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NiOOH/FeOOH Supported on Reduced Graphene Oxide Composite Electrodes for Ethanol Electrooxidation

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Abstract: In this work nickel (Ni) and Ni-Fe bimetallic microparticles were electrosynthesized at reduction potentials in the range from -0.70 V to -1.20 V (50 mV s^{-1}) by cyclic voltammetry (CV) onto graphite/paraffin electrode surface modified with nanosheets of reduced graphene oxide (RGO). Previously, the RGO was electrodeposited by CV from a suspension of 1 mg mL^{-1} of graphene oxide in PBS solution with pH 9.18, in the potential range from -1.50 V to 0.50 V (10 mV s^{-1}). After electrodeposition of metals, the oxyhydroxides were formed by CV in an alkaline medium of 0.10 mol L^{-1} of NaOH in the potential range from -0.20 V to 1.0 V (100 mV s^{-1}) with successive scans until stabilization of currents. In order to characterize the developed electrodes composites, the surfaces were investigated by SEM and EDX. Electrochemical performance of the developed electrodes composites, ethanol electrooxidation was carried out in an alkaline medium of 0.10 mol L^{-1} of NaOH in the potential range from -0.20 V to 1.0 V (100 mV s^{-1}) by CV. The electrodes were able to induce the electrooxidation of ethanol at a potential of 0.55 V for the electrode made of NiOOH/FeOOH and around of 0.60 V for the electrode modified with NiOOH.

Keywords: Composite; RGO; Oxyhydroxide; Ethanol; Electrooxidation

1. Introduction

The composite materials have become very attractive in several areas of knowledge due to the different benefits that the synergies between the manufactured materials have brought to society [1]. This type of material consists of joining several materials to form another material with better properties [2]. Carbon-based composite materials have shown great advances in science, and can be used in several sets with graphene oxide (GO) catalysts and metal nanoparticles for application in sensors [3], fuel cell [4], supercapacitors [5], and other applications.

Oliveira and collaborators [6] developed composite sensors made of nanoparticles of nickel oxyhydroxide anchored in graphene nanosheets supported onto graphite/epoxy for oxidation and determination of glycerol, ethanol and methanol. The authors report that the nickel nanocomposite showed low detection limits (LOD) for alcohols.

Eshghi and colleagues [7] developed electrocatalysts based on PdNiFe nanoparticles supported onto MnO2/Vulcan XC-72R for anodic ethanol oxidation in direct alkaline ethanol cell (DEAFC). The authors concluded that the manufactured electrocatalysts have significantly high current density, excellent catalyst durability and cyclic stability for ethanol oxidation.

Therefore, it is possible to observe that graphene oxide combined with metals oxyhydroxide on the carbon surface is an interesting alternative, such as electrocatalysts [8]. In this work sought to obtain the electrosynthesis of a composite material, using the simple methodology, based on metal oxyhydroxide and reduced graphene oxide in the graphite/paraffin support by the cyclic voltammetry technique, aiming at the potential of this composite in devices such as fuel cells.

2. Materials and Methods

2.1. Preparation of Composite Graphite/Epoxy Electrodes

The electrodes were made using a syring and a copper wire was connect. After the electrodes (EGP) were confection, a composite graphite-paraffin mixture was prepared [9]. The mixture of graphite and paraffin was carried out with constant heating of 80 ℃, the resulting slurry homogenized was inserted into syringe and cured at room temperature for 1 day. After, the electrodes were polished in sandpaper with deionized water of granulometry 300, 600, 800, 1200 and 4000, respectively, until you get a clear and homogeneous surface.

2.2. Electrosynthesis of Iron-Nickel Oxyhydroxide Microparticles on Reduced Graphene Oxide

The electrodeposition of the Ni and Fe oxyhydroxide onto graphene oxide (GO) nanosheets was done in 3 stages, similar to literature [6, 10]. A 1.0 mg mL^{-1} solution of GO was prepared in 0.07 mol L^{-1} of PBS. Thereby, the electrodeposition of the graphene oxide occurred by cyclic voltammetry (CV) for 10 sucessive potential cycles in the potential range from -1.50 V to 0.50 V (vs Ag/AgCl) at 10 mV s^{-1} in GO dispersion with magnetic stirring.

