Co:TiO_2 films obtained by CBPLD for the OER and ORR in alkaline media

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ABSTRACT

Co:TiO_2 films were obtained on glass substrates and glassy carbon by Crossed Beam Pulsed Laser Deposition (CBPLD). Two crossed plasmas were produced by ablating simultaneously two targets, TiO_2 and Co, in vacuum. The ablation conditions on the Co target were varied in order to prepare Co:TiO_2 films with different Co content. The composition of the films was analyzed by X-ray Photoelectron Spectroscopy (XPS) the results showed that: depending on the synthesis condition the Co content in the films varies from 1.2 to 5.1 at. % . The microstructure was studied by microRaman Spectroscopy; it was found the presence of $CoTiO_3$ and the rutile phase of TiO_2. The electrochemical performance for the Oxygen Evolution Reaction (OER) was studied by cyclic voltammetry and the Oxygen Reduction Reaction by rotating disk electrode (RDE) using a standard three electrode cell in alkaline media (0.5 M KOH) being the prepared films the working electrode. For the OER, the current densities obtained in samples with different cobalt content at 1.4 mV vs. NHE vary from 3.2 to 8.3 mA cm^{-2}. The Tafel slopes values obtained were in the range of 30 to 90 mV/decade and the exchange current densities from $1.9x10^{-4}$ to $1.0x10^{-5}$ A/cm^2. These films were studied in the ORR, achieve a reaction via 4electrons with a current density around to 1.5 mA/cm^2 at 800mv and 1600rpm.

1. Introduction

Bifunctional electrocatalysts are of particular interest for use in unified regenerative fuel cells (URFC), in these systems one electrode is used solely for the oxygen reactions, oxygen evolution reaction (OER) in the electrolysis mode, oxygen reduction reaction (ORR) in the fuel cell mode [1]. The main trend for the electrochemical mechanism of OER or ORR is to involve at least one reaction step with fairly slow electron transfer. For this reason, one of the major aspects to be considered for improving the overall kinetic of the OER or ORR is the nature of the electrocatalyst which must be the most efficient and resistant to anodic corrosion during the water electrolysis reaction; it is well known that electrocatalysis depends on both electronic and geometrical factors [2].

In recent years, the electro-catalytic properties of transition metal oxides have received considerable attention specially, the mixed oxide valances, due to their low cost, thermodynamic stability, low electrical resistance, stability in alkaline solution and good electro-catalytic properties [3],. In the literature many research work has been done to synthetized this kind of materials by different techniques such as reactive PLD [4], sol gel [5], CVD [6] modified Adams methods, being the synthesis technique is fundamental in the physical properties of the electrocatalysts, in this work we proposed a variation of PLD [7] so called Crossed Beam Pulsed Laser Deposition to obtain Co:TiO_2 thin films electrodes and the determination of their electrochemical performance in alkaline media, this media is a a less corrosive environment for non- noble metals electrocatalysts [8].

2. Experimental

Preparation of the electrodes.

To develop the electrodes, we can use the variation of the PLD technique so called Crossed Beam Pulsed Laser Deposition (CBPLD). The Co: TiO_2 electrodes were obtained on glass and glassy carbon substrates at the same time; two crossed plasmas were produced by ablating simultaneously TiO_2 disk, 99.99% purity and Co targets also of 99.99% purity in positioned perpendicularly to each other were simultaneously ablated. The ablation was performed using a Nd:YAG laser with emission at the second harmonic (λ=532nm) with a pulse duration of 5 ns. Over glass substrate of 1cm^2, the distance target-substrate was of 4.2 cm at a working pressure of $5x10^{-6}$ Torr at room temperature. In order to vary the Cobalt content in the films, the average kinetic energy of cobalt ions (E_{Co}) was changed, keeping the same plasma conditions for TiO_2 deposition

Physical characterization

The composition of the films was analyzed by X-ray Photoelectron Spectroscopy (XPS) with a JEOL JS 9200 with a standard Mg Kα excitation source (1253.6 eV), binding energies were calibrated respect to the carbon signal (285eV). Whilst the film structure was studied by Raman Spectroscopy in a Lab-Ram HR, Jobin Yvon system equipped with an Olympus BX40 confocal microscope. A Nd:YAG laser beam (532 nm) was focused by an 100X

microscope objective onto an ≈ 1 μm diameter on the sample surface. The electrochemical performance for the Oxygen Evolution Reaction (OER) was studied by cyclic voltammetry, the oxygen reduction reaction (ORR) was studied by linear voltammetry mean rotating disk electrode technique (RDE), both in a standard three electrode cell using a potentiostat/galvanostat EG&G 273A and a small glass cell with alkaline media (KOH 0.5M) at 23 °C, applied the thin films obtained like working electrode and the Calomel as a reference electrode, while platinum grid was employed as the counter electrode.

