

# Electrosynthesis of Composites Consisting of FeOOH and Reduced Graphene Oxide in Graphite Electrodes

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## Abstract:

Carbon-based composite nanomaterials, such as graphene oxide, have demonstrated a great potential for applications in several areas. The present work sought to obtain, via electrosynthesis, a composite material based on graphene oxide and iron oxyhydroxide deposited onto graphite pencil surface. The electrodes modifications by electrosynthesis was performed using the cyclic voltammetry technique. The graphene oxide and the electrosynthesized FeOOH cuboids were characterized by SEM-FEG, EDX. The cyclic voltammetry was used to characterize the electrochemical behavior of the graphite pencil electrode (PEG). The composites electrodes of PEG modified with GO/FeOOH (PEG/GO/FeOOH) were formed in two stages. In the first stage, there was the formation of FeHCF in PEG/GO, and subsequently, there was the formation of PEG/GO/FeOOH in alkaline medium.

**Keywords:** graphene; electrosynthesis; iron oxyhydroxide; ethanol

## 1. Introduction

Composite nanomaterials have generated great interest in several areas of knowledge [1]. This type of material consists of joining several materials in order to form another material with better properties [2]. Carbon-based composite nanomaterials have demonstrated great advances in science, which can be used together with graphene oxide (GO) and metal particle catalysts for application in supercapacitors [3], electrocatalysts for fuel cells [4], reduction oxygen [5], water purification [6] and among other applications.

According to Zhu and coauthors [7] graphene oxide can be considered an excellent material, due to its mechanical and electrical properties. Moreover, its high tolerance to chemical changes is beneficial, because it provides controlled chemical environments for active metal species, due to its functional groups (COOH, OH and O

which are reactive species that provide help in the heterogeneous nucleation of metallic nanoparticles [5, 8].

Hao Sun and collaborators [9] used FeOOH nanorods to support hollow platinum nanostructures. It was reported that FeOOH nanorods provided remarkable catalytic activity and better stability for the methanol oxidation reaction, due to their structural properties such as their high contact surface to 3D reagent and a more homogeneous distribution of the nanostructures on the surface.

Thus, it is possible to observe that graphene oxide combined with iron oxyhydroxide on a carbon surface is an interesting alternative for obtaining nanomaterials, such as electrocatalysts [9]. Thus, the present work sought to obtain, via electrosynthesis, a composite material, through a simple methodology, based on electrodeposition of graphene oxide and iron oxyhydroxide onto graphite pencil electrode surface by cyclic

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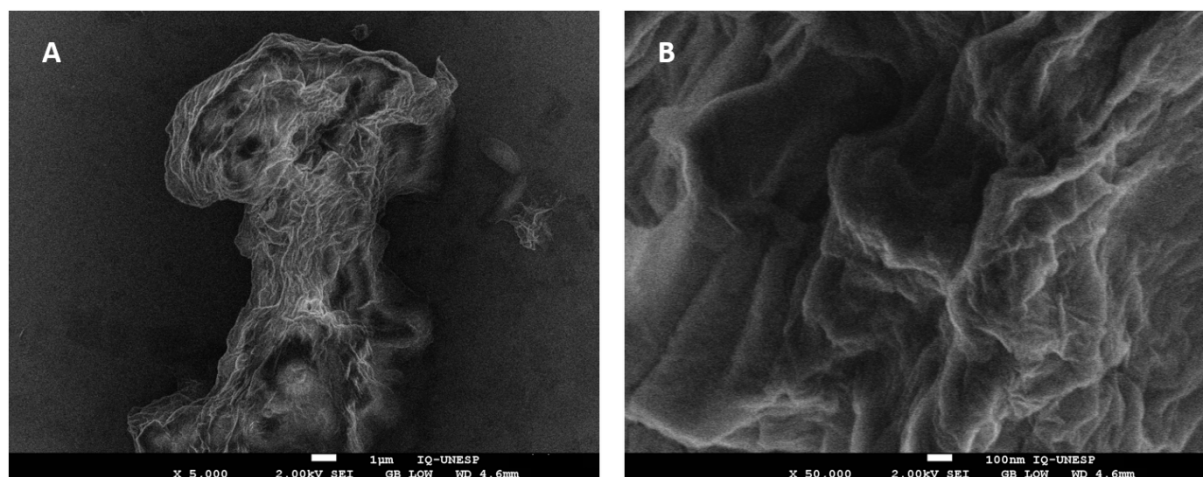
voltammetry technique, aiming at the potential of this composite in devices, such as supercapacitors and electrocatalysts in fuel cells.

