation of the Pt-Co films. After the initial increase of the absolute value of current density, a quasi-stationary value is attained by the curves corresponding to the solution with Na_2PtCl_6 2 mM. It indicates that the deposit surface is maintained during the film growth. However, the potentiostatic curves of the solution containing Na_2PtCl_6 4 mM show a continuous increase of the current density, which can reflect a gradual rise of the deposits roughness.

Table 1. Experimental conditions for the preparation of Pt-Co films by electrodeposition on Si/Ti/Au substrates and features of the deposits.

| $[\text{Na}_2\text{PtCl}_6]$ mM | E range V | Q C cm^{-2} | Thickness nm | wt. % Pt | Colour | Aspect | Pt-Co sample type |
|------------------------------------|----------------|-------------------------|-----------------|----------|--------|--------|-------------------|
| 2 | (-0.70, -0.80) | 7 | 500 | 70-77 | grey | flat | A |
| | | 11 | 930 | 70-77 | grey | flat | |
| 4 | (-0.65, -0.70) | 7 | 500 | 88-91 | black | rough | B |
| | | 11 | 930 | 88-91 | black | rough | |

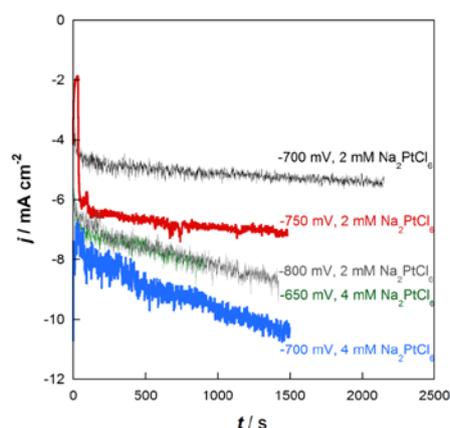


Figure 1. Chronoamperometric curves for electrodeposition of Pt-Co films on Si/Ti/Au substrates.

The morphology of Pt-Co films can be observed in Figure 2. These scanning electron micrographs show the surface appearance of the samples as-prepared and after an activation step by cyclic voltammetry. Regarding the as-deposited micrographs, the films with 70-77 wt. % of Pt content (Pt-Co A) present uniform morphology with rounded composed grains, whereas the Pt-Co deposits with 88-91 wt. % of Pt (Pt-Co B) present an irregular columnar morphology. These observations are related to the observed black colour of the Pt-Co B deposits and the shape of the chronoamperometric deposition curves. Moreover, the incorporation of cobalt into the deposits favours the formation of more uniform flat deposits, as observed for Pt-Co A and A'.

The activation of the catalysts surface previous to the methanol oxidation test in H_2SO_4 medium is usually performed by successive voltammetric cycles until stationary profile. The possible modification of the Pt-Co films during the activation was analysed. Composition, morphology and crystalline structure was determined after the activation and compared with that of the as-deposited films. Figure 3 shows the typical voltammograms of the two types of Pt-Co films (A and B) in deoxygenated H_2SO_4 0.5 M. Solid lines correspond to the first scan and dotted lines correspond to the stationary cyclic voltammetry after 40 scans. Current density is referred to geometric area of the working electrodes (between 0.2 and 0.25 cm^2). The anodic scans show a signal below 200 mV assigned to desorption of

hydrogen atoms of platinum active sites. At higher potentials, other oxidation signal appears above 600 mV owing to the formation of oxidized species of platinum and cobalt. The backward sweep shows a peak around 500 mV assigned to reduction of oxidized surface of materials and other cathodic signal generated by the adsorption of hydrogen atoms on the platinum sites. After the activation (40 voltammetric scans until stationary profiles), the Pt-Co deposits type A clearly changed, both in composition and morphology (Figure 2). Significant decrease of the cobalt percentage was observed, resulting very flat cracked films of composition around Pt_3Co (A' films). However, the initially platinum-richer deposits (type B) maintain their composition and similar morphology during the activation process, although some refinement in the grain size was observed (B' films). The stability of the Pt-Co type B deposits (Pt_3Co) is, therefore, clearly higher.