3. Results and discussion

The parameters and conditions of the films synthesis was already reported [7]. The cobalt content in the films was calculated by XPS measurements. Figure 1 shows the Co content in titanium oxide as a function of the Co ions mean kinetic energy. It can be seen that the cobalt content varies from 1.2 at. % up to 5.1 at %, depending on the Co ions means kinetic energy. In this case the increasing of Co ions mean kinetic energy increases the Co doping of titanium oxide.

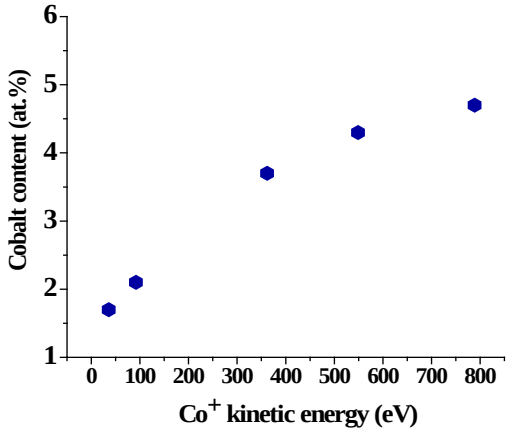
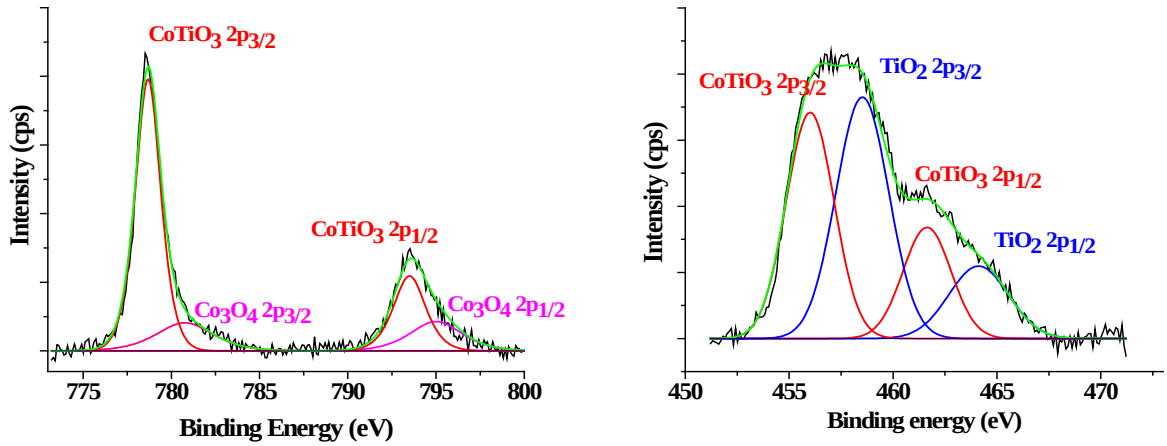


Figure 1 Variation of the cobalt content (atomic percent) in the films as a function of E_{Co}

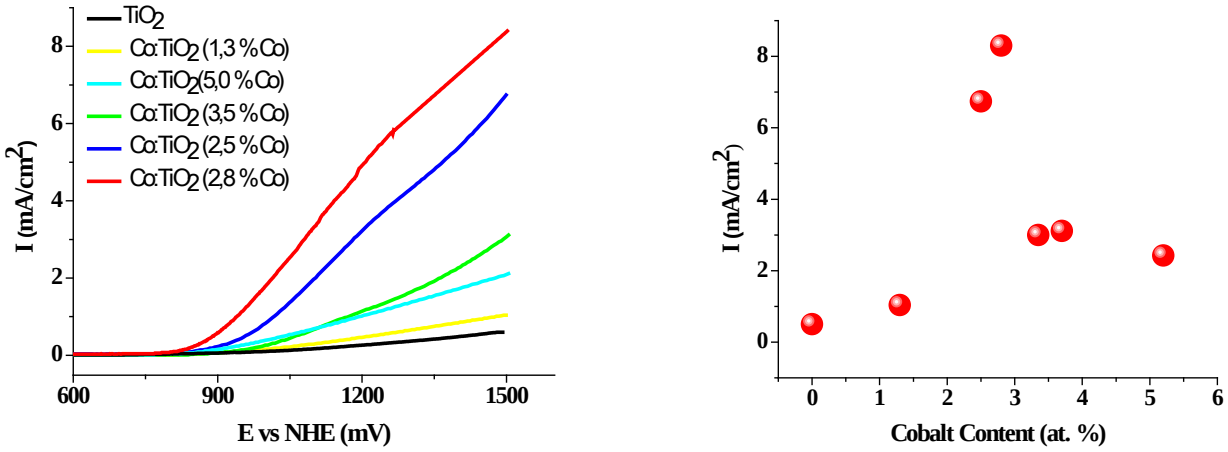
The analysis of the XPS is presented in the Figure 2, where shows the Ti and Co 2p photoelectron spectrum of the Co: TiO_2 film with 5.1 at.% of Co. The spectrum was deconvoluted using Gaussian functions in order to obtain information about the interaction of the Ti atoms with the Co and O atoms. The obtained results reveal the presence of Ti-Co-O bonds corresponding to $CoTiO_3$ and Ti-O bonds attributed to TiO_2 in its rutile phase and little signal of the Co-O bonds corresponding to Co_3O_4.



(a) (b)

Figure 2. a) XPS spectra in the high resolution for the cobalt region and b) XPS spectra in the high resolution for the titanium region.

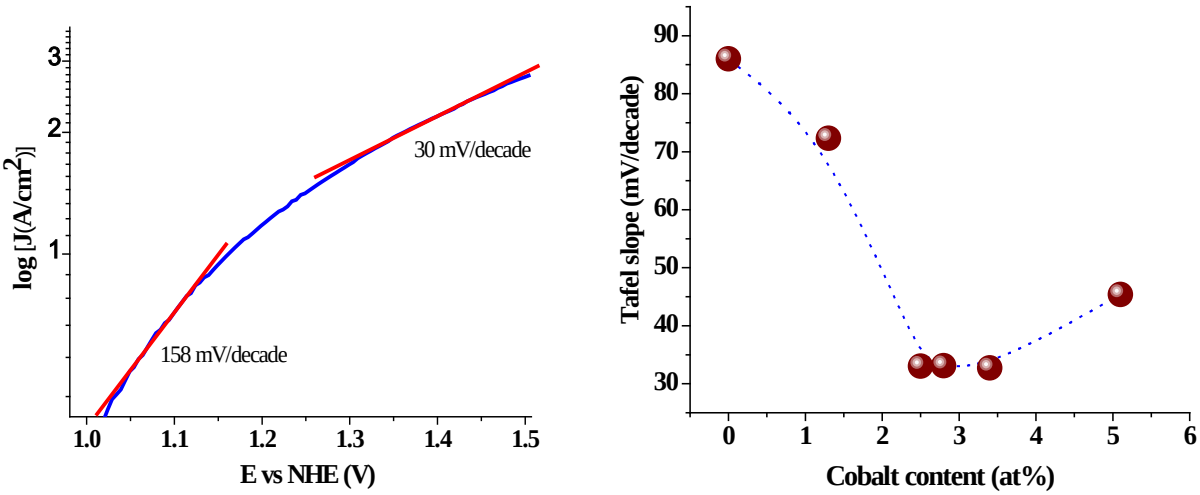
The effect of the cobalt content for the oxygen evolution reaction was analyzed by voltammetry measurements in the range of 600 to 1500 mV, no great changes were observed for the potential of oxygen evolution with the different cobalt content. However the voltamperograms of the anode with different cobalt content, Figure 3a shows that the current density (mA cm^{-2}) obtained at 1400 mV increased with the Co content: 1.2 < 2.5<2.8 after this value of Cobalt content the current density decreases: 2.8>3.7>5.1. Figure 3b shows the current density at 1400 mV in function of the cobalt content in order to display the optimal composition of the electrode allows obtaining the highest current density.



