



# Nickel/cobalt alloys modified electrodes: Synthesis, characterization and optimization of the electrocatalytical response



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## ABSTRACT

In this work we present the electrochemical deposition of nickel/cobalt alloys onto platinum electrodes followed by their conversion into the respective electrocatalytic hydroxide form. The modified electrodes were analyzed by cyclic voltammetry and by scanning electron microscopy (SEM). The electrocatalytic behavior was analyzed using glucose as electrochemical probe obtaining the sensitivities of detection. The sensitivities were normalized by the amount of active material onto the electrode surface. The presence of cobalt into the nickel hydroxide matrix led to a shift in the redox pair, achieving by this way the electrocatalytic form at lower potentials. The SEM images showed the presence of nanostructures at lower deposition times and the formation of a unique material which is not the simply deposition of nickel and cobalt separately. The composite was also studied by FTIR spectroscopy. We elaborated a detailed factorial design by using the electrode modified by the 50:50 (Ni:Co) proportion and 5 s of deposition as central point in order to find out the best electrode modification.

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## 1. Introduction

The research in modified electrodes has been widely reported along the years. In analytical sciences they represent a cheaper and straightforward methodology compared with the classical biosensors. Besides their utilization as electrochemical sensors they cover many other classical applications such as fuel cells, electrochromism, solar cells, drug delivery amongst others. Many different electrocatalytic materials can be found in literature such as conducting polymers [1–3], metal complexes [4,5] and transition metal oxides [6–8]. Amongst the commonly used inorganic materials, we can mention those ones based on nickel, copper and cobalt oxides. The presence of the oxidized forms  $M^{III}OOH$  provides an intense electrocatalytic performance, being able to oxidize many different organic molecules such as alcohols, aminoacids, sugars, nitrites and nitrates [9–14]. Besides, another interesting point is the easy and low cost electrode modification, either in the forms of thin films or in the nanometric scale.

Nickel hydroxide is a very interesting material with broad applications covering classic alkaline batteries, electrochromism, capacitors and electrocatalytic electrodes [15–20]. Independently in which area it will be applied, it is necessary to overcome two

major limitations related to nickel hydroxide: (i) its chemical stability and (ii) the oxygen evolution reaction, which is very close to  $Ni^{II}(OH)_2/Ni^{III}OOH$  process. By this way is well established in the literature the incorporation of small amounts of a second cation in the  $Ni(OH)_2$  structure in order to stabilize the high electroactive  $\alpha$ - $Ni(OH)_2$  phase avoiding the conversion into the  $\beta$ - $Ni(OH)_2$  phase, which is highly packed presenting lower electrochemical performance [18,21,22]. The goal of this strategy is to maintain the opened and disarranged structure of  $\alpha$ - $Ni(OH)_2$  that presents a higher electrochemical performance but it is invariably transformed into the  $\beta$  structure with lower charge capacity and leading to mechanical stress of the films when oxidized to the  $\gamma$ - $NiOOH$  phase [21,22]. The use of additives, such as  $Cu^{2+}$ ,  $Al^{3+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  have been widely employed strategy toward the stabilization of the  $\alpha$ - $Ni(OH)_2$  [23–28].

The incorporation of cobalt into the  $Ni(OH)_2$  structure is also found in literature leading to a significant improvement in the electrochemical properties of nickel hydroxide, shifting the  $Ni^{II}(OH)_2/Ni^{III}OOH$  redox process to cathodic potentials and increasing the reversibility of the system by increasing the conductivity of the discharged phase [29–31]. These are remarkable achievements for sensor technology as it is possible to split apart the oxygen reaction and the electrocatalytic  $Ni^{III}OOH$  peak and also avoid further interference signal provoked by any redox specie within this potential window. The presence of cobalt also hinders to a structural modification of the  $Ni(OH)_2$ , leading to a very

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disarranged structure by increasing the lattice defects and exposing the electrocatalytic sites, being an interesting feature for heterogeneous electrocatalysis for either fuel cells and analytical sciences.

