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Non-enzymatic sensing of carbohydrates using a nickel–chromium alloy electrode

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ABSTRACT

A highly sensitive non-enzymatic carbohydrates sensor based on a nickel hydroxide film on a nickel alloy electrode was developed. The electro-catalytic film is formed by using a potential scan program developed in our research group. This program facilitated the formation of stable proportions of Ni(II)/Ni(III) oxy-hydroxides which are necessary for the electro-catalysis. The structural morphology and roughness of the oxy-hydroxides were characterized by using scanning electron microscopy and atomic force microscopy. The electrochemical behavior of the electrodes in 0.10 M NaOH and in the presence of carbohydrates was characterized by cyclic voltammetry and chronoamperometry, showing good catalytic activity for the anodic oxidation of carbohydrates. Fast and significant amperometric responses were obtained with the renewable nickel hydroxide films, which were easily constructed on the electrodes' surfaces by potential cycling. The good analytical performance, low cost and straightforward preparation method make this alloy a promising electrode for the development of effective non-enzymatic carbohydrates sensor.

1. Introduction

The determination and quantification of sugars has a great significance in many fields such as food industries, biotechnology, medical applications, wastewater treatment, and many others [1–4]. Enzymatic sensors based on the immobilization of enzymes on various substrates are the topics of most of the previous studies on this subject [5,6]. However, the greatest problem is naturally insufficient stability and loss of enzyme activity during immobilization process which affects sensitivity and reproducibility of sensor.

The glucose detection industry is dominated by use of enzymatic electrodes, in which the enzyme glucose oxidase is predominantly used. It is a highly selective enzyme, and works at a wide range of pHs relative to other enzymes [7]. Enzyme modified electrodes, however, suffer from limited stability and variable sensitivity, requiring increasingly elaborate fabrication and immobilization methods to overcome these boundaries [8].

Non-enzymatic amperometric sensor for direct determination of glucose is an attractive alternative technique to solve the disadvantages of enzymatic biosensors. A number of metal electrode materials, namely copper [9–11], gold [12,13], platinum [14,15], and nickel [16,17], have been explored extensively in their application to catalytic oxidation of carbohydrates. Nickel alloys have also been frequently used in non-enzymatic glucose detection, with alloys such as Ni–Cu [18,19], Ni–Ti [20,21] and Ni–Cr [19,22]. Particularly, the Ni–Cr (80:20) alloy was proposed as an excellent electrode material for the amperometric detection of carbohydrates after anion-exchange high performance liquid chromatographic separations [19,23]. Moreover, this alloy showed enhanced sensitivity and signal stability when compared with pure nickel electrodes [24].

Nickel and nickel oxy-hydroxide electrodes are good materials for the oxidation of organic compounds in alkaline solutions [25–27]. Various authors have demonstrated that nickel oxy-hydroxide has good electro-catalytic properties for the oxidation of different molecules. For example, aspirin [28], methane [29], acetylcholine [30], and glucose [31,18] were easily oxidized on nickel oxy-hydroxide-modified nickel electrodes. A catalytic reaction mechanism [32] has been generally used to explain the results obtained in the electro-oxidation of several organic molecules at oxy-hydroxide-modified metal electrodes (see for example [33,34] and references therein). According to this mechanism, $Ni(OH)_2$ is first oxidized to NiOOH, which then reacts with the organic molecule to regenerate the starting material.

In previous studies we developed potential scan programs for cyclic voltammetry that allowed us to obtain stable proportions of nickel α- and β-oxy-hydroxides on the electrode surfaces [35].

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We also proposed an electro-catalytic mechanism based on the cyclic voltammetric (CV) response of glucose at Ni and Ni–Cr alloys (namely 90:10 and 80:20 Ni–Cr alloys) [22]. The proposed mechanism helped us to explain the curved nature of the calibration plots, that is, the electro-catalytic peak current as a function of glucose concentration.

In this work we report an alternative route to the enzymatic detection of carbohydrates by applying the electro-catalytic properties of a nickel oxy-hydroxide film on a Ni–Cr (80:20) alloy electrode for the electro-oxidation of glucose, fructose, lactose and sucrose in alkaline solution. The electro-catalytic properties for the oxidation of those carbohydrates were evaluated by chronoamperomety, and the proposed electrode showed an excellent catalytic activity. The developed surface can be used directly as non-enzymatic carbohydrate sensor.

2. Materials and methods

Working electrodes were made of Ni–Cr (80:20) (Goodfellow, England, catalog number NI055150) wires of 0.10 cm diameter embedded in Teflon shrinkable tubes. They were polished with sand paper and then with fine alumina down to 0.05 μm, rinsed with triply distilled water, ultrasonicated during 5 min, rinsed again with triply distilled water and immersed in the electrochemical cell. The exposed circular area obtained after polishing was ca. 7.8×10^{-3} cm^2. In order to minimize oxides formation −1.00 V was applied to the working electrodes for about 60 s before CV experiments. A platinum foil of a larger area (ca. 0.8 cm^2) was used as the counter electrode. All potentials are referred to the saturated calomel electrode (SCE). This electrode was placed in a Luggin capillary in the electrochemical cell.