## 2. Results and Discussion

### Characterization of graphene oxide by SEM

The microscopy characterization was

performed using the SEM-FEG. It was possible to study the characteristic morphology of the synthesized graphene. According to Figure 1 (A and B), the graphene oxide sheets dispersed on the graphite surface were observed, where according to literature [10, 17] the wrinkled nature of the sheets favors the changes on the surface due to the increase in surface area.

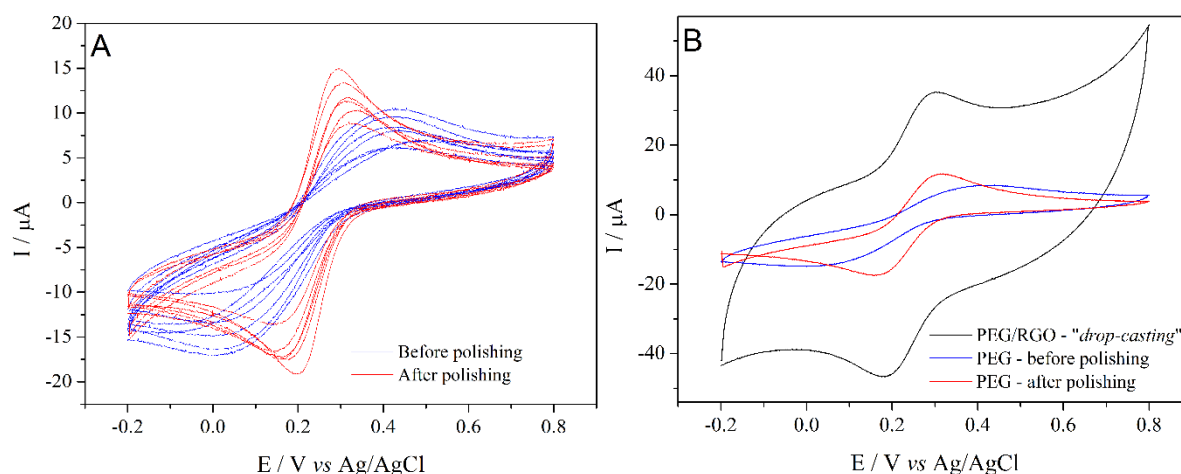


**Figure 1.** SEM-FEG images for the graphene oxide (GO) sheets dispersed on the graphite surface with magnifications: (A) 5000x and (B) 50000x.

### Graphite pencil electrode - voltammetric study

The cyclic voltammetry technique was used to characterize the electrochemical behavior of the graphite pencil electrode (PEG) and GO modified electrodes (Figure 2). The PEGs were polished in sandpaper with different grain sizes of 600, 800,

1200 and on bond paper, respectively. Figure 2-A shows the difference between voltammograms before and after polishing at different electrodes ( $n = 5$ ). Figure 2-B shows the difference between the three steps before (—) and after polishing (—) of PEG and the PEG/GO voltammogram (—).



**Figure 2.** **A** – Cyclic voltammograms of PEGs before (—) and after (—) polishing. **B** – Cyclic voltammograms before (—) and after (—) polishing and after deposition of graphene oxide (GO) (—) using the drop-casting technique on the PEG surface. All voltammograms were obtained in solution of  $5 \text{ mmol L}^{-1}$  of  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $1.0 \text{ mol L}^{-1}$  of  $\text{KCl}$  at a scan rate speed of  $50 \text{ mV s}^{-1}$ .