After electrodeposition of RGO, the deposition of iron and nickel was carried out as described elsewhere [5]. The metals were electrodeposited by CV for 25 sucessives potential sweeps between -0.70 V and -1.20 V (50 mV s^{-1}) in a solution of 1.0 mol L^{-1} $FeSO_4$ and 5.0 mmol L^{-1} of $NiCl_2$. The formation of iron-nickel oxyhydroxide nanoparticles on the electrode surface was performed by cyclic voltammetry during 50 sucessives potential cycles from -0.20 V at 1.0 V (vs Ag/AgCl) at 100 mV s^{-1} in alkali solution of 0.10 mol L^{-1} of sodium hydroxide (NaOH) for surface passivation [11, 12].

2.3. Characterization by Scanning Electron Microscopy

The spectroscopic characterizations of the modified composites electrodes were carried out in a graphite/paraffin electrode (EGP). Scanning electron microscopy (SEM) performed the morphological characterization of the composite surface using a Jeol scanning electron microscope, model JSM 7500F with X-ray spectroscopy module (EDX).

2.4. Measuring Procedure

The measurement cell was formed by the 1 work electrode plus a reference Ag/AgCl (KCl, 3 mol L^{-1}) and platinum wire auxiliary electrode. Cyclic voltammetry measurements were taken using a AUTOLAB PGSTAT204 potentiostat (Metrohm, Netherlands), using the NOVA 2.1 software. For carrying out the experiments, the potential range was -0.20 V and 1.0 V (vs Ag/AgCl) using a scan rate of 50 mV s^{-1}. All electroanalytical experiments were carried out at room temperature (25 ° C).

3. Results

3.1. Caracterization of Composite Surface of EG/RGO/NiOOH-FeOOH

The successful electrosynthesis of nickel-iron oxyhydroxide microparticles on RGO was confirmed by SEM and EDX. Figure 1-A shows the electrode surface only with RGO/FeOOH, the microscopy showed a distribution of cuboids over the electrode surface. Figure 1-C shows the electrode surface only with RGO/NiOOH, the microscopy showed an excellent homogeneous distribution of microspheres. The EDX spectroscopies confirmed the presence of Ni and Fe on the surfaces, the spectra also showed the presence of C, O and K.

