Journal of Electroanalytical Chemistry 765 (2016) 126–131

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Evaluation of the electrocatalytical properties of $NiCo(OH)_2$ composite modified electrodes

Ana Leticia Soares [1], Ana Luiza Lorenzen [1], Ariane Schmidt, Marcio Vidotti *

Grupo de Pesquisas em Macromoléculas e Interfaces, Universidade Federal do Paraná, CP 19032, CEP 81531-980, Curitiba, Brazil

ARTICLE INFO

Article history:
Received 4 May 2015
Received in revised form 5 August 2015
Accepted 7 August 2015
Available online 13 August 2015

Keywords:
Nickel hydroxide
Cobalt
Rotating disk electrode
Electrocatalysis
Morphology

ABSTRACT

In this contribution we describe a detailed electrochemical study on the nickel hydroxide modified electrodes synthesized in the presence of different amounts of cobalt, producing tunable composite electrodes towards the electrocatalytic oxidation of glucose. The modified electrodes were studied by means of the sensitivity of detection where the results were further investigated by analyzing the heterogeneous charge transfer rate, obtained by using rotating disk electrode. It was found that despite of the higher sensitivity found, the composite electrodes have almost the same value of k indicating that the material morphology plays an important role in the electrocatalytic reaction. The modified electrode surfaces were studied by SEM images and found different sizes and morphologies of each composite deposited.

1. Introduction

Classically, nickel hydroxide electrodes have been the subject of study of many studies along the past years due to its extensive application in secondary batteries and energy storage devices [1,2]. Nowadays it is possible to find out the utilization of this versatile material in electrochromism, where due to the intense coloration achieved in the oxidized form ($Ni^{III}OOH$) in comparison with the reduced $Ni(OH)_2$, electrodes of good contrast are assembled [3–5]. Another important application is centered on its electrocatalytic properties where many different organic molecules can be immediately oxidized onto the electrode surface, it is possible to find many different electrochemical sensors in literature focused on the detection of carbohydrates, aminoacids, biological molecules, among others [6–10].

In a few lines, $Ni(OH)_2$ can be found in two different phases named as α and β. The difference between them can be summarized as the number of structural defects and the interlamellar space between the hydroxide sheets. In the α phase, the structure has many structural defects and a spacing of about 9 Å, being highly disordered, on the other hand, the β phase is closely packed in a 4 Å interlamellar distance. By this way the α phase is more electroactive than the β phase but unconditionally will be converted to the later one, which is thermodynamically stable [11–14]. Many efforts have been made in order to stabilize the α-$Ni(OH)_2$ by adding additives into the inorganic matrix, Al, Co, Mn, Fe, Ce, Cd and Zn can be easily found in literature [15–17]. Among the different additives, cobalt plays an important role as it has some interesting similarities with nickel, such as the ionic radii and the M–O bond energy. Probably the most interesting effect of the use of cobalt in nickel hydroxide electrodes is the shifting of redox potentials towards less positive potentials [18–21]. This effect can be explained by the increase of the composite conductivity, the redox pair $Co(OH)_2/CoOOH$ is highly irreversible, so, once formed the most of the $Co^{III}OOH$ sites is maintained into the inorganic structure [22], increasing by this way the overall conductivity, leading by this way the shifting of the oxidation peak towards less positive potentials. It is important to point out that the reduced form $Ni(OH)_2$ is much less conductive than the $Ni^{III}OOH$ one [23]. The mentioned effects occur due to the chemical similarities between cobalt and nickel atoms, so that the Co^{2+} replaces some Ni^{2+} sites in its hydrate oxide structure, forming a composite material, and besides the peak shifting mentioned before, the inclusion of Co^{2+} also is responsible for the increase of the number of structural defects within the material, leading to more disordered structure [24], affecting by this way the overall morphology of the composite.

