

## Electrocatalytic oxidation of ethanol on the surface of the POAP/ phosphoric acid-doped ionic liquid-functionalized graphene oxide nanocomposite film

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### ABSTRACT

In situ electropolymerization as a facile synthetic procedure has been used to obtain highly active composites of ionic liquid functionalized graphene oxide (FGO) and poly ortho aminophenol (POAP). Surface and electrochemical analysis have been used for characterisation of FGO-POAP composite film. Nickel was accumulated by complex formation between Ni (II) in solution and amines sites in the polymer backbone to obtain Ni-FGO-POAP/ graphite electrode. Surface morphology of composite was characterized by scanning electron microscopy. The electrochemical performance of Ni-FGO-POAP composite electrodes was investigated by cyclic voltammetry and Chronoamperometry. Compared with Ni- POAP, a Ni-FGO-POAP electrode shows a higher catalytic performance in the electrocatalytic oxidation of ethanol. Under the CA regimes the reaction followed a Cottrellian behavior. Developing a simple and green route for synthesis of FGO-POAP and long life cycle and stability of nanocomposite are main important factor in presented work.

**Keywords:** POAP, Nanocomposite, Graphene, Electrocatalyst, Ethanol.

### 1. Introduction

Polyaniline (PANI) is one of the most important conducting polymers because of its unique electrical, optical, and optoelectrical properties, as well as its ease of preparation and its excellent environment stability. Aminophenols are interesting members of the class of substituted anilines. The hydroxyl group in the phenyl ring can be oxidized to quinone and quinone can be reduced again. POAP gives a surface film of interesting electrochemical and electrochromic properties when it is electropolymerised in acidic solution. This film is electroactive in aqueous and non-aqueous solutions containing protons but no response is observed at pH-value higher than pH 7. The variety of results for conductivity of the POAP film reported in the literature [1-3] show that the electrochemical response of POAP is strongly influenced by the

experimental procedure used to produce the polymer film, dopant anions and the purity starting monomer [1-3]. Carbon-based nanomaterials having a high surface area and good electrical conductivity have been attracted the attention of scientific community for different applications. These carbon based nanomaterials (activated carbon, carbon nanotubes, and graphene) have been used as substrate for metal oxide nanoparticles and conductive polymers for supercapacitor applications [4-8]. These conducting carbon materials provide a fast electron transfer rate during Faradaic charge transfer reactions and hence enhance the capacitance [9-13]. Polymer-carbon nanocomposites provide the solution for the insulating nature of conducting polymers at dedoped states by using carbon nanomaterials as substrate to grow nanostructured polymers [4-8]. The functionalization of graphene enhances the capacitance as well as provides anchoring sites for decoration of metal oxide nanoparticles and conductive polymer. Newly, the functionalized GO (FGO) nanosheets have been developed as attractive fillers for electrode and

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membrane modifications. The functional groups of FGO could ease the dispersion of FGO in organic solvents; so the composite membranes with improved distribution of nanofillers in polymer matrix could be expected [14], while the GO particles can hardly be dispersed in some organic solvents and the aggregation problems may occur. Additionally, the functional groups on the FGO structure can enhance the water retention and proton conductivity of the membranes [14-16].

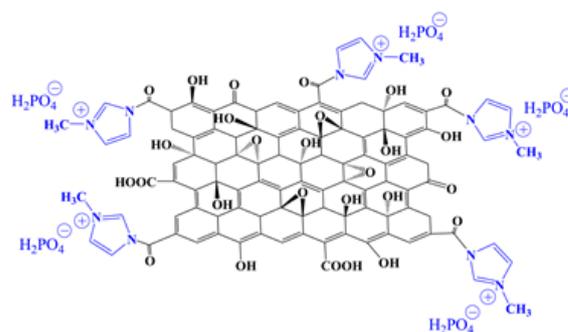
During the past few years, a large number of papers published concerning electrocatalytic properties of platinum group metals and their alloys incorporated into polymeric backbone. It has been shown that such modified electrodes with Pt micro particles exhibit a better catalytic effect than smooth platinum for the oxidation of methanol [17-20]. The use of Ni as the catalyst for alcohol electro-oxidation is of interest because it is an inexpensive metal. Many electrodes that include nickel as a component in their manufacture can be used as catalysts in fuel cells. Nickel is commonly used as an electrocatalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis. One of the most important uses of nickel as a catalyst is to oxidize alcohols. Several investigations on the electro-oxidation of alcohols on Ni have been reported [21-25]. We have combined the advantageous features of polymer modification, dispersion of metallic particles into an organic polymer. All these results encouraged us to continue the studies with new polymer materials. In this work, we combined the above-mentioned advantageous features with the aim of the electrocatalytic oxidation of ethanol by the use of poly ortho amino phenol (POAP) as a new polymer.