For the formation of the oxy-hydroxides film on the electrode's surface, the potential of the working electrode was swept from 0.00 V to 0.60 V during 5 CV cycles, then a smaller potential range from 0.10 V to 0.60 V was swept during 10 CV cycles. Finally, an even smaller potential range (from 0.20 V to 0.60 V) was swept during the remaining CV cycles (a total of 600 CV cycles) at a potential sweep rate of 0.05 V/s in 0.10 M NaOH. This program facilitated the development of approximately equal quantities of α-Ni(OH)$_2$ and β-Ni(OH)$_2$ [35].

The electrochemical cell was a conventional two compartments glass cell. Autolab model PGSTAT-30 or PGSTSAT-12 potentiostats were used to control the potential between the working and reference electrodes. The potentiostats were controlled by PC compatible computers using the PGSTAT software version 4.9006. Graphics were obtained with a conventional printer. The temperature of the electrochemical cell was kept at 25.0 ± 0.2 °C.

Atomic force microscopy (AFM) images were performed in tapping mode with a NanoScope V scanning probe microscope, silicon tip, spring constant: 42 N/m (Bruker) operating at ambient conditions. The analyses were made at the Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Universidad Nacional de la Plata (Argentina).

The elemental analyses of the electrode's surfaces were performed by using an EDAX Genesis 2000 energy dispersive spectroscopy system coupled with a LEO1450VP scanning electron microscope (SEM). The analyses were made at the Electron Microscopy Laboratory and Microanalysis (LabMEM) of the National University of San Luis (Argentina).

Sodium hydroxide solutions were prepared with triply distilled water and analytical grade reagents (Merck, Argentina). The solutions were thoroughly degassed by bubbling high purity N$_2$ prior to electrochemical experiments. Contact with atmospheric CO$_2$ was minimized by maintaining N$_2$ over the solutions during the electrochemical experiments.

The fitting of the voltammetric traces by hyperbolic functions was performed by using the software Origin 8.0.

For the calibration curves experiment, amperometric measurements were carried out at 0.5 V while adding from 60 μL to 200 μL of 10 mM glucose into 60 mL of 0.10 M NaOH solution under a magnetically stirred condition to obtain a step-by-step increase of the final concentration, that is, from approximately 10 μM to 600 μM.

3. Results and discussion

3.1. Morphology of Ni and Ni–Cr (80:20) alloy electrode

The morphology of the oxy-hydroxide film formed on the nickel–chromium alloy electrodes in sodium hydroxide solution was examined by AFM and SEM [36]. The electrodes' surfaces were prepared by voltammetric cycling between 0.20 V and 0.60 V during 600 cycles. Fig. 1A and B shows representative photomicrographs of the electrodes' surfaces after the voltammetric treatment. A greater roughness at the Ni–Cr (80:20) alloy electrode was observed in the morphology analysis of the oxy-hydroxide films [22]. The increase in roughness was confirmed by the root mean square (RSM) roughness values of 3.0 and 4.3 nm obtained from the area (500 × 500 nm) of the nickel oxy-hydroxide film on the surface of the electrodes [37,38]. The forming a rougher nickel oxy-hydroxide film in the presence of chromium indicates that a larger surface area is exposed in the electrochemical experiments, suggesting the possibility of a greater electro-catalytic behavior.

The chemical contrast image indicates that chromium is homogeneously distributed in the nickel matrix at the Ni–Cr (80:20) alloy electrode, Fig. 1C. The results of chemical composition analysis obtained by EDAX revealed that the alloy contains 80% Ni and 20% Cr, Fig. 1D.

3.2. Catalytic oxidation of carbohydrates

The Ni–Cr (80:20) alloy electrode showed good catalytic activity for the anodic oxidation of carbohydrates in 0.10 M NaOH. Fig. 2 shows the cyclic voltammetric responses in the absence and in the presence of different concentration of glucose, Fig. 2A and of sucrose, Fig. 2B.

An oxidative current peak, at approximately 0.45 V on the positive going potential scan, is observed in the cyclic voltammetric current density vs. potential (j/E) profiles obtained with the working electrode Ni–Cr (80:20) in the absence of carbohydrates. The bell shaped peak is indicative of a surface confined electrochemical reaction. This oxidative current peak has been ascribed to the oxidation of Ni(II) to Ni(III), as shown in Eq. (1)

$$\mathrm{Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e} \tag{1}$$

A pair of reductive current peaks is observed during the negative going potential scan. The reductive current peak observed at approximately 0.38 V has been ascribed to the reduction of β-NiOOH to β-Ni(OH)$_2$, while that observed at approximately 0.30 V has been ascribed to the reduction of γ-NiOOH to α-Ni(OH)$_2$ [35].

An increment of the peak current and oxidative charge under the peak observed at 0.45 V is observed when glucose is added to the electrolyte solution. A decrease of peak currents and reductive charges is observed in the reductive waves obtained during the negative going potential scan. This behavior is characteristic of electro-catalytic mechanisms [32]. Equivalent behaviors are observed when different carbohydrates are added to the electrolyte solution. Fig. 2B shows the j/E behavior of the nickel oxy-hydroxide film on a Ni–Cr (80:20) alloy electrode when different concentrations of sucrose were added to the electrolyte solution.