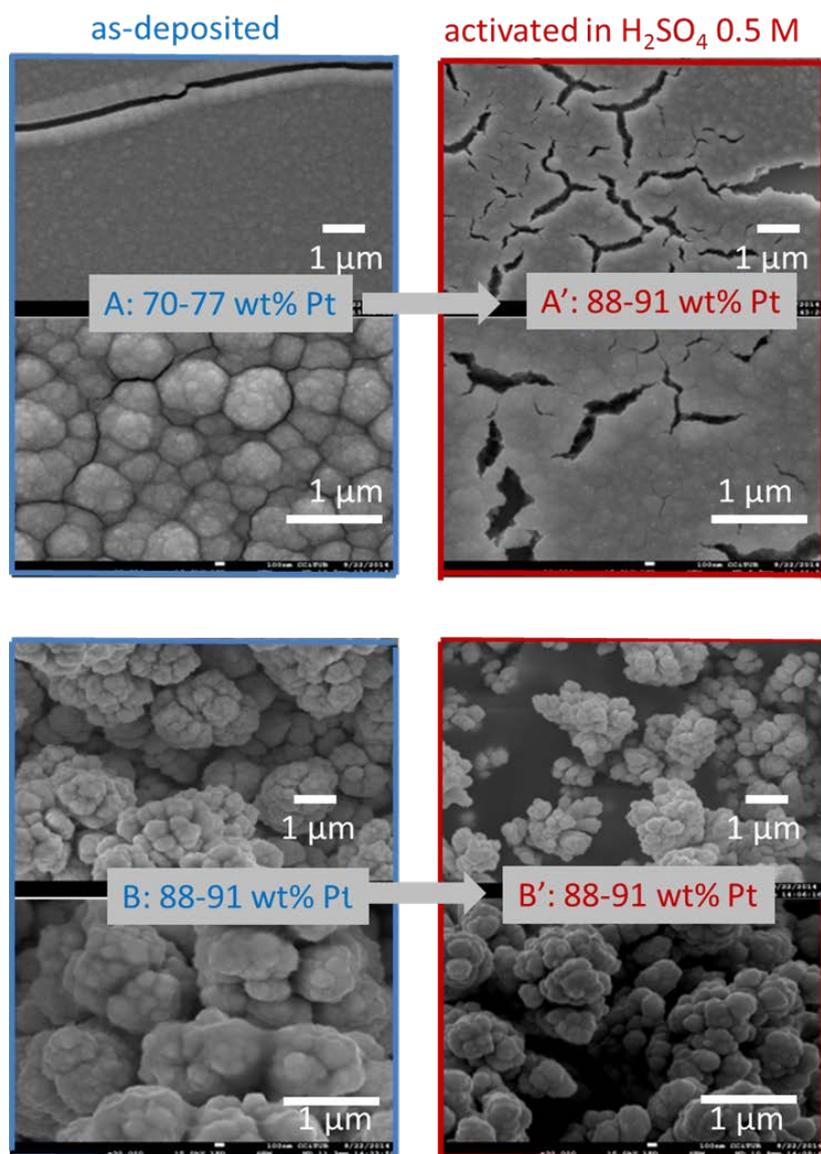


Figure 2. FE-SEM micrographs for Pt-Co films electrodeposited on Si/Ti/Au substrates. Images on the left side correspond to as-deposited materials and on the right side correspond to the materials subjected to the activation process in acid medium.

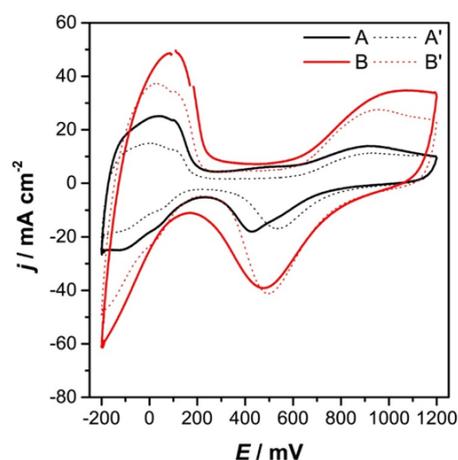


Figure 3. Cyclic voltammetry curves of the Pt-Co films recorded in 0.5 M H₂SO₄ at the sweep rate of 100 mV s⁻¹. As-deposited films are depicted as solid lines and the materials after activation are represented as dotted lines.

