Simultaneous electrochemical determination of glucose and ethanol on glassy carbon electrode modified with nickel oxides.

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Abstract
In this paper we present the simultaneous electrocatalytic oxidation of glucose and ethanol, in alkaline solution, at a glassy carbon electrode (GCE) modified with nickel oxides. This electrochemical sensor has the particularity to separate the oxidation peaks of glucose and ethanol by more than 100mV, allowing their dosage simultaneously. The proposed electrochemical sensor has a fast response to the simultaneous oxidation of ethanol with a sensitivity of 1.0 10⁻³ A L mol⁻¹ in the range 0 – 9.3 10⁻² mol L⁻¹, with a limit of detection of 7.2 10⁻³ mol L⁻¹, and glucose with a sensitivity of 5.0 A L mol⁻¹ in the range 0 – 3.0 10⁻⁵ mol L⁻¹ and with a limit of detection of 2.9 10⁻⁶ mol L⁻¹.

Keywords: Ethanol, Glucose, Cyclic Voltammetry, Nickel Oxide Film, Mediator

1. Introduction
To our knowledge, the use of sensors dates back to 1952 and was interested in phonocardiography [1]. Since, the development of electrochemical detection systems for small organic molecules gained considerable attention [2,3]. In analytical science, electrochemical detection systems represent a simple and less expensive way than traditional methods. Numerous attempts have been undertaken to develop methods of detection. Many studies focused on the use of electrocatalysts based on noble metals such as platinum [4,6], gold [7,9], rhodium [10,11] and iridium [12,13]. Others works on electrochemical sensors were more oriented towards oxides of transition metals, such as titanium [14,15], vanadium [16,17], Chromium [18,19], manganese [20], iron [21], cobalt [22,23], nickel [24], copper [25,26], zinc [27, 28] and ruthenium [29]. The presence of the oxidized form in the sensors provides an intense electrocatalytic performance and makes them able to oxidize various organic molecules, such as alcohols, amino acids, sugars, nitrites, sulphites, etc ... [30,35]. Furthermore, sensors based on metal oxides have the advantage of being inexpensive. Among these sensors, the nickel oxides exhibit excellent performance with respect to the electrocatalytic oxidation of organic molecules, in particular [36,37]. Nickel oxides are used as catalyst for the glucose electrooxidation. The importance of controlling glucose levels in the blood by a simple, compact and reliable device, has led many researchers to focus their efforts on the determination of glucose sensor based on metal oxides [38,39].

Given the importance of the determination of glucose and ethanol in the blood, we thought it is useful to contribute to the development of an electrochemical sensor that gives in a single operation the rate of glucose and the ethanol. For this purpose, we have modified a glassy carbon electrode with nickel oxides and we have used it to selectively determine glucose and ethanol in an alkaline solution.
2. Experimental

2.1 Materials and Reagents
Boric acid, nickel chloride, sodium hydroxide, ethanol and D-glucose used in this work were of analytical grade and were purchased from Merck. These reagents were used without further purification. All solutions were prepared with distilled water. Electrochemical study was realised in a three-electrode cell powered by a potentiostat model Versastat3, controlled by Versa-Studio software. Along this work, we used a KCl saturated calomel electrode (SCE) as reference (XR 110, Radiometer), an auxiliary filiform platinum electrode (XM 110, Radiometer) and a disk shaped glassy carbon of 3 mm diameter mounted on a rotating electrode. All studies were carried out at 25 ± 0.1 °C.

2.2 Electrode modification
The GCE was polished to a mirror finish before each modification by means of a polishing machine (Mercapol B), with a 0.3µm alumina, rinsed several times with distilled water and mounted on a rotating electrode. The GCE modification was achieved in two sequential steps. In the first one, a metallic nickel film was electrochemically deposited on GCE, from 10⁻² mol L⁻¹ NiCl₂ and 10⁻¹ mol L⁻¹ boric acid, by cyclic voltammetry, in the potential range -0.05V to -1.05V with a potential scan rate of 0.05Vs⁻¹, for 19 cycles [40]. In a second step, the nickel coated GCE was oxidized in NaOH pH 12, by cycling the potential from 0.1V to 0.7V, in the anodic direction. Ten cycles were performed at 0.1 Vs⁻¹. The voltammogram recorded in this step is characterized by anodic and cathodic peaks located at 0.430V and 0.350 V, respectively. These two peaks are attributed to the electrochemical system NiOOH/Ni(OH)₂ [36,41]. After this, the nickel oxide coated GCE was used for the simultaneous determination of glucose and ethanol.

3. Results and discussion

3.1 Determination of ethanol concentration.
The GCE modified with NiOOH/Ni(OH)₂ is used to the determination of the ethanol in NaOH at pH12. Fig.1 shows, that in absence of ethanol, the electrochemical process of NiOOH/Ni(OH)₂ is characterized by anodic and cathodic peaks located at 0.430V and 0.350V; respectively (curve a). The ethanol is not electroactive in bare GCE (curve b), but it becomes oxidizable on the modified electrode (curve c). The second anodic peak of curve (c) is located at 0.573V and lies in the stability domain of NiO₂.

![Figure 1: Voltammograms recorded before and after ethanol oxidation: (a) voltammogram of NiOOH/GCE in absence of ethanol; (b) and (c) 2.8 10⁻² mol L⁻¹ of ethanol on bare GCE and NiOOH/GCE, respectively in 0.1Vs⁻¹; 25 °C; 10³ rpm.](image-url)
Fig. 2: Voltammograms (without backward trajec) recorded during ethanol oxidation on NiOOH/GCE, in NaOH pH=12; 0.1Vs$^{-1}$; 25°C; 10$^3$rpm; inset: Calibration curve of ethanol oxidation on NiOOH/GCE in NaOH pH=12; 0.1Vs$^{-1}$; 25°C; 10$^3$rpm.

