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Electrocatalysis of Ethanol and Methanol Electrooxidation by Composite Electrodes with NiOOH/FeOOH Supported on Reduced Graphene Oxide onto Composite Electrodes †

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Abstract: This paper presents graphite/paraffin composite electrodes modified with microparticles of nickel (Ni) and Ni-Fe alloy anchored in reduced graphene oxide (rGO); these electrodes were made by electrosynthesis. Firstly, the electrodeposition of reduced graphene oxide was made by cyclic voltammetry (CV) onto the graphite/paraffin electrodes' surface. After electrodeposition of the rGO, iron and nickel were electrodeposited by CV with successive scans. Finally, the formation of iron-nickel oxyhydroxide on the electrode surface was performed by cyclic voltammetry in alkaline medium. The composites were investigated by field emission gun scanning electron microscopy (FEG-SEM); it was observed that the Ni microparticles had spherical shapes, while the Ni-Fe alloy did not present a defined shape. The composite electrodes were used to analysis ethanol and methanol electrooxidation in an alkaline medium of 0.10 mol L^{-1} of NaOH in a potential range of from −0.20 to 1.0 V (vs. Ag/AgCl) at 50 mV s^{-1} by CV. The electrodes were able to make the electrooxidation of ethanol at a potential of around 0.57 V for the electrode constituted by the Ni-Fe alloy and around 0.61 V for the electrode modified with Ni, and for methanol in a potential around 0.57 V for the Ni-Fe alloy and around 0.66 V for the Ni electrode. The Ni-Fe alloy electrodes showed the electrocatalysis of the alcohols in relation to Ni electrodes.

Keywords: electrocatalysis; ethanol; methanol; graphene oxide; oxyhydroxide; composite

1. Introduction

Composite materials are have shown great attractions in manifold areas of knowledge [1]. The composites are formed by the joining of two or more materials and a new material is formed with specific properties due to the synergistic effect of the precursor materials characteristics [2]. Carbon-based composite materials have demonstrated great advances in science, which can be used together with graphene oxide (GO) and metal particle catalysts for application in sensors [3], supercapacitors [4], electrocatalysts for fuel cells [5] and reducing oxygen [6], among other applications.

Oliveira and collaborators [7] developed composite electrodes of nanoparticles of nickel oxyhydroxide deposited on reduced graphene oxide nanosheets on graphite/epoxy surfaces for the oxidation and determination of alcoholic compounds. The authors reported that the electrodes

modified with graphene and nickel showed low limits of detection (LOD) for alcohols; in addition, they also performed Principal Component Analysis (PCA) to analyze the relationship of the compounds and the electrodes in the same solution.

Nacef and colleagues [8] developed graphite electrodes with nickel particles for the catalytic oxidation of alcohols. Nickel was electrodeposited by cyclic voltammetry (CV) on the surface of a commercial graphite B grade Rotring®, the electrodes were characterized by CV, SEM and EDX. The electrodes were applied in the oxidation of methanol, ethanol and glycerol in alkaline NaOH solution at an ambient temperature of 25 °C.

Eshghi and collaborators [9] developed electrocatalysts based on palladium alloy nanoparticles supported on MnO_2/Vulcan XC-72R for ethanol oxidation in a direct alkaline ethanol fuel cell (DEAFC). The catalysts were characterized by XRD, SEM, EDX and elemental mapping techniques, presenting excellent distributions on the study surface. Electrochemical studies were performed by CV, chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The developed electrocatalysts have high current density, good durability and high stability.

According to the literature, it can be observed that the use of carbon-based composites constituted of particles of metallic oxides and carbon nanomaterials, such as graphene, present good results as electrocatalysts [10]. Therefore, in this work, a composite material based on metallic oxyhydroxide and reduced graphene oxide supported in graphite/paraffin was carried out by electrosynthesis, using the CV technique. These composite materials were electrosynthesized, glimpsing a potential application in energy devices, such as fuel cells.