Another point of interest is the development of electrochemical glucose sensor itself. The use of biosensors for the glucose detection has been described along the past years [32,33] and with the boost of the nanoscience nowadays many different modified electrodes can be found in literature [34–37]. In spite of the excellent selectivity provided by the use of enzymes (mainly *Glucose oxidase*) several limitations are also found such as the high cost for the enzyme purification, limited electrolyte conditions, durability and reliability of the modified electrode, among others. In this context the development of electrocatalytic materials based on the direct detection of glucose is desirable in order to overcome the limitations found in the biosensors modified electrodes.

Although widely spread in different analytical methodologies, the use of multivariate methods in electroanalytical analysis is fewer when compared to spectroscopic and chromatographic methods [38]. Studies have shown that it is possible to reduce the number of experiments in electrochemistry, beyond reduce the aggregate cost using this approach [38], moreover this technique provides relevant information about the system in study, in many cases improving analytical response and facilitating the understanding of the interaction between the various factors that affect the analyzes, especially in the development of electrochemical sensors [39–44].

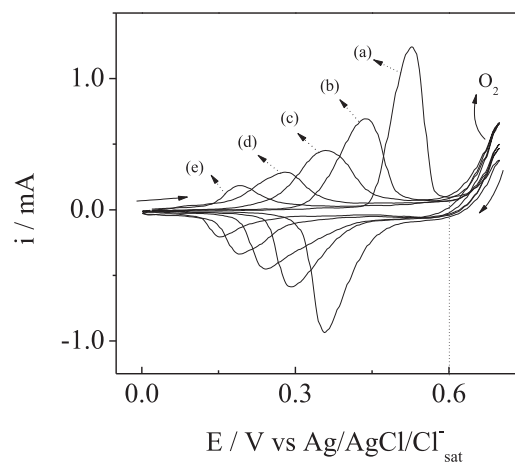
Thus, from the formation of electrocatalytic material between hydroxide nickel and cobalt, it is proposed the modification of electrodes by multivariate optimization in order to increase the utilization of chemometrics analysis not just for classic analytical methods but collaborated in the development materials.

## 2. Materials and methods

KOH, NiSO<sub>4</sub>, CoSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, KCl, glucose, (Synth) were used as received without any purification step. All solutions were prepared using Milli-Q water, resistivity of 18.2 MΩ cm at room temperature. Before each experiment the platinum electrode ( $A = 0.19 \text{ cm}^2$ ) was polished with alumina 0.3 and 0.05 μm, rinsed with water and kept in ultrasonic bath with ethanol during 5 min. Indium tin oxide (ITO, sheet resistance <15 Ω/sq) electrodes were purchased from Delta Technologies. Electrochemical experiments were performed in an Autolab PGSTAT 30 potentiostat using Pt foil and Ag/AgCl/Cl<sup>-</sup><sub>(sat)</sub> as counter and reference electrode respectively. The scanning electron microscopy (SEM) images were obtained in a Jeol JSM 6360 LV on the as-growth samples on ITO electrodes. The substrates in which the samples grew were put directly on the sample holder of the equipment and at least five different points of the sample were analyzed in order to assure the homogeneity. The Infrared spectra were obtained in a Bio-Rad Excalibur FTS 3500GX spectrometer, using KBr pellets.

The chemical precipitation of mixed oxides was done in order to corroborate the formation of a material which is not the simply mixture of nickel and cobalt hydroxides. To do so, 10 mL of 1.5 mol L<sup>-1</sup> solutions of cobalt and nickel sulphates were mixed at 50:50 proportion (mol:mol) and aliquots of KOH 3.0 mol L<sup>-1</sup> were added under intense magnetic stirring at low temperature (with ice bath), the pure hydroxides were also obtained by the same methodology. After 15 min, the samples were filtered and washed with cold water and the solids were dried at low pressure and room temperature. Four different solid samples were analyzed: pure Ni(OH)<sub>2</sub>, pure Co(OH)<sub>2</sub>, the composite Ni<sub>50</sub>Co<sub>50</sub>(OH)<sub>2</sub> and a simply mixture of the pure powders of nickel and cobalt hydroxides.

The metallic Ni/Co alloys were directly deposited on platinum or ITO electrodes (both presenting the geometric area of 0.19 cm<sup>2</sup>) by



**Fig. 1.** Cyclic voltammograms performed at Ni/Co modified electrodes, electrolyte: KOH 0.1 mol L<sup>-1</sup>, scan rate of 50 mV s<sup>-1</sup>. The electrodes were modified by applying -1.1 V during 5 s. Tested electrodes: (a) Ni(OH)<sub>2</sub>, (b) Ni<sub>75</sub>Co<sub>25</sub>(OH)<sub>2</sub>, (c) Ni<sub>50</sub>Co<sub>50</sub>(OH)<sub>2</sub>, (d) Ni<sub>25</sub>Co<sub>75</sub>(OH)<sub>2</sub> and (e) Co(OH)<sub>2</sub>.

applying -1.1 V vs Ag/AgCl during different times using electrolytes containing different proportions of cobalt and nickel sulphate salts. Then the modified electrodes were submitted to cyclic voltammograms in KOH 0.1 mol L<sup>-1</sup> in order to convert the alloys into their respective oxide form. The description of the modified electrodes was done by the respective proportion (mol/mol) of Ni<sup>2+</sup> and Co<sup>2+</sup> in the synthetic solution, for example, the electrode Ni<sub>25</sub>Co<sub>75</sub>(OH)<sub>2</sub> was modified in a solution containing the proportion of 25% (2.5 mmol L<sup>-1</sup>) of Ni<sup>2+</sup> and 75% (7.5 mmol L<sup>-1</sup>) of Co<sup>2+</sup> (mol/mol). The ionic strength for all synthetic solutions was the same (10 mmol L<sup>-1</sup>).

## 3. Results and discussion

Fig. 1 shows the voltammetric behavior of the modified electrodes by different proportions of Ni:Co by the deposition time of 5 s. As commented previously, the intrinsic conductivity of the Ni(OH)<sub>2</sub> is enhanced by the incorporation of irreversible Co<sup>III</sup>OOH, by this way the oxidation peak of the Ni<sup>II</sup>(OH)<sub>2</sub>/Ni<sup>III</sup>OOH process is shifted to lower potentials as the amount of cobalt in the inorganic structure increases [23,30,31]. This potential shifting is indeed a great feature taking into account the development of modified electrodes toward electrocatalytic systems, for example, in sensor technology the selectivity can be improved as the analyte of interest can be detected in a region with no contribution from interfering species with higher oxidation potentials, in fuel cells this effect also represent the possibility of collecting the electrons from the carbon sources by applying less positive potentials which in a long term operation can promote interesting savings in energy. In the system presented herein the electrocatalytic form can be obtained in a potential which there is no contribution from the oxidation of OH<sup>-</sup> producing O<sub>2</sub>, starting at about 0.6 V.

The metal/alloy depositions were also analyzed by linear voltammetry, as seen in Fig. 2. These experiments were done by using both Pt and ITO as substrates by running to the negative potential. It is possible to verify that using platinum (A) that the cathodic wave for the reduction of Ni<sup>2+</sup> is centered at about -0.37 V, the Co<sup>2+</sup> at about -0.44 V and -0.52 V for the composite deposition. This result is quite interesting as it shows that there are no individual peaks that would be attributed to the separately reduction of Ni<sup>2+</sup> and Co<sup>2+</sup>, on the other hand, these two acting together reducing as unique composite, in agreement with the results found in Fig. 1 where the different modified electrodes showed a distinct redox process rather than two individually voltammetric waves

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