In the present work, room temperature electrochemically synthesized FGO-POAP electrode is presented as an efficient electrode material in electrooxidation of ethanol. Our goals in this paper were increasing the electrocatalytic activity of POAP by using FGO (Fig. 1) to form a composite electrode and moreover increase electrocatalytic activity. The electrochemical responses of nanocomposite were tested by cyclic voltammetry, chronoamperometry and impedance spectroscopy techniques.

## 2. Experimental

### 2.1. Reagent and materials

All the chemical materials used in this work, obtained from Merck Chemical Co., were of analytical grade and used without further purification. Double distilled water was used throughout the experiments.



**Fig. 1.** Molecular structure of functionalized graphene oxide [2].

### 2.2. Characterization

All electrochemical experiments were carried out by an Autolab General Purpose System PGSTAT 30 (Ecochime, Netherlands). A conventional three electrode cell with an Ag/AgCl reference electrode (Argentel, 3 M KCl) was used in order to carry out the electropolymerization of the POAP. A platinum wire and a graphite rod electrode was used as the counter and working electrodes respectively. Morphological investigations of the compounds were carried out by using FESEM analysis (Mira 3-XMU).

### 2.3. Preparation of GO and functionalized GO (FGO)

Firstly, GO was synthesized according to the modified hummers method from oxidation of natural graphite [23]. Then, 4.0 g of dry GO and 40 mL of thionyl chloride were placed into a 100 mL round-bottomed flask equipped with a condenser and magnetic stirrer. The mixture was then refluxed at 70°C for 48 h. After that, the extra thionyl chloride was extracted from the mixture using rotary and vacuum pump. The product was washed by dichloromethane several times and dried in vacuum oven at 60°C overnight. Afterwards, 2.0 g of the resulting acylated graphene oxide (GO-Cl) with 40 mL of 1-methylimidazole were put into a 100 mL round-bottomed flask topped with a condenser and stirred at 50°C for 48 h. The resulting FGO was filtered and washed with dichloromethane and deionized water several times and dried in vacuum oven at 60°C overnight. FGO nanosheets with chloride counter ions were added to 30 mL of phosphoric acid 85% and stirred in room temperature for 6 h in order to exchange the chloride ions with  $\text{H}_2\text{PO}_4^-$  [14].

### 2.4. Synthesis of POAP and FGO-POAP nanocomposite

POAP/ FGO composites were prepared by in a stirring solution containing 0.01 M monomer, 0.5 M  $\text{HClO}_4$ , 0.1 M  $\text{LiCO}_4$  and  $5.0 \times 10^{-3}$  M sodium dodecyl sulfate (SDS) on the surface of the graphite electrode.

Before polymerization of POAP/ FGO, the FGO dispersion was prepared as follows:

5 mg FGO was added into a 1 mL dimethyl formamide (DMF) under ultrasonication for 2 h, and a stable mixture was obtained. Consequently, POAP was coated on the electrode by an electrochemical process by CV for 10 cycles from an aqueous solution containing 0.5 M HClO<sub>4</sub>, 0.01 M OAP and 5.0 × 10<sup>-3</sup> M SDS, in which the potential range was between -0.25 and 0.90 V and at a scan rate of 50 mV s<sup>-1</sup>. After polymerization, 5 μL FGO (0.05 wt %) dispersion was dropped on the electrode immediately. After drying, the working electrode was scanned by CV in the above OAP solution for 10 cycles again [26]. In order to incorporate Ni (II) ions into the POAP film, the freshly electropolymerized working electrode was placed at open circuit in a well stirred aqueous solution of 0.1 mol L<sup>-1</sup> Ni (NO<sub>3</sub>)<sub>2</sub>. Nickel was accumulated by complex formation between Ni (II) in solution and amines sites in the polymer backbone [24, 27] in a given period of time.

The mass of electrodeposited films was approximated assuming a current efficiency for the electropolymerization process of 100%, using Faraday's law.

### 3. Results and Discussion

SEM images of FGO and electrosynthesized FGO-POAP have been shown in Fig. 2. It can be seen from the SEM image of FGO that the Individual FGO nanosheets have flaky and wrinkled paper-like structures which have been exfoliated through the horizontal expansion of the compact layers of graphene oxide nanosheets from the natural graphite. SEM

image of FGO-POAP composite shows porous structure and presence of the FGO in the electrosynthesized composite film.

Fig. 3 shows cyclic voltammograms of Ni-POAP and Ni- POAP/FGO electrode in 1.0 M NaOH solution in the potential sweep rate of 10 mV s<sup>-1</sup>. The larger Ni response at the Ni-FGO-POAP in respect to Ