

ELECTROCHEMICAL DETERMINATION OF ETHANOL, 2-PROPANOL AND 1-BUTANOL ON GLASSY CARBON ELECTRODE MODIFIED WITH NICKEL OXIDE FILM

A. Benchettara and A. Benchettara*

Laboratory of Electrochemistry-Corrosion, Metallurgy and Inorganic Chemistry-Fac.
Chemistry USTHB-BP 32 El Alia Bab Ezzouar Algiers 16111, Algeria.

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ABSTRACT

In this work, we present the modification of a glassy carbon electrode with nickel oxide film which is performed in two successive steps. In the first one, the electrochemical deposition of metallic nickel on the glassy carbon electrode (GCE) is achieved in 0.1M boric acid; in the second step, the metallic deposit is anodically oxidized in 0.1M NaOH. These two operations were carried out in a three electrode cell with a filiform platinum auxiliary electrode, a SCE as potential reference and a working microelectrode of modified glassy carbon with nickel oxides. This electrode is characterized by several electrochemical techniques and is used for the catalytic determination of ethanol, 2-propanol and 1-butanol in 0.1 M NaOH. The proposed chemical mechanism shows that NiO₂ acts as a mediator.

Key words: Sensor; Electrodeposition; Electrocatalysis; Alcohol; Mediator.

1. INTRODUCTION

For sixty years, the development of electrochemical detection systems for small organic molecules gained considerable attention [1,2]. In analytical science they represent a simpler and less expensive method compared to conventional biosensors.

Author Correspondence, e-mail: bbenchettara@hotmail.com

Tel.: +213 550253916; fax: +213 21247311.

[ICID: 1124392](#)

Many attempts were established to develop methods of detection, early work focused on the use of electro catalysts based on noble metals than that Pt [3-5] and Au [6-10].

Recent works are more oriented towards oxides of transition metals for example NiO_x [11], FeOOH [12], CuO [13], MnO₂[14] , RuO₂ [15], Cu₂O and Co₃O₄ [16-17].The presence of oxidized forms provides an intense electro catalytic behaviour, being capable of oxidizing many various organic molecules such as alcohols, amino acids, sugars and nitrites [18-23]. Furthermore, another interesting point in the modification of the electrode is the simplicity and low cost, either in the form of thin films or in the nanoscale.

Among these oxides, nickel oxide (NiO) is a very interesting material which presents an excellent performance in alkaline medium [24-26], with wide applications covering conventional alkaline batteries, electro chromic, capacitors and electro catalytic electrodes.

Nickel oxide is used as a catalyst for the electro oxidation of alcohols. The catalytic behaviour of some alcohols has been studied by several authors [27-29]. The level of concentration of alcohol in the human body can be a bio-brand for many applications such as the determination of blood alcohol concentration, which is a parameter very important for the safety of drivers of vehicles. There is therefore an interest in developing methods to detect alcohol. In this article, a glassy carbon electrode was coated with nickel oxides by electrochemical technique and characterized by cyclic voltammetry to evaluate its performance for electro oxidation of ethanol, 2-propanol and 1-butanol.

2. MATERIALS AND METHODS

Boric acid, nickel chloride, sodium hydroxide, and alcohols used in this work were manufactured by Merck and Sigma-Aldrich. Electrochemical study was realized in a three-electrode cell powered by a potentiostat model Versastat 3 and controlled by Versastudio software. Along this work, we used a saturated calomel electrode (SCE) as reference, an auxiliary filiform platinum electrode and a static glassy carbon microelectrode. All studies were carried out at 25°C. The glassy carbon microelectrode used is polished before each modification using a polishing machine with 0.3µm alumina and then rinsed several times with distilled water. The solution was stirred during electrodeposition and alcohol determination at a constant speed.

3. RESULTS AND DISCUSSION

3.1 Electrode modification

The glassy carbon microelectrode (GCE) is polished to a mirror finish before each modification by means of a polishing machine, with 0.3 μm alumina, rinsed several times with distilled water. The GCE modification is achieved in two sequential steps. In the first one, the reduction of Ni^{2+} is achieved on GCE, from an aqueous solution of $10^{-2} \text{ mol L}^{-1} \text{ NiCl}_2$, acidified with 0.1 mol L^{-1} boric acid, by cyclic voltammetry, in the potential range -0.05 ; -1.05V , (19 cycles), figure 1. At the end of the 19th cycle, the working electrode is removed from the micro electrolysis bath and washed several times with distilled water. A deposit of metallic nickel is visible to the naked eye on the glassy carbon electrode. In a second step, the glassy carbon electrode, coated with a film of metallic nickel (Ni / GCE), is immersed in a solution of 0.1 M sodium hydroxide. After a few seconds of immersion, the free potential of the new interface stabilizes. Once the steady state is reached, a cyclic potential ramp is applied from 0.1V to 0.7V, in the anodic direction, in order to obtain nickel oxides. Twenty cycles are performed at a scan rate potential of 100 mV s^{-1} (figure 2). After this, NiOx/Ni/GCE is removed from the alkaline bath and thoroughly washed with distilled water.

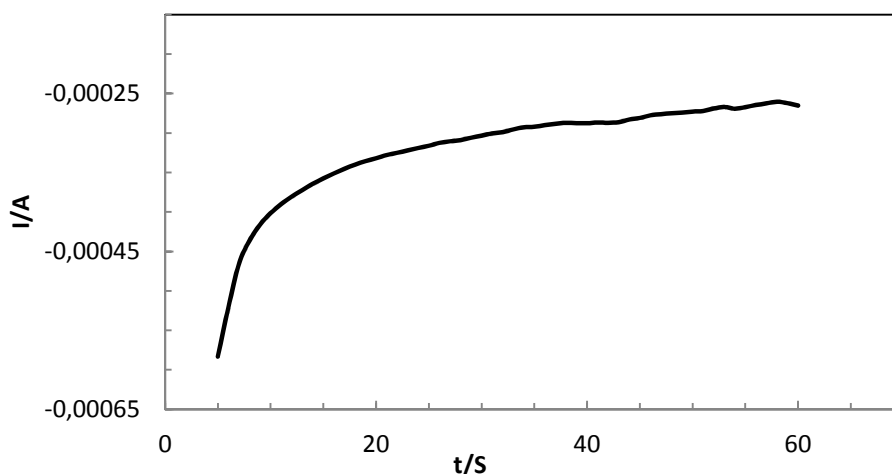


Fig.1. Chronoamperogram of the cathodic reduction of $10^{-2} \text{ mol L}^{-1} \text{ Ni}^{2+}$ on glassy carbon in $0.1 \text{ mol L}^{-1} \text{ H}_3\text{BO}_3$; 50 mV s^{-1} ; 25°C .

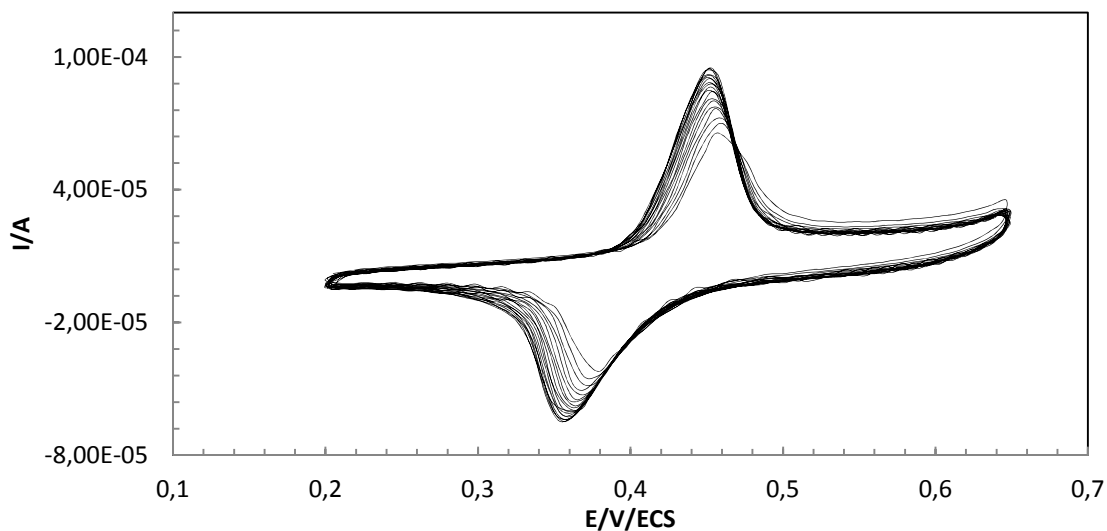


Fig.2. The voltammograms recorded during oxidation of Ni film in 0.1 mol L⁻¹ NaOH; 100mVs⁻¹; 25°C.

The voltammograms of figure 2 show an anodic peak located at 450 mV and a cathodic peak, at 350 mV. These peaks become more intense by increasing the number of cycles until the 20th cycle. This increase in intensity is due to the accumulation of nickel oxides on the surface electrode. Once the working electrode surface is completely covered by nickel oxides, the nickel oxidation is stopped, and the peaks reach optimum values.

3.2. Characterization and kinetics

The anodic and cathodic potentials peaks of the voltammograms of figure (2) are located in the stability domains of NiOOH and Ni(OH)₂, respectively. The anodic oxidation of Ni has thus led to the formation of the redox system NiOOH/Ni(OH)₂ [29]



A study of the rate scanning potential was performed on the previous redox system (Fig.3), in the range 0.030V/s – 0.250V/s.

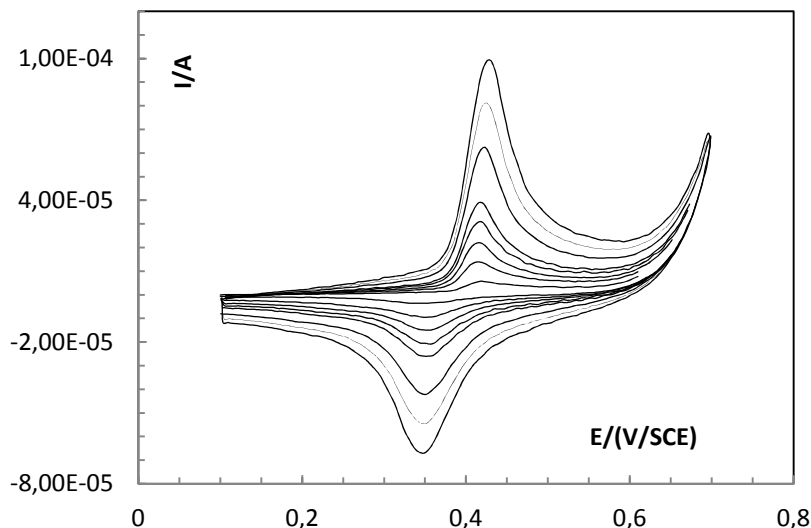


Fig.3. Effect of potential scan rate on the oxidation of Ni in NaOH 0.1mol L⁻¹; 25°C.

Figure 3 shows that both anodic and cathodic peak currents increase linearly with increasing potential scan rate. In contrast, anodic and cathodic peak potentials remain almost constant during the scan rate potential effect. The system is then quasi reversible. The plot of the anodic peak currents as a function of the potential scan rate (v) $I_{pa} = f(v)$ of the previous voltammograms is shown in figure 4.