The main difference between solid and dotted lines in Figure 3 is the decrease of the current density observed for both A and B samples. The electrochemically active surface area of the electrodes was estimated from the cyclic voltammetry profiles to quantify these differences. At the beginning of the CV measurements, sample A displays an ECSA value of 257 cm² Pt per cm² of geometric area of the film. After the stabilization of CV response, this sample (A') only reaches 165 cm² Pt. This difference may be related to the morphological changes commented above. Nevertheless, as the morphologic changes observed by SEM for sample B are not as noticeable, the ECSA values are more similar (432 and 400 cm² Pt for B and B', respectively). It is worth noting that the signal around 500 mV is shifted to higher potential for sample A. This fact indicates that the surface of material is getting rich in platinum, probably due to the dissolution of oxidized cobalt in the solution or the redistribution of the surface metals. As commented above, sample A displays a decrease in the cobalt content after activation process, which could explain this shift since platinum is more noble than cobalt.

In order to determine possible evolution of the crystalline structure during the activation process to a more stable one, an accurate study of the as-deposited and activated deposits has been performed. The X-ray diffractograms of the blank substrate (Si/Ti/Au), the as-deposited Pt-Co films (type A and B) and the corresponding ones after the activation (A' and B') were recorded. The profiles of the Pt-Co deposits show the peaks of the gold substrate and the corresponding ones to the alloy (Figure 4). The wideness of the diffraction peaks reveals the nanocrystalline nature of the films. In each case, the deposits present five diffraction peaks, indexed as the corresponding to an *fcc* phase. The position of each peak appears between the lines corresponding to Pt *fcc* and Co *fcc*, which indicates a lattice parameter of the samples between that of the *fcc* phases of Co and Pt. In all cases the peaks appear near to the positions of the Pt reflections, as corresponds to Pt-rich films. The specific position varies as a function of the Pt percentage: Films type A (70-77 wt. % Pt) were more shifted to the position of the pure Co peaks than films type B (88-91 wt. % Pt), as corresponds to the different composition. The relationship between the position of the diffraction peak and the composition of the deposits corroborates that the electrodeposition in the selected conditions leads to Pt-Co solid solution formation.

The position of the peaks for the films A', B and B' is the same, as can be expected due to the same composition of the films. The X-ray diffraction study corroborates that the crystalline phase of the platinum-rich Pt-Co as-deposited films is *fcc*, with a cell parameter distorted by the incorporation of more or less cobalt to the crystalline cell. The *fcc* phase is maintained after the activation of the films, without modification of the cell parameter in the case of Pt-Co B deposits, and variation in the case of the A ones, as a consequence of the main loss of the cobalt during the process. Therefore, the films type B, corresponding to a Pt₃Co phase, maintain constant composition, morphology and crystalline structure during the voltammetric scans, which reflects the high stability of this kind of films. However, the Pt-Co deposits with lower platinum percentage (Pt-Co type A), result less stable. The changes of morphology

and composition observed after the successive cyclic voltammeteries reflect also an evolution of the X-ray diffractograms and a decrease of the ECSA value.

The oxidation of methanol was studied using the four types of Pt-Co films as catalysts. Figure 5 displays typical voltammograms recorded in the presence of methanol. The shape of the voltammograms is quite similar in all cases. During the anodic sweep, voltammograms show the hydrogen desorption region notably reduced by the dissociative adsorption of methanol on metal surface. The methanol oxidation signal starts below 300 mV and the current increases with the potential. Wide anodic peaks centred at 790 (samples A and A') and 880 mV (samples B and B') were obtained in the forward scan, and other narrower oxidation peaks were observed at lower potentials in the backward scan. In the same way, the region related to the hydrogen adsorption shows low response compared to the measurements carried out in the absence of methanol. The main differences in the catalytic behaviour of the Pt-Co films might be due to the morphology and the effective area of the deposits, as showed in Figure 2. Pt-Co B and B' display similar methanol oxidation activities and those are significantly higher than Pt-Co A and A' films, accordingly to the higher roughness of the deposits (as expected from the ECSA values). Moreover, the activity of the sample Pt-Co A is much higher than that of Pt-Co A', as expected of the morphologic changes observed by FE-SEM.