Fig.2 shows that the second anodic peak increases with increasing ethanol concentration. During ethanol determination, the anodic and cathodic current peaks of NiOOH/Ni(OH)$_2$ system remain almost constant. The constancy of the reduction peak current of NiOOH to Ni(OH)$_2$ is interpreted by the fact that the amount of NiOOH consumed during the formation of NiO$_2$ (Eq.1) is exactly compensated by the amount of NiOOH produced during the reduction of NiO$_2$ by ethanol (Eq.2).

\[ 4\text{NiOOH} (s) + 4\text{OH}^-(aq) \rightarrow 4\text{NiO}_2(s) + 4\text{e} + 4\text{H}_2\text{O}(l) \quad \text{Eq. (1)} \]

\[ \text{CH}_3\text{CH}_2\text{OH} (ad) + 4\text{NiO}_2(s) + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- (aq) + 4\text{NiOOH} (s) \quad \text{Eq. (2)} \]

The current of the first anodic peak remains almost constant since Ni(OH)$_2$ does not participate to the ethanol oxidation.

### 3.2 Determination of glucose concentration

Fig.3 shows voltammograms recorded at 0.1V/s after each addition of glucose. The anodic potential peaks, during glucose oxidation, shift toward more anodic value with increasing glucose concentration and are located in the range 0.430-0.480V, while peak currents increase proportionally to the glucose concentration.

The potential of the cathodic peaks remains constant during glucose determination and is located at 0.350V, while the peak currents decrease [41]. The adsorption of glucose on the active anodic sites of the interface(NiOOH/Ni(OH)$_2$) explains the shift of the potential in the forward scan, while the desorption of products lead to free cathodic sites, thus the reduction potential of NiOOH/Ni(OH)$_2$ remains constant. The cathodic peak represents the electrochemical reduction of NiOOH formed during the modification step of the electrode. Its intensity is maximal in the absence of glucose. But, when adding the glucose in the measuring cell, a quantity of NiOOH reacts with glucose. The remaining amount of NiOOH decreases with increasing glucose concentration, which explains the decrease in the cathodic peak current according to equation (3):

\[ \text{NiOOH} (s) + \text{1e} + \text{H}_2\text{O}(l) \rightarrow \text{Ni(OH)}_2(s) + \text{OH}^- (aq) \quad \text{Eq. (3)} \]
Equation (4) represents the oxidation of glucose by NiOOH; the accumulation of Ni(OH)$_2$ explains the increase of the current anodic peak during glucose determination.

$$\text{GluCHO}^{(ads)} + 2 \text{NiOOH}^{(s)} + \text{OH}^{-}^{(aq)} \rightarrow \text{GluCOO}^{-}^{(aq)} + 2\text{Ni(OH)}_2^{(s)} \quad \text{Eq. (4)}$$

3.3 Simultaneous determination of glucose and ethanol.

Fig.4 includes the potential-pH equilibrium diagrams for nickel-water, ethanol-water and glucose-water system, at 25°C. The diagram of figure (4) is constructed by adding to the nickel-water equilibrium diagram [43], those of ethanol-water and glucose-water by considering their standard potentials and their acidity constants.

**Figure 4:** Potential-pH equilibrium diagrams of glucose/water ethanol/water and nickel /water at 25°C.
Fig. 4 shows that equilibrium potentials of glucose/gluconate and ethanol/ethanoate are pH dependent. It is well known that two peaks do not overlap when their potentials are separated by at least 100mV. At pH 12.7, the anodic peak potentials of glucose and ethanol are separated by 113mV, and then their simultaneous determination becomes selective.

Fig. 5 shows the voltammograms of the simultaneous determination of glucose and ethanol in NaOH aqueous solution, on modified GCE. Figure (5a, b) shows the simultaneous determination of ethanol in the concentration range 1.4 $10^{-2}$ mol L$^{-1}$ to 9.3 $10^{-2}$ mol L$^{-1}$ and glucose in the concentration range 2.5 $10^{-4}$ mol L$^{-1}$ to 1.2 $10^{-3}$ mol L$^{-1}$. These two determinations are performed with limits of detection of 1.4 $10^{-2}$ mol L$^{-1}$ and 2.1 $10^{-4}$ mol L$^{-1}$, respectively.

**Figure 5:** Voltammograms recorded during oxidation of glucose-ethanol mixture, on NiOOH/GCE, NaOH pH=12.7; 0.1Vs$^{-1}$; 25°C; 10$^3$ rpm; inset: (a) Calibration curve of glucose oxidation, in presence of ethanol, on NiOOH/GCE, in NaOH pH=12.7; 0.1Vs$^{-1}$; 25°C; 10$^3$ rpm; (b) Calibration curve of ethanol oxidation, in presence of glucose, on NiOOH/GCE, in NaOH pH=12.7; 0.1Vs$^{-1}$; 25°C; 10$^3$ rpm.

**Conclusion**

1. A non-enzymatic sensor for selective determination of glucose and ethanol was manufactured successfully using nickel oxide NiOOH as sensing material, with a sensitivity of 48 $\mu$A mM$^{-1}$ and 1.9 $\mu$A mM$^{-1}$ respectively.
2. The catalytic oxidation of ethanol is mediated by NiO$_2$.
3. This electrochemical sensor is used to the simultaneous determination of glucose and ethanol in alkaline solution.
4. The electrochemical sensor is used to measure trace amounts of glucose in the presence of an excess of ethanol.

**References**