2. Materials and Methods

2.1. Preparation of Composite Electrodes

As described in the literature [11,12], the electrodes (EC) were prepared by inserting the graphite and paraffin composite into a plastic syringe and connected to a copper wire. After being made, the electrodes were polished with sandpapers 1200 and 4000 until there was a clear and homogeneous surface. At the end of the process, the electrodes were cleaned with deionized water.

The electrodeposition of Ni and Fe oxyhydroxide (NiOOH and FeOOH) on reduced graphene oxide (rGO) nanosheets was performed similar to the literature: [12–14]. The electrodeposition of graphene oxide was made by CV with 10 successive potential cycles in the potential range from −1.50 to 0.50 V (vs. Ag/AgCl) at 10 mV s^{-1} in dispersion 1 mg mL^{-1} of GO in phosphate buffer solution (pH 9.00) with magnetic stirring.

After electrodeposition of the rGO, deposition of iron and nickel was performed as described elsewhere [12]. Fe and Ni were electrodeposited by CV during 25 successive scans of potential from −0.70 to −1.20 V (vs. Ag/AgCl) at 50 mV s^{-1} in a solution of 1.0 mol L^{-1} of $FeSO_4$ and 5.0 mmol L^{-1} of $NiCl_2$. The formation of iron–nickel oxyhydroxide on the electrode surface was performed by cyclic voltammetry for 50 successive cycles of potential from −0.20 to 1.0 V (vs. Ag/AgCl) at 100 mV s^{-1} in 0.10 mol L^{-1} of sodium hydroxide (NaOH) for surface passivation [15,16].

2.2. Apparatus

The surface morphological characterizations of the composite surfaces were performed using a Jeol scanning electron microscope, model JSM 7500 F. The three-electrode electrochemical cell was used. The electrode of Ag/AgCl (KCl at 3 mol L^{-1}) was used as a reference electrode, a platinum wire was used as an auxiliary electrode and the composite electrodes were used as work-modified electrodes. All electrochemical measurements were carried out at room temperature (25 °C) with an AUTOLAB PGSTAT204 potentiostat (Metrohm, Herisau, Switzerland).

3. Results

3.1. Morphological Characterization

The surface morphology of the composite electrodes was studied by SEM. Figure 1A shows the composite electrode surface modified with NiOOH and the SEM image showed a distribution of clusters over the electrode surface. Figure 1B shows the composite electrode surface modified with FeOOH and the SEM image showed the distribution of microcubes. Figure 1C shows the composite electrode surface modified with NiOOH and FeOOH, and the SEM image showed undefined scattere shapes. It can be observed that the nickel had a good distribution on the electrode surface and also formed particle clusters; however, the iron presented smaller amounts of microcube particles. The mixture of the two did not present defined shapes, only undefined features. The same situation was reported by Oliveira and collaborators [12,13], but the presence of NiOOH and FeOOH was confirmed by EDX and the mapping of elements on the surface of the electrodes.

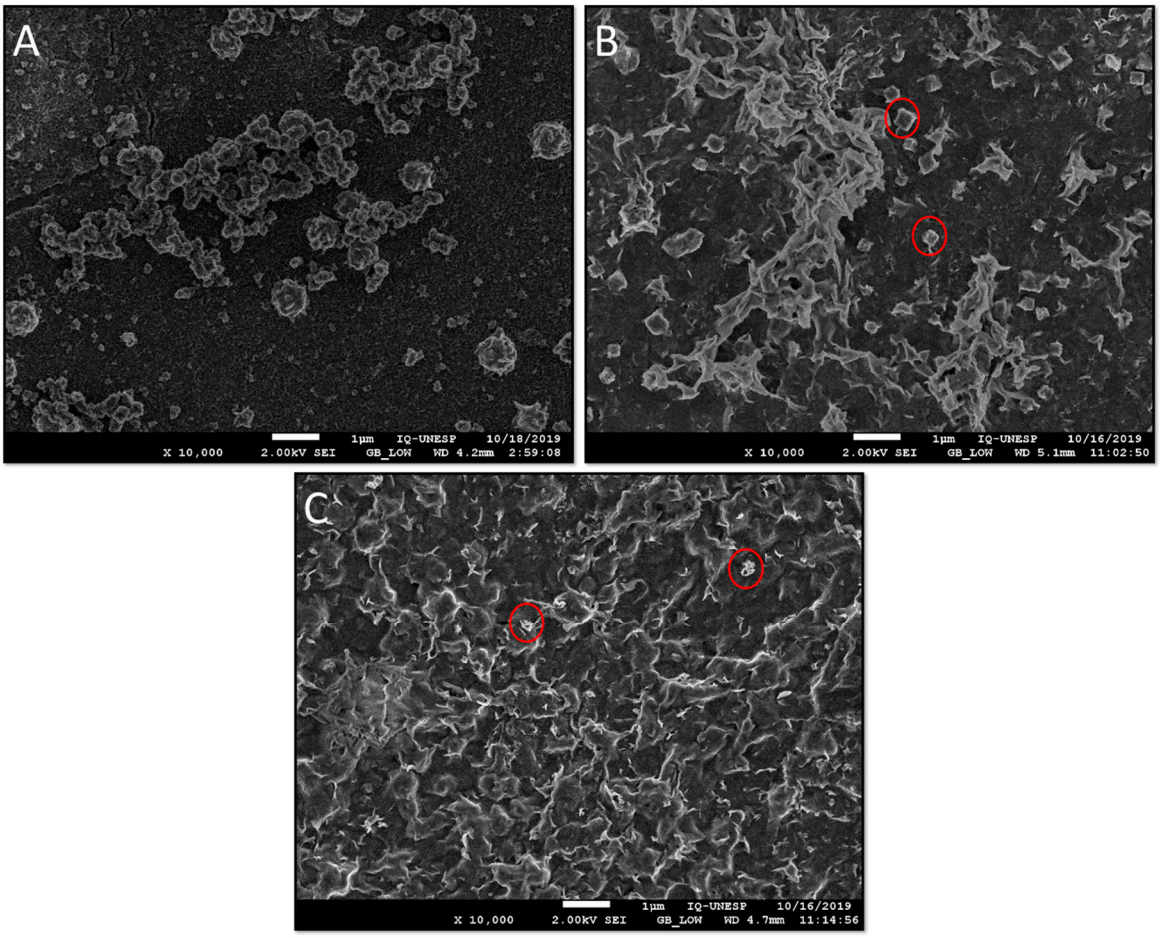

Figure 1. SEM image of the surfaces of the composite electrodes: (**A**) EC/rGO/NiOOH; (**B**) EC/rGO/FeOOH; (**C**) EC/rGO/NiOOH-FeOOH.

3.2. Electrooxidation of Ethanol and Methanol in Alkaline Medium

After the development of the electrodes, they were applied in the electrooxidation of ethanol and methanol. Figure 2A shows the cyclic voltammograms of the EC/rGO/NiOOH electrode in the absence and presence of 10 mmol L^{-1} of methanol and ethanol; the electrode showed an oxidation peak at the potential of 0.61 V for ethanol and 0.66 V for methanol. The electrooxidation process of ethanol and methanol occurs due to the presence of the Ni(III)/Ni(II) redox couple, present in the modified composite electrode [16,17]. Figure 2B shows the cyclic voltammograms of the EC/rGO/NiOOH-FeOOH electrode in the absence and presence of 10 mmol L^{-1} of methanol and