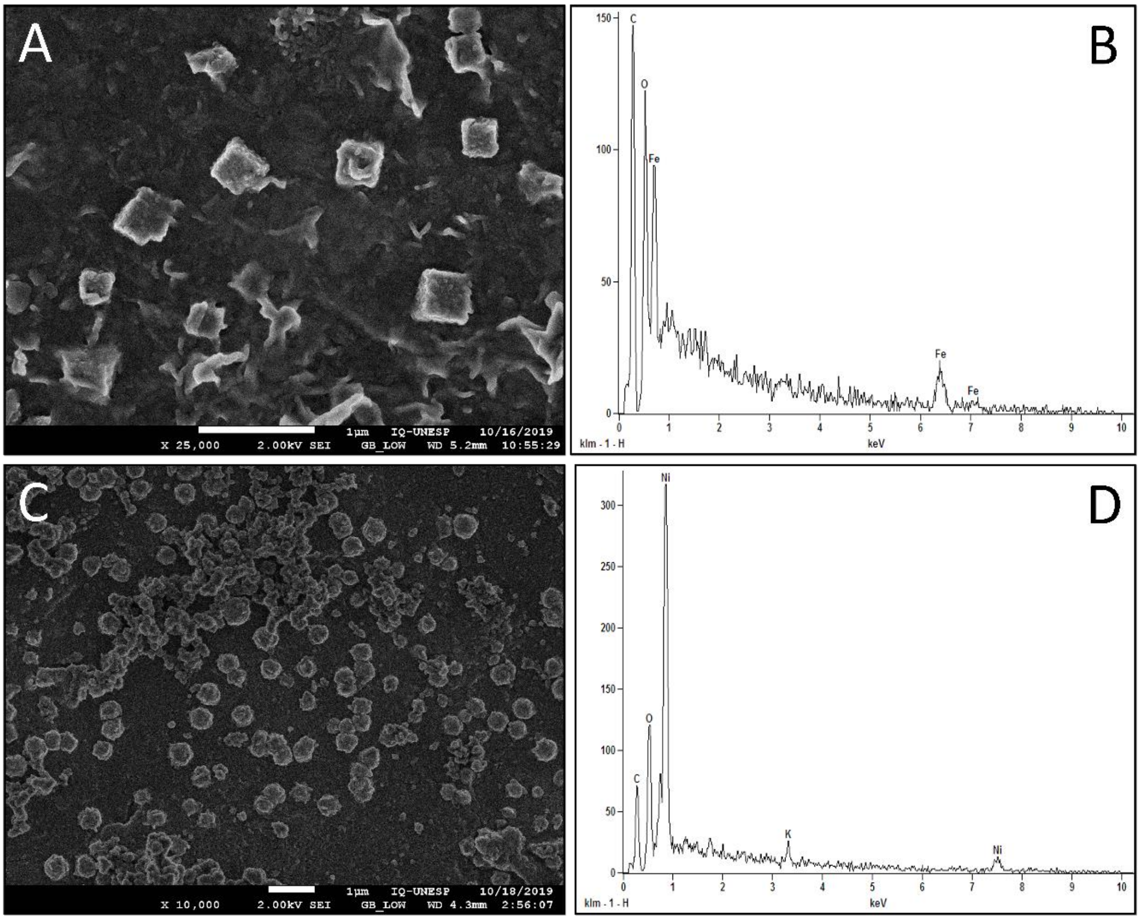

Figure 1. (**A**) SEM image for the EGP/RGO/FeOOH surface; (**B**) EDS spectrum for the EGP/RGO/FeOOH surface; (**C**) SEM image for the EGP/RGO/NiOOH surface; (**D**) EDS spectrum for the EGP/RGO/NiOOH surface.

The Figure 2-A shows the surface of the EGP/RGO/NiOOH-FeOOH electrode, the surface had different characteristics than expected, as iron had formed cuboids and nickel had formed spheres, it was expected microparticles with shapes similar to those previously formed , however, microscopies showed several elevations with connected "wires". In Figure 2-B it is possible to observe the EDX spectrum of the EGP/RGO/NiOOH-FeOOH electrode, the EDX showed that the surface is composed of Ni, Fe, O, C and K, analysis showed a high amount of nickel and reasonable amounts of iron on the electrode surface, showing that the electrodeposition of the bimetallic microparticles was successful. Figure 2-C and Figure 2-D shows the mapping of the microparticles on the electrode surface, it is possible to observe that the nickel had a good distribution on the electrode surface and also formed particle clusters, however the iron presented smaller amounts of particles.