Cobalt hydroxide electrodes can also be found in literature on the construction of electrochemical sensors [25–28], but some recent studies performed by our group using chemometrics and hydroxide formation from metallic nanostructures [29] demonstrated that the material itself has a poor electrocatalytic behavior and for electrochemical sensors its use together with nickel for electrochemical sensors seems to be a very interesting choice. Nevertheless, to the best of our knowledge, there are no reports in literature that explores the real effect of cobalt into the nickel hydroxide for electrochemical modified electrodes towards electrocatalysis, by this way this work discusses the electrocatalytic properties of $NiCo(OH)_2$ composite electrodes studied by the

---

* Corresponding author.
E-mail address: mvidotti@ufpr.br (M. Vidotti).

[1] Both authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jelechem.2015.08.011
1572-6657/

oxidation of glucose, by using rotating disk electrode and scanning electron microscopy. The studies presented herein could boost the development of electrochemical sensors and other nickel based devices.

2. Materials and methods

$Ni(NO_3)_2$ (Aldrich), $Co(NO_3)_2$ (Aldrich), KOH (Synth), HNO_3 (Synth) and glucose (Synth) were used as received without any purification step. All solutions were prepared using Milli-Q water, resistivity of 18.2 MΩ cm by using a Millipore system.

Electrochemical experiments were performed in an Autolab PGSTAT 30 potentiostat in a three electrode conventional electrochemical cell, using platinum ($A = 0.031\ cm^2$ for static and $0.126\ cm^2$ for RDE experiments) and ITO (Delta technologies, $R < 5\ \Omega$) as working electrodes, Pt foil and $Ag/AgCl/Cl^-_{(sat)}$ as counter and reference electrode respectively. SEM images were obtained using a Tescan Vega3LMU equipment under voltage of 15 kV, at least 5 different regions of three different modified electrodes were analyzed in order to assure both homogeneity and reproducibility. Rotating disk electrode experiments were performed in a RRDE-3A equipment by BAS. All electrochemical experiments were also performed in triplicate.

The nickel hydroxide electrodes were electrochemically modified by following the Corrigan's method [30] which is commonly referred as the electrochemical reduction of nitrate producing an interfacial increment of pH followed by the chemical precipitation of $Ni(OH)_2$, accordingly to Eqs. (1) and (2).

$$NO^-_{3(aq)} + 7H_2O_{(l)} + 8e^- \rightarrow NH^+_{4(aq)} + 10\,OH^-_{(aq)}. \quad (1)$$

$$2OH^-_{(aq)} + Ni^{2+}_{(aq)} \rightarrow Ni(OH)_{2(s)}. \quad (2)$$

The amount of material deposited was controlled by the cut off charge value passed through and for all experiments was limited to −2.0 mC by applying −1.1 V in electrolytes containing different proportions of Ni^{2+} and Co^{2+} in order to obtain different types of deposited $Ni_XCo_Y(OH)_2$ modified electrodes. From now on, the electrodes are labeled accordingly to the proportion of Ni^{2+} and Co^{2+} in the synthetic solution, X and Y, respectively.

3. Results and discussion

The effect of cobalt on the electrochemical properties of nickel hydroxide electrodes is described as an increment on the intrinsic electric conductivity of the material, especially in the reduced form, leading to a shifting in the redox pair towards lower potentials [31,32], this is a very interesting feature, taking into account the use of this material for electrochemical sensors as the catalytic form $Ni^{III}OOH$ can be obtained in an energetic region far from many interferent species. Herein the sensitivity values were determined by cyclic voltammetry in the diffusional limited region, in electrolytes containing different concentrations of glucose. In Fig. 1 are shown the representative voltammograms of a $Ni_{95}Co_{05}(OH)_2$, $Ni_{50}Co_{50}(OH)_2$ and $Co(OH)_2$ modified electrodes in the presence of different glucose concentrations, ranging from 0.2 up to 1.2 mmol L^{-1} in a KOH 0.1 mol L^{-1} electrolyte, depicted in the figures the respective calibration curves of the modified electrodes.

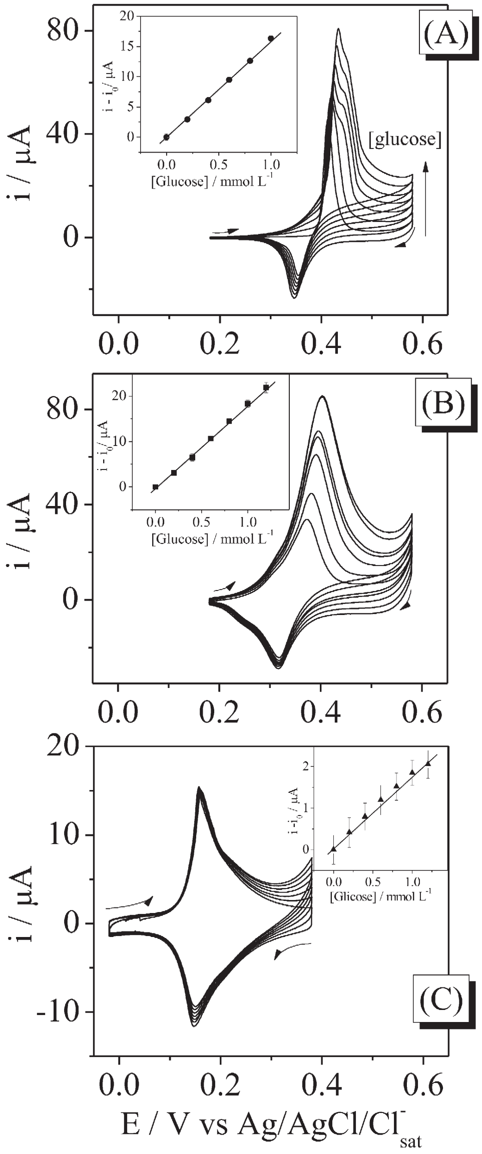

Fig. 1. Representative cyclic voltammograms performed in KOH 0.1 mol L^{-1} containing different amounts of glucose, scan rate of 10 mV s^{-1} at different modified electrodes: (A) $Ni_{95}Co_{05}(OH)_2$, (B) $Ni_{50}Co_{50}(OH)_2$ and (C) $Co(OH)_2$. Inserted the respective calibration curves obtained (S/N = 3).

The voltammograms showed the well known electrocatalytic behavior for the oxidation of organic molecules performed by the $Ni^{II}(OH)_2/Ni^{III}OOH$ redox pair, it is important to note the low electrocatalytic effect by the $Co(OH)_2$ modified electrode. To obtain the calibration curves, the electrocatalytic response was obtained at 0.55 V for $Ni_XCo_Y(OH)_2$ and at 0.3 V for the pure $Co(OH)_2$ electrodes, in a diffusion controlled regime. It is very hard to compare the values of sensitivity presented herein with other ones published elsewhere as it is important to mention that different parameters can be changed such as: amount of electrocatalytic material, geometric electrode area, electrolyte concentration, technique employed in the detection, thermodynamic form of $Ni(OH)_2$ present, among others, a review of these works can be found in [33–35]. Nevertheless these values obtained herein can be readily compared among them in the scope of this work.

All calibration curves showed a linear behavior in the range studied and at first view the sensibilities look similar apart from the $Co(OH)_2$ modified electrode. The low sensitivity presented by the $Co(OH)_2$ are in concordance with our previous report [29] indicating that the Ni^{III} sites are the main responsible for the electrocatalytic oxidation of glucose. By this way it is necessary a proper relationship between the sensitivity and the amount of nickel present in each modified electrode. To do so, it was found that the number of moles of electroactive $Ni^{III}OOH$ [36] by means of integrating the voltammetric electric charge (Q_{volt}) passed through the electrode in the cathodic process at slow scan rate (2 mV s^{-1}), the cathodic reaction was chosen in order to avoid any interference from the oxygen reaction that occurs at the proximity of the $Ni^{III}OOH$ peak. The amounts of nickel and cobalt were estimated by its proportion in the synthetic solution, although the real proportion