(a) (b)

Figure 3 a) electrochemical performance for (OER) in alkaline media employed the Co: TiO_2 films with different Co content. b) Effect of the cobalt content in the electrochemical performance at 1400mV

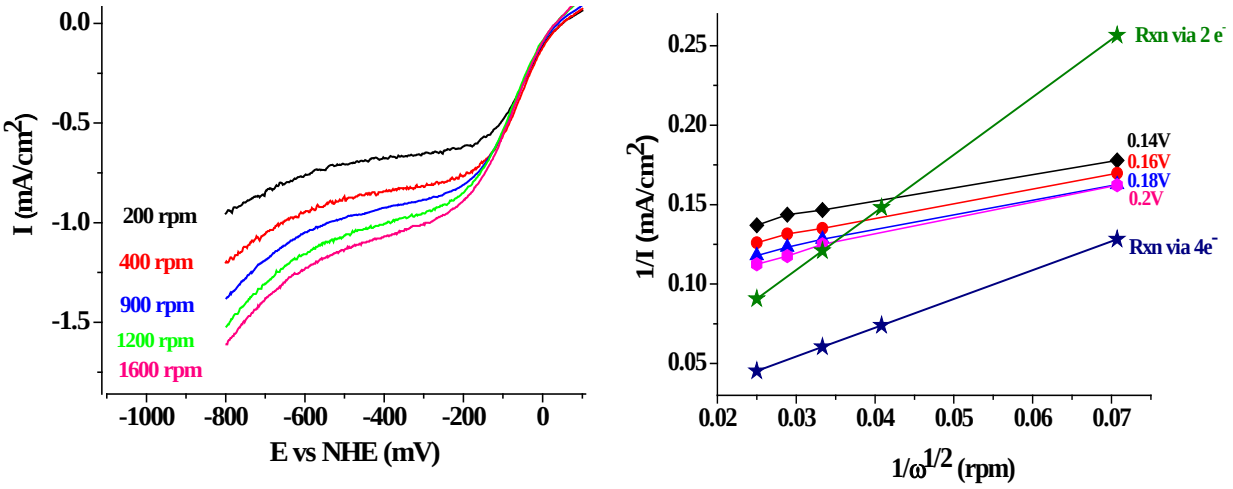
The OER kinetic was determinate for each electrode, determination of the Tafel slope were calculated from the current-potential plots at low and high voltage, the obtained results are reported in figure 4a) for Co:TiO_2 (2.8% at of Co). Figure 4b) shows the dependence of the Tafel slopes at high voltage as a function of the cobalt content. The best performance for the OER was obtained with the titanium oxide doped with 2.8% of Cobalt [9]. This material was also tested for cronoamperometry during the oxygen evolving and no changes in the current density were observed for 21 h of continuous work at 800 mV.



(a) (b)

Figure 4 a) Tafel plot for the anodic branch with linear regression showing low and high potentials. b) Effect t of the cobalt content on the Tafel Slope of the Co: TiO_2 electrodes.

The ORR polarization curves obtained in the Co: TiO_2 with 2.5% at of cobalt in the disk at rotation rates from 200 to 1600 rpm in an oxygen saturated 0.5M KOH solution are shown in the figure 5a. The figure 5b) shows the Koutecky Levich plots for the ORR on Co: TiO_2, the theoretical plots for the 2e- and 4e- transfer processes toward the ORR are also displayed for comparison. The experimental plots of Koutecky Levich slopes of Co: TiO_2 show a linear and parallel feature corresponding most to theoretical $4e^-$ than $2e^-$ transfer [10].



(a) (b)

Figure 5. a) Oxygen reduction polarization curves at Co:TiO_2 with 2.5% at of Co. b) Koutecky Levich plot and theoretical values for the 4 and 2 e- pathway.

This suggest that the ORR processes over with Co:TiO_2 (2.5% at of Co) electrocatalyst is a 4e- transfer pathway[11]. For the ORR also the Co:TiO_2 (2.5% at of Co) give the highest current density for this reaction.

$4e^-$ pathway: $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

$2e^-$ pathway: $O_2 + 2e^- + 2H_2O \rightarrow HO_2^- + OH^-$

$HO_2^- + 2e^- + 2H_2O \rightarrow 3\ OH^-$

This material will be interesting for the ORR in alkaline media on alkaline membranes, however the study of rotating disk ring electrode technique is necessary to verify the non-generation of H_2O_2, and to verify the proposed pathway.

4. Conclusions

Crossed Beam Pulsed Laser Deposition (CBPLD) allowed the synthesis of at Co:TiO_2 with different cobalt content by varying the kinetic energy of cobalt ions. The best performance for the OER and ORR was obtained with the Co:TiO_2 (2.5% at of Co) electro catalyst, this material was stable after 21 hours evolving hydrogen. These open the possibility to use this material as bifunctional electro catalysts in a unified regenerative fuel cell.

5. Acknowledgment

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6. References

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