In short, two types of Pt-Co films with different platinum content ($Pt_{0.7 \leq x \leq 1}Co$ and Pt_3Co) have been selected to study their performance as methanol oxidation catalysts and their evolution after the electrochemical tests. The $Pt_{0.7 \leq x \leq 1}Co$ samples evolve structurally to Pt_3Co during the activation process and the morphological changes result in a considerable loss of surface area. These new features of the films cause a loss of activity towards methanol oxidation reaction.

4 Conclusions

The preparation of Pt-Co sub-micrometric films with different percentage of platinum has been possible using electrodeposition technique, by adjusting the platinum salt concentration in the solution and applying defined potentials. Two types of platinum-rich films containing around 70 and 91 wt. % of Pt have been selected to test their stability during the activation in H_2SO_4 to be used as catalysts for methanol electro-oxidation in acidic medium. Although their crystalline phase is the same (*fcc* phase with cell parameters proportional to the platinum percentage), their morphology is clearly different. The Pt-Co films with around 70 wt. % of Pt present uniform granular morphology that evolves to a flatter cracked one during the voltammetric cycling process in H_2SO_4 medium. A clear loss of cobalt occurs to attain a value around 91 wt. % of Pt for the stabilized stationary deposit. However, the Pt-Co films with initially around 91 wt. % of Pt show high stability, maintaining their morphology, diffraction profile and composition during the voltammetric activation process.

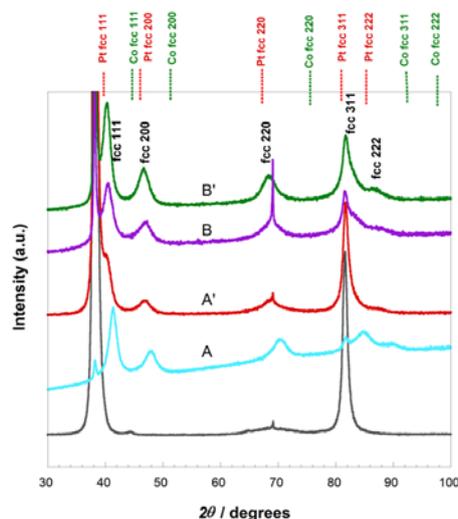


Figure 4. X-ray diffraction patterns of the Si/Ti/Au substrate, the Pt-Co as-deposited films (type A and B) and the Pt-Co films after activation (A' and B').

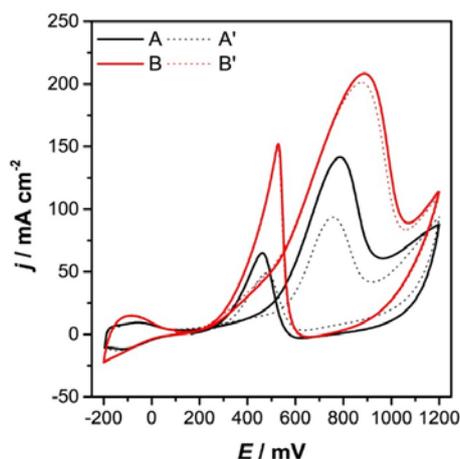


Figure 5. Cyclic voltammograms of the Pt-Co films recorded in 0.5 M H₂SO₄ and 1.0 M methanol at the sweep rate of 100 mV s⁻¹. As-deposited films are depicted as solid lines and the materials after activation are represented as dotted lines.

Therefore, Pt-Co films of around 91 wt. % of Pt, corresponding to Pt₃Co, are stable in aggressive medium (sulphuric acid) and during their voltammetric activation. Platinum films with lower Pt-content evolve to the same stable composition during the activation in sulphuric medium, but the mass loss and the flat resulting films discourage their use as catalyst for methanol oxidation. Moreover, the electrochemically active surface area of the Pt-Co films resulted 1.7 times higher for Pt₃Co than for the Pt_{0.7<x<1}Co samples before the activation and 2.4 times after the activation. Also, the Pt_{0.7<x<1}Co films lose a 65 % of active surface area during the voltammetric activation. Pt₃Co electrodeposited and activated films show higher performance for methanol electro-oxidation, maintained during several voltammetric cycles.

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