The electrochemical parameters of the PEG and PEG/GO electrodes are shown in Table 1 and were obtained according to the literature [11, 12]. As the voltammograms presented inclined baselines, and in goal to obtain more accurate

values, Eq. 1 was used to calculate the ratio of  $|I_{pa}/I_{pc}|$ .

$$\frac{|I_{pa}|}{|I_{pc}|} = \frac{(I_{pa})_0}{I_{pc}} + \frac{0,485(I_{\lambda})_0}{I_{pc}} + 0,086 \quad (\text{Eq. 1})$$

**Table 1.** Electrochemical parameters of the PEG and PEG/GO electrodes obtained from the voltammograms in Figure 2.

Parameters	PEG (unpolished)	PEG (polished)	PEG/GO
$E_{pa}$ (V)	$0.434 \pm 0.030$	$0.311 \pm 0.011$	$0.287 \pm 0.003$
$E_{pc}$ (V)	$-0.006 \pm 0.044$	$0.172 \pm 0.019$	$0.197 \pm 0.007$
$\Delta E_p$ (V)	$0.440 \pm 0.072$	$0.140 \pm 0.030$	$0.090 \pm 0.010$
$E'^{\circ}$ (V)	$0.214 \pm 0.012$	$0.242 \pm 0.004$	$0.242 \pm 0.003$
$I_{pa0}$ ( $\mu\text{A}$ )	$7.965 \pm 1.643$	$12.089 \pm 2.307$	$30.512 \pm 3.327$
$I_{pc}$ ( $\mu\text{A}$ )	$-13.820 \pm 2.460$	$-16.975 \pm 1.988$	$-42.912 \pm 4.428$
$I_{(\lambda)0}$ ( $\mu\text{A}$ )	$5.325 \pm 1.181$	$5.254 \pm 1.402$	$50.259 \pm 11.442$
$ I_{pa}/I_{pc} $	$0.676 \pm 0.053$	$0.771 \pm 0.089$	$1.188 \pm 0.085$

After analyzing the voltammograms in Figure 2 and the data in Table 1, it was observed that the electrodes before polishing showed values of  $\Delta E_p$  of  $0.440 \pm 0.072$  mV,  $E'^{\circ}$  of  $0.214 \pm 0.012$  V and  $I_{pa}/I_{pc}$  ratio of  $0.676 \pm 0.053$  below the expected for the  $\text{K}_3\text{Fe}(\text{CN})_6$  reversible  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  redox process, since for a reversible system a  $\Delta E_p$  value of 59 mV and an  $I_{pa}/I_{pc}$  ratio close to 1 are expected [11, 15]. After polishing, there was an improvement in the electrochemical parameters, as there was a reduction in the value of  $\Delta E_p$  to  $0.140 \pm 0.030$  mV and an increase in the value of the  $I_{pa}/I_{pc}$  ratio to  $0.771 \pm 0.089$ . The values of standard deviation from electrochemical parameters is attributed to the matrix effect, since it is composed of graphite pencil and all the graphite used were the same batch from the same brand. However, there is a difference in the batch and that probably influenced the results. The advantage of using graphite pencil as working electrodes is the gains in mechanical strength, easy surface recovery and the very low-cost for an electrochemical system.

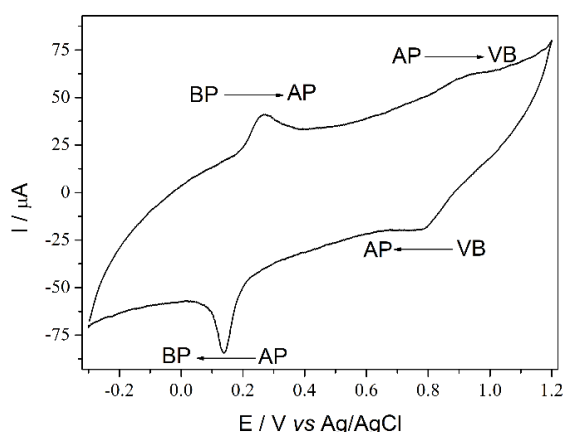
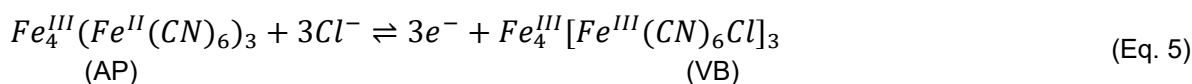
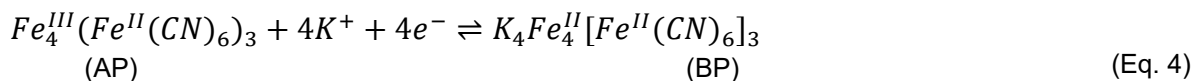
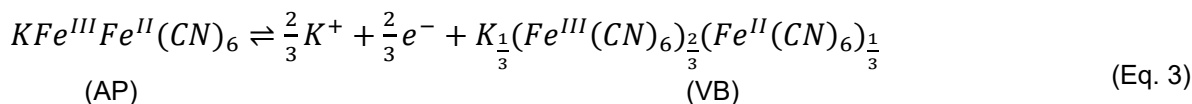
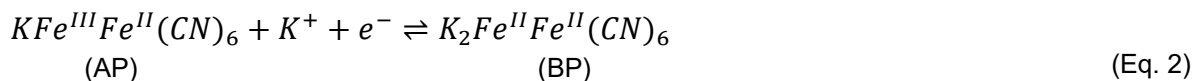
After the formation of the PEG and voltammetric study, the graphene synthesized was added by a drop-casting process onto electrode surface by adding 10  $\mu\text{L}$  of suspension of 0.5  $\text{mg mL}^{-1}$  of graphene oxide in phosphate buffer solution, after drying the electrodes were applied to cyclic voltammetry study in KCl and  $\text{K}_3\text{Fe}(\text{CN})_6$ . After modifying the surface with

graphene oxide and analyzing the results referring to Figure 2-B and data from Table 1, it was observed that the PEG/GO electrodes showed electrochemical parameters characteristic of a reversible system as expected, showing values of the relationship  $I_{pa}/I_{pc}$   $1.188 \pm 0.085$  and  $\Delta E_p$  value of  $0.090 \pm 0.010$  V and there was still an increase in anodic and cathodic peak current values ( $I_{pa}$  and  $I_{pc}$ ), so the values indicate that with the addition of GO there was an improvement in electrochemical properties compared with PEG electrodes before and after polishing.

### Electrosynthesis, characterization and study of the composite by cyclic voltammetry

For a better performance of the electrodes, the deposition of graphene was performed by drop-casting according to the literature [13], from a suspension of 0.5  $\text{mg mL}^{-1}$  of graphene oxide in phosphate buffer pH 9.18. After deposition of GO on the PEG surface (PEG/GO), the deposit of iron hexacyanoferrate ( $\text{FeHCF}$ ) was formed on the surface of the PEG/GO electrode by cyclic voltammetry [18] through 25 successive cyclic voltammograms from a solution containing 0.5  $\text{mol L}^{-1}$  of KCl, 2.5  $\text{mmol L}^{-1}$  of  $\text{Fe}(\text{NO}_3)_3$  and 2.5  $\text{mmol L}^{-1}$  of  $\text{K}_3\text{Fe}(\text{CN})_6$  with a potential range of -0.3 V to 1.2 V at a scan rate of 100  $\text{mV s}^{-1}$ . Figure 3 shows the PEG/GO modified with  $\text{FeHCF}$  in KCl solution.

The voltammogram in Figure 3 shows two redox pairs with formal potential around +0.20 and +0.84 V, respectively, attributed to the processes represented in Eq. 2-5 characteristic of the



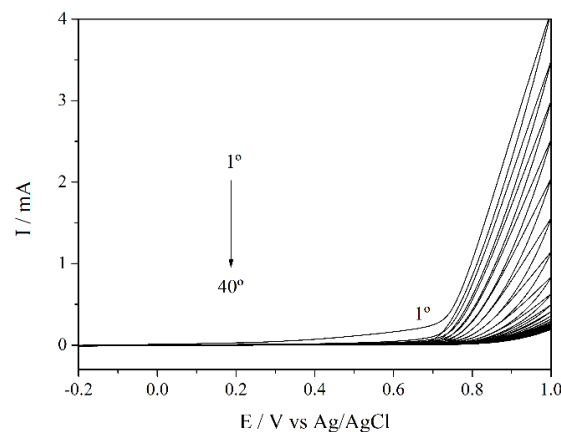
**Figure 3.** Cyclic voltammogram showing FeHCF formed in a solution containing 0.1 mol L<sup>-1</sup> KCl with a potential of -0.3 V to 1.2 V at a scan rate of 100 mV s<sup>-1</sup>.

The formation of FeOOH occurred after cycling PEG/GO/FeHCF during 40 successive scans in the range of -0.2 to 1.0 V ( $\nu = 100 \text{ mV s}^{-1}$ ) in 0.1 mol L<sup>-1</sup> NaOH solution. During this process, FeHCF is decomposed and there is the formation of the species of FeOOH on the surface of PEG/GO/FeHCF, this modified electrode being called PEG/GO/FeOOH. Figure 4 shows the formation of FeOOH using the cyclic voltammetry technique.