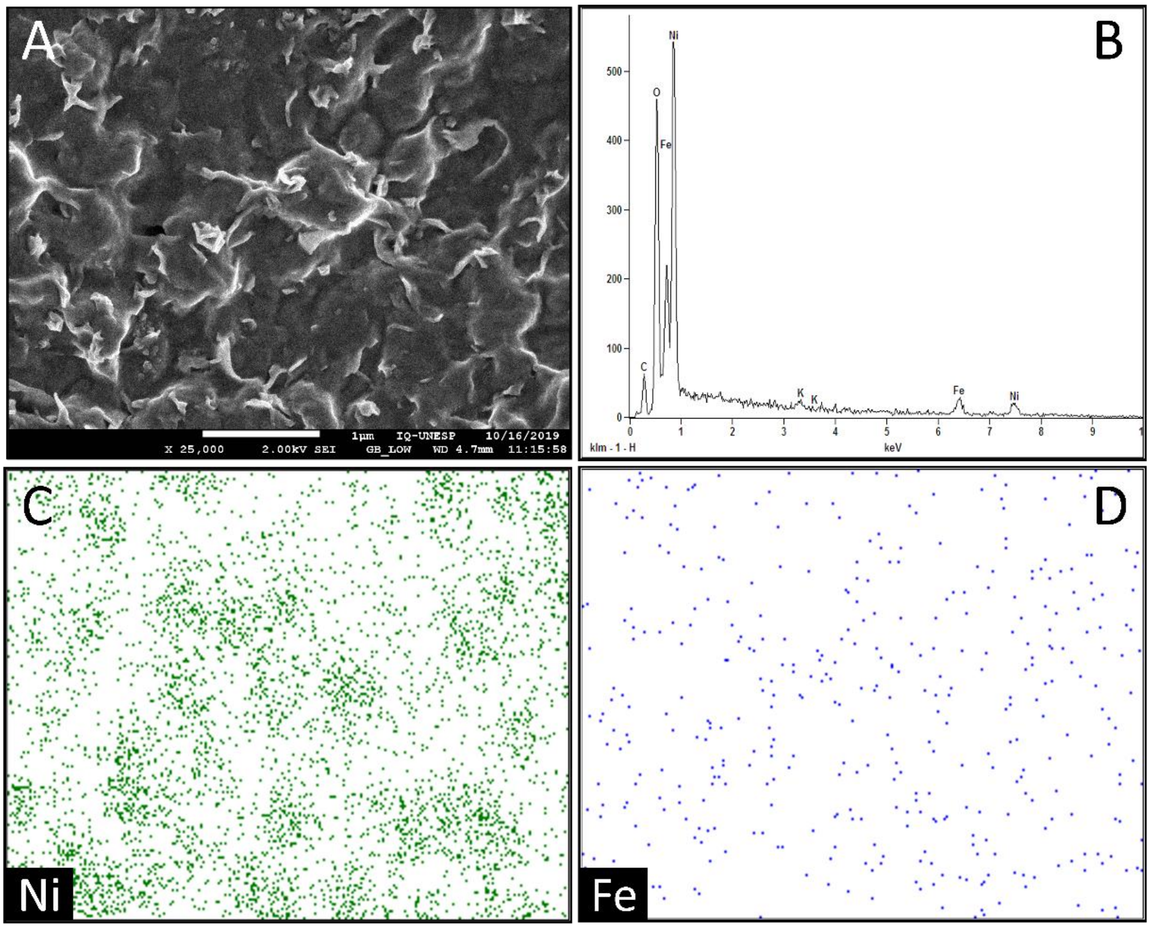

Figure 2. (**A**) SEM image for the EGP/RGO/NiOOH-FeOOH surface; (**B**) EDS spectrum for the EGP/RGO/NiOOH-FeOOH surface; (**C**) Mapping the Ni distribution on the surface; (**D**) Mapping the Fe distribution on the surface.

3.2. Electrochemical Application of Modified Electrode in Alcohol Oxidation

Figure 3-A shows the EGP/RGO/NiOOH electrode in the absence and presence of 10 mmol L^{-1} of ethanol, in voltammetry cyclic (VC) the electrode showed an oxidation peak close to the potential of 0.60 V. The results that can be Ni (III) / Ni (II) redox can catalyze an ethanol electrooxidation [12-14]. As you can see in Figure 3-B the EGP/RGO/FeOOH electrode did not show an oxidation peak for ethanol. Figure 3-C shows the EGP/RGO/NiOOH-FeOOH electrode in the absence and presence of 10 mmol L^{-1} of ethanol, in VC the electrode showed an oxidation peak close to the 0.50 V potential, a behavior similar to nickel and different from iron. With the addition of iron, the electrode showed smaller anodic and cathodic peaks, however it presented a electrocatalytic of ethanol process compared to the other electrodes, shifting the oxidation potential of ethanol to a more negative potential, in this case from 0.60 V to 0.55 V. Qiu and collaborators [15] showed that Fe in alkaline solutions does not have current density at the studied potential, but that it has redox potential and is between -0.60 V and -1.20 V and that the addition of Fe can reduce the electrochemical oxidation from Ni (OH) 2 to 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 Fe did not improve the anodic peak, the Ni electrode starts ethanol oxidation at 600 mV with an anode current of 180 μA, and the Ni-Fe electrode starts at 550 mV with an anode current 480 μA, confirming the electrocatalysis of the compound and a much larger amount of current.

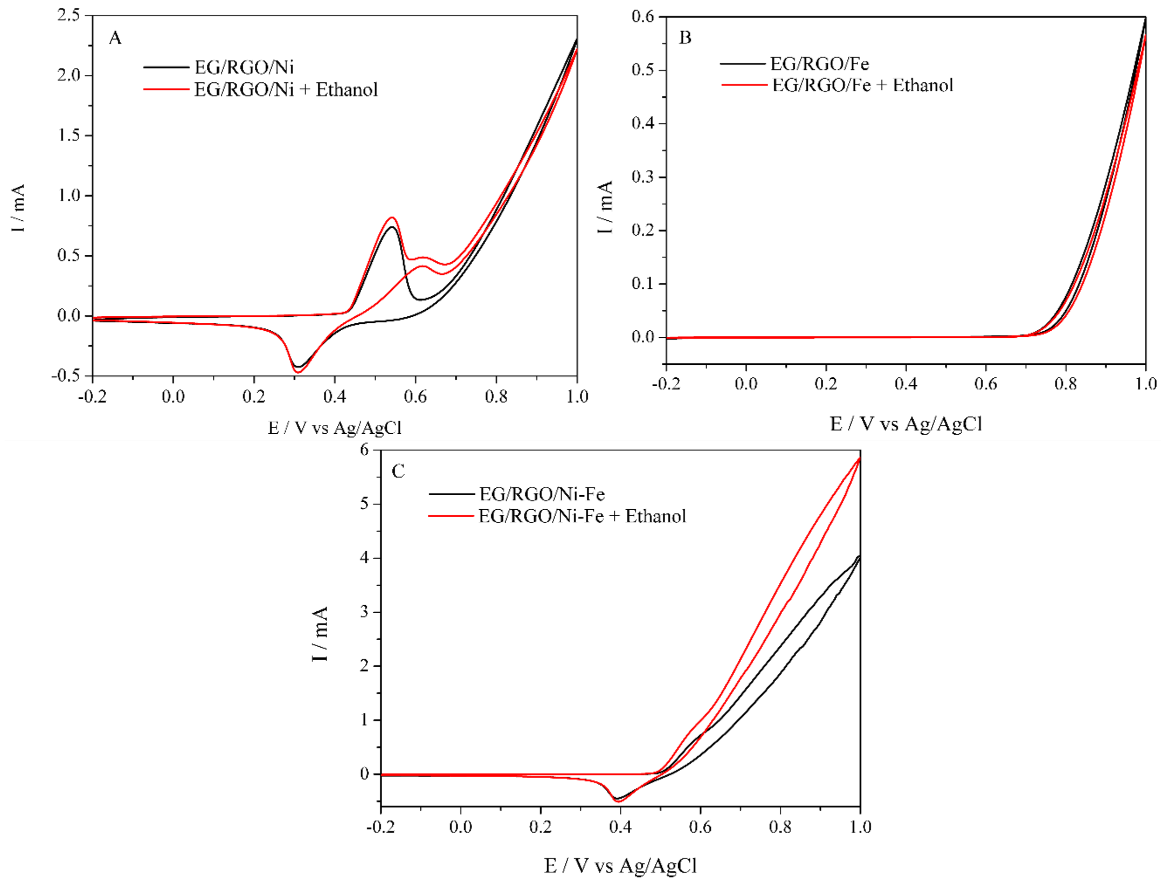

Figure 3. Cyclic voltammograms obtained for 10 mmol L^{-1} ethanol oxidation by (**A**) EGP/RGO/NiOOH; (**B**) EGP/RGO/FeOOH; (**C**) EGP/RGO/NiOOH-FeOOH.

4. Conclusions

In summary, the composites were prepared in 3 steps by electrodeposition method. The characterization SEM showed that the microparticles of NiOOH, FeOOH and the mixture of the two materials. EDX confirmed the success of the electrosynthesis of the composites in the reduced graphene oxide nano sheets. The composites EG/RGO/NiOOH and EG/RGO/NiOOH-FeOOH exhibited electrochemical behavior in the oxidation of ethanol with the increase of the anodic peak, however the composite EG/RGO/FeOOH did not show a response to alcohol. Although the FeOOH composite did not respond, in synergy with the NiOOH composite there was an electrocatalysis, displacing the oxidation potential.

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

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