ethanol; the electrode showed an oxidation peak at the potential of 0.57 V for both alcohols, and the electrochemical behavior was similar to the composite electrode modified with NiOOH. With the addition of FeOOH, the electrodes showed a similar electrocatalytic process of ethanol and methanol in relation to the EC/rGO/NiOOH, however, a shift was observed in the oxidation potential of ethanol and methanol to a more negative potential, in this case from ~0.66 to ~0.57 V. Oliveira and collaborators [12] showed that the electrodes modified with only FeOOH in alkaline medium do not show a electrocatalytic current at the studied potential in the presence of alcohols. However, Qiu and collaborators [18] observed that electrodes modified with only FeOOH have a redox potential between −0.60 and −1.20 V and that the addition of FeOOH can reduce the electrochemical oxidation of $Ni(OH)_2$ in NiOOH due to the decrease in the amount of active Ni site on the surface, thus the decrease in the amount of electrons transferred by the Ni atom can also be altered. Although the addition of FeOOH did not improve the anodic peak, the NiOOH/FeOOH electrode showed a catalytic current of the studied compounds with a considerable increase in current, such as observed in Figure 2B. The images of ethanol oxidation can be seen in the work of Oliveira and collaborators [12]. In Table 1, it is possible to observe the values of the oxidation potentials obtained for ethanol and methanol.

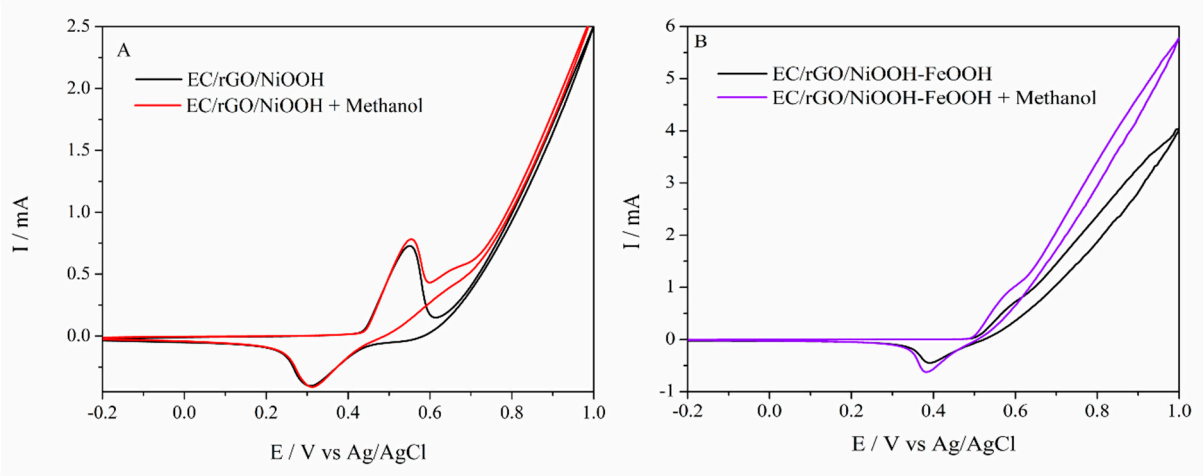

Figure 2. CVs obtained for 10 mmol L^{-1} methanol oxidation by (**A**) EC/rGO/NiOOH; (**B**) EC/rGO/NiOOH-FeOOH.

Table 1. Potential values obtained in the electrooxidation of alcohol by composite electrodes.

Electrode	Potential (V)
Ethanol	
EC/rGO/NiOOH	0.61
EC/rGO/NiOOH-FeOOH	0.57
Methanol	
EC/rGO/NiOOH	0.66
EC/rGO/NiOOH-FeOOH	0.57

4. Conclusions

In this paper, composite electrodes of graphite and paraffin sensors modified with nickel and iron oxyhydroxide and reduced graphene oxide were developed using a simple and fast method by cyclic voltammetry electrodeposition. The electrodes' surfaces were characterized by FEG-SEM, and microparticles in different shapes were obtained. The electrodes were applied to the electrooxidation of ethanol and methanol in alkaline sodium hydroxide medium. The composite rGO/NiOOH and rGO/NiOOH-FeOOH electrodes developed showed good results in relation to the electrooxidation of alcohols, with a considerable increase in the anodic peak. The combination of nickel and iron promoted an electrocatalytic synergy in the electrooxidation of ethanol and methanol, improving the

results obtained and showing good alternatives for the electrooxidation of alcoholic compounds in alkaline medium.

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Conflicts of Interest: The authors declare no conflict of interest.

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