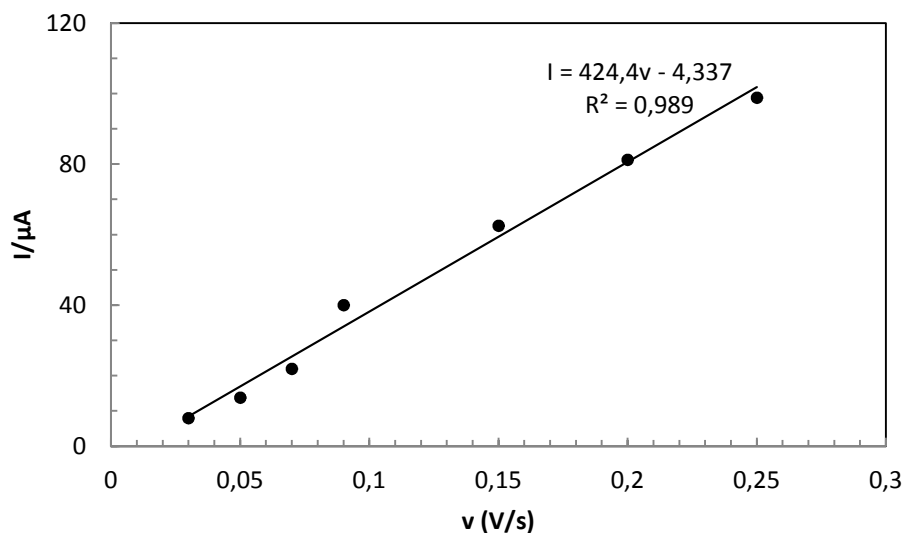


Fig.4. Anodic peak intensity $I_{p,a}$ vs v of Ni oxidation on glassy carbon electrode in the range 0.030 -0.250 V/s; NaOH 0.1 mol.L⁻¹; 25°C.

From Laviron equation,

$$I_{pa} = \frac{n^2 F^2 A \Gamma v}{4RT}$$

the average surface concentration (Γ) of electro-active sites (NiOOH) on the surface of glassy carbon electrode can be estimated based on the slope of I_p vs. Γ was calculated to be $6.45 \cdot 10^{-9}$ mol.cm⁻².

4. APPLICATION

4.1 Determination of ethanol, 2-propanol and 1-butanol concentration

The glassy carbon electrode modified with a film of NiOOH/Ni(OH)₂ is used for the anodic oxidation of the three alcohols to their respective alkylate, in 0.1M NaOH. Figures (5-7) represent the voltammograms recorded during the oxidation of ethanol, 2-propanol and 1-butanol, respectively.

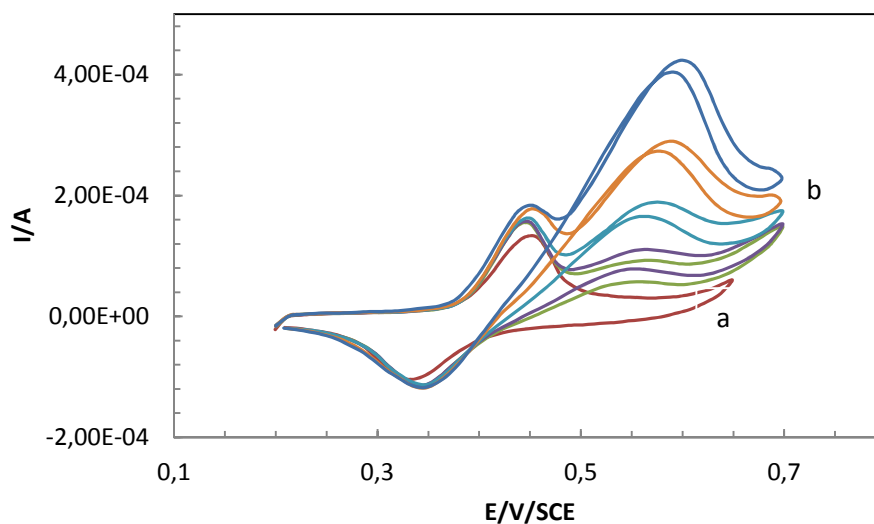


Fig.5. Voltamperograms recorded during ethanol oxidation in 0.1 mol. L⁻¹ NaOH; at scan rate equal to 0.1 V s⁻¹; 25 °C.

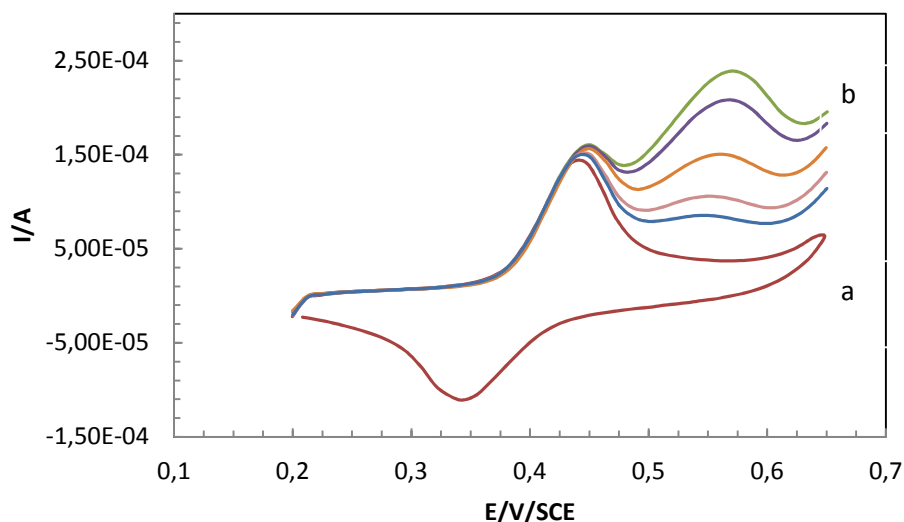


Fig.6. Voltamperograms recorded during 2-propanol oxidation in 0.1 mol.L⁻¹ NaOH; at scan rate equal to 0.1 V s⁻¹; 25 °C.

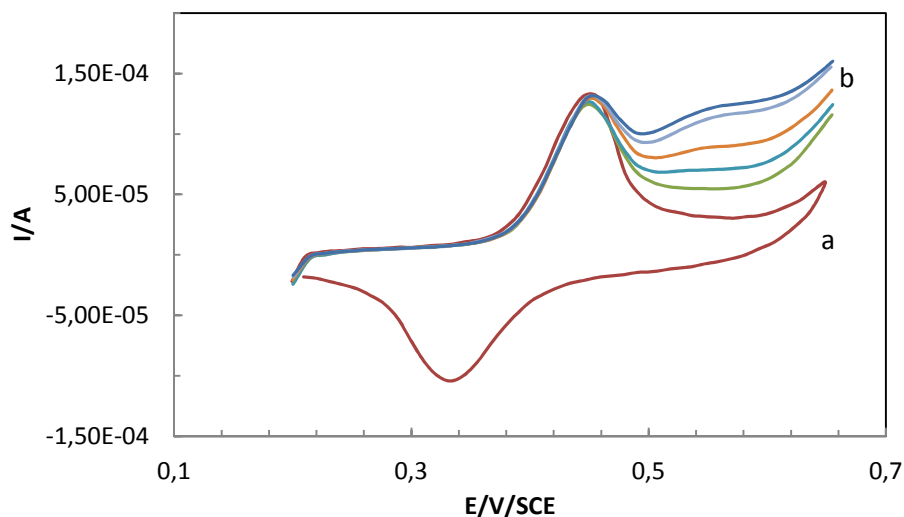
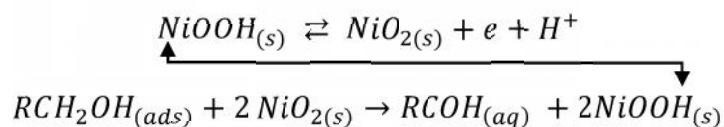
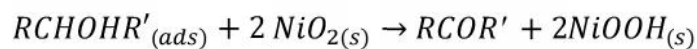


Fig.7. Voltamperograms recorded during 1-butanol oxidation in 0.1 mol.L⁻¹ NaOH; at scan rate equal to 0.1 V s⁻¹; 25 °C.

In the absence of alcohols, figures (5a, 6a, 7a) show two anodic and cathodic peaks, E_1 and E_2 , located at 350 mV and 450 mV, respectively. They correspond to the electrochemical process of $\text{NiOOH} / \text{Ni}(\text{OH})_2$. In the presence of alcohols, figures (5b, 6b, 7b) show a second anodic peak E_3 located at 600 mV; E_3 lies in the stability domain of NiO_2 . This observation leads us to propose the following mechanism where NiO_2 is the mediator which catalyses the alcohol oxidation.



or



4.1.2 Calibration curve of alcohols

Figure 8 includes the calibration straight lines of the three alcohols, on the glassy carbon electrode modified with NiOOH/ Ni(OH)₂, in 0.1 mol L⁻¹ NaOH.

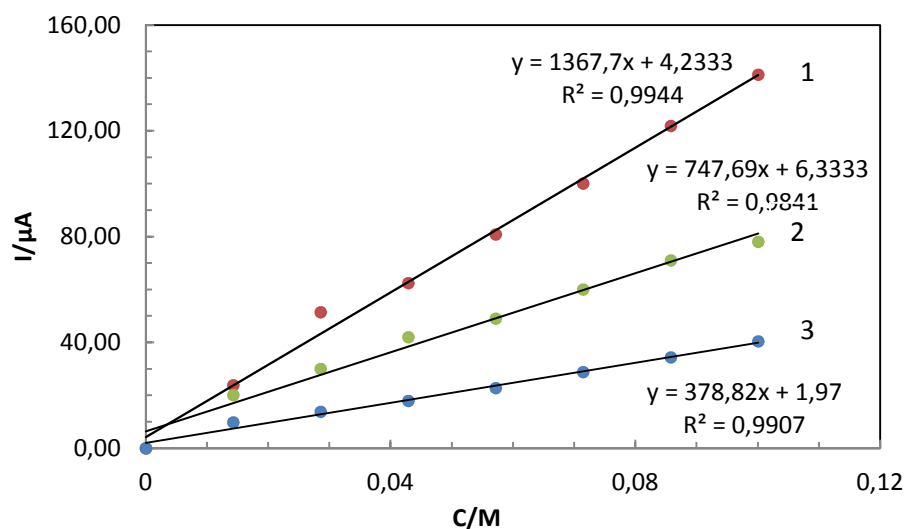


Fig.8. Calibration curves of: (1) ethanol, (2) 2-propanol, (3) 1-butanol, on GC modified with NiOOH/ Ni(OH)₂, in 0.1 mol L⁻¹ NaOH; 25°C; 0.1Vs⁻¹.

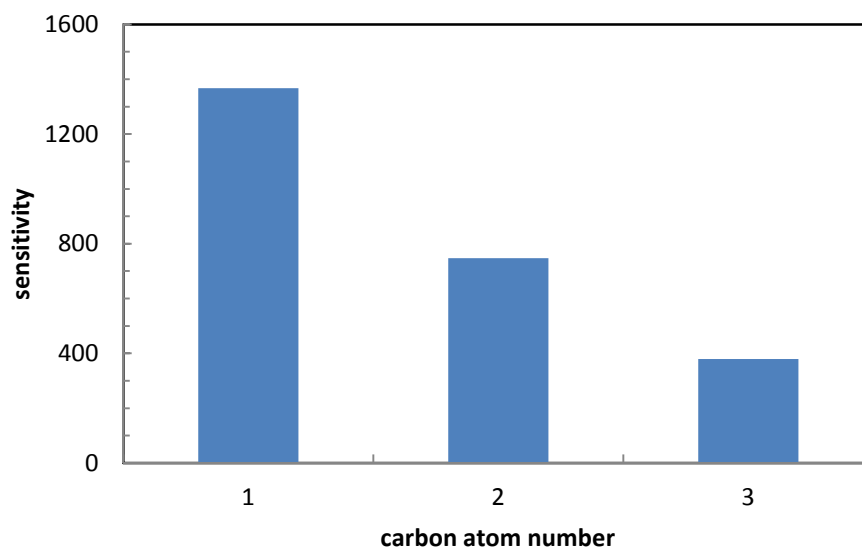


Fig.9. Sensitivity of alcohol determination vs carbon atom number of alcohols

7. CONCLUSION

In conclusion, a non-enzymatic alcohol sensor was manufactured successfully using NiOOH/Ni(OH)₂ as sensing materials. The electrochemical detection of alcohols is achieved through the formation of the mediator NiO₂. The sensitivity of alcohol determination depends upon the length of the carbon chain.

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