Figure 5-A shows the surface of the PEG/GO/FeOOH electrode with several cuboids scattered. In Figure 5-B it is possible to observe the EDX spectrum of the PEG/GO/FeOOH electrode, the EDX showed that the surface is composed of Fe, O and C, as expected due to the

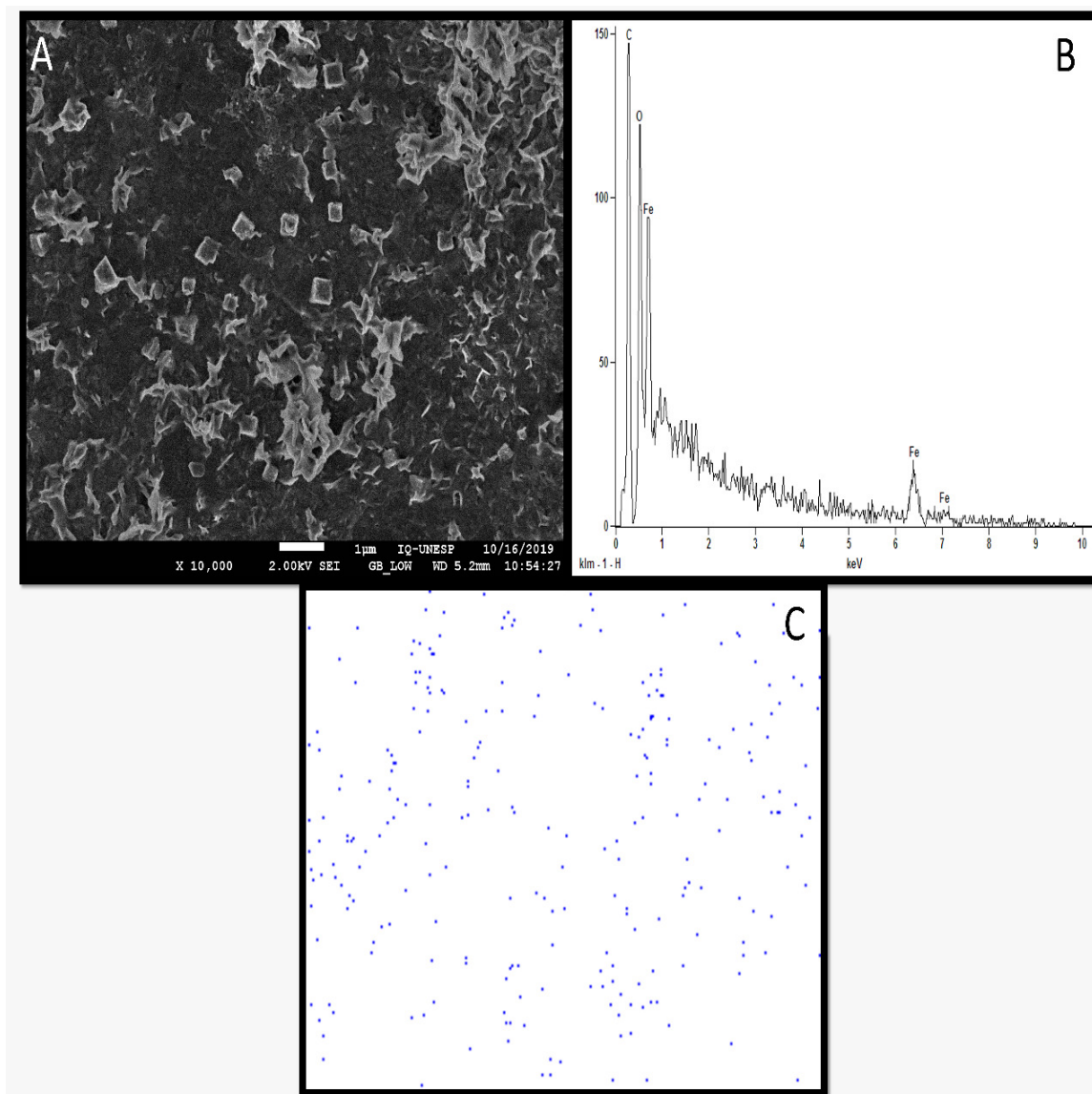
FeHCF compound [14, 15], therefore the voltammogram in Figure 3 indicates the successful formation of the FeHCF complex on the surface of the PEG/GO.

electrosynthesis of iron oxyhydroxide. Figure 5-C shows the mapping of microparticles on the electrode surface, it is possible to observe that a reasonable number of particles was formed.

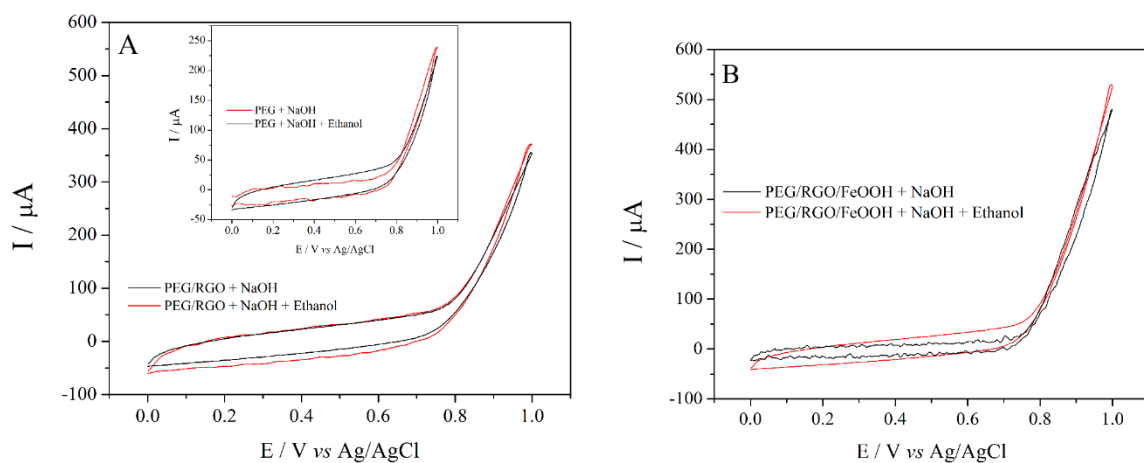


**Figure 4.** Cyclic voltammogram showing FeOOH formation in a solution containing 0.1 mol L<sup>-1</sup> NaOH with a potential of -0.2 V to 1.0 V at a scan rate speed of 100 mV s<sup>-1</sup>.

Figure 6-A shows the behavior of the PEG (inserted) and PEG/GO electrodes in NaOH medium and after the addition of 1 mmol L<sup>-1</sup> of ethanol. It was possible to observe that there was no increase in anode and cathode currents after the addition of ethanol. In Figure 6-B we can see the PEG/GO/FeOOH voltammograms and as in Figure 6-A voltammograms, no peak formation was observed, however there was a small increase in the anodic and cathodic currents indicating that PEG/GO/FeOOH presented better catalytic activity compared to PEG and PEG/GO.



**Figure 5.** **A** – SEM-FEG image of the cuboids formed in the electrosynthesis of FeOOH on reduced graphene oxide. **B** – EDX spectrum for the PEG/GO/FeOOH electrode. **C** – Mapping the Fe distribution on the electrode surface.



**Figure 6.** Cyclic voltammograms of the **(A)** PEG, PEG/GO and **(B)** PEG/GO/FeOOH working electrodes in 0.1 mol L<sup>-1</sup> NaOH solution, under 0 V to 1.0 V potential with a scan rate speed of 100 mV s<sup>-1</sup>, in the presence and absence of 1 mmol L<sup>-1</sup> of ethanol.

### 3. Material and Methods

#### Reagents and solutions

For the preparation of aqueous solutions, was used deionized water prepared by reverse osmosis. Graphite, potassium chloride, potassium permanganate, sodium nitrate, sulfuric acid, hydrogen peroxide (30%), hydrazine sulfate, ammonium hydroxide, potassium ferricyanide, iron nitrate, hydrochloric acid, sodium hydroxide, buffer phosphate, ethyl alcohol were purchased by Sigma-Aldrich and used as received.

#### Graphene oxide synthesis

Graphene oxide was prepared and purified according to the modified Hummers method [16] and described in the work of Luo and collaborators [17]. 5 g of graphite and 2.5 g of  $\text{NaNO}_3$  were mixed with 120 mL of  $\text{H}_2\text{SO}_4$  (95%) and the mixture was stirred for 30 min in an ice bath. Under vigorous stirring, 15 g of potassium permanganate were added to the suspension and maintaining the system temperature below 20 °C. The ice bath was removed, and the mixture was stirred at room temperature for one day. As the reaction continued, the mixture gradually became pasty and the color became light brown. At the end of the period, 150 mL of water was added slowly with vigorous and constant stirring. The reaction temperature increased to approximately 98 °C and effervescence was observed in the mixture and the suspension changed to yellow. The diluted suspension was kept under stirring for one day, after which 50 mL of hydrogen peroxide (30%) was added. At the end of the process, the mixture formed was purified by washing and centrifuging with HCl (5%) and deionized water several times until pH 7.0 was obtained in the supernatant. After vacuum filtration, graphite oxide was added in a phosphate buffer solution (PBS) of 100 mmol  $\text{L}^{-1}$  and pH 9.18 forming a suspension in the proportion of 5 mg  $\text{mL}^{-1}$ . The graphite oxide suspension was placed in an ultrasonic bath for 12 hours to obtain graphene oxide (GO) via exfoliation [18].

#### Characterization of synthesized graphene oxide

The synthesized graphene oxide was characterized by high-resolution scanning

electron microscopy (SEM-FEG) and cyclic voltammetry. The measurements were performed using a High-Resolution Scanning Electron Microscope with emission of electrons by a Field Emission Gun, model JSM 7500F from Jeol with an X-ray energy dispersion spectroscopy (EDS) module. The characterization by cyclic voltammetry of graphene oxide was carried out from the deposition of the GO by drop-casting on the surface of the pencil graphite electrodes (PEG), where 10  $\mu\text{L}$  of a suspension of GO at 0.5 mg  $\text{mL}^{-1}$  was pipetted in PBS solution and added to the PEG surface and left to stand for 24 hours at room temperature for drying.

#### Electrosynthesis of composites

The electrosynthesis of the catalysts based on graphene oxide (GO) and iron oxyhydroxide ( $\text{FeOOH}$ ) was carried out in two stages on the surface of pencil graphite electrodes (PEG). The first stage consisted of electrodeposition iron hexacyanoferrate ( $\text{FeHCF}$ ) in PEG (GO/ $\text{FeHCF}$ ) similar to the procedure used by Oliveira and coworkers [19], where by means of the cyclic voltammetry technique, the graphite electrodes were subjected to 25 successive voltammograms at 100  $\text{mV s}^{-1}$  in a potential range of -0.3 V to 1.2 V in an electrochemical cell containing a solution of 0.10 mol  $\text{L}^{-1}$  KCl with 4.0 mmol  $\text{Fe}(\text{NO}_3)_3$  and 4.0 mmol  $\text{K}_3\text{Fe}(\text{CN})_6$ . Subsequently, the formation of the  $\text{FeHCF}$  compound on the electrode surface was analyzed in a KCl 0.1 mol  $\text{L}^{-1}$  solution at a potential range of -0.3 V to 1.2 V at a scan rate of 50  $\text{mV s}^{-1}$ . In the second stage of the process,  $\text{FeOOH}$  was formed from the GO/ $\text{FeHCF}$  electrode in 0.10 mol  $\text{L}^{-1}$  NaOH solution by cyclic voltammetry with 40 successive sweeps in a potential range from -0.2 to 1.0 V with a scan rate of 100  $\text{mV s}^{-1}$ .

#### Morphological characterization of composites

The synthesized iron oxyhydroxide ( $\text{FeOOH}$ ) was characterized by high resolution scanning electron microscopy (SEM-FEG). The measurements were performed using a High-Resolution Scanning Electron Microscope with emission of electrons by a Field Emission Gun, model JSM 7500F from Jeol with an X-ray energy dispersion spectroscopy (EDX) module. The electrode was prepared according to the

methodology described in methods.

#### 4. Conclusions

The work presented interesting results with the possibility of obtaining a composite of iron oxyhydroxide and reduced graphene oxide by cyclic voltammetry, a simple and low-cost process. PEG/GO/FeOOH should still be studied more intensively with a view to other applications using electrochemical and spectroscopic techniques, however the results presented here serve as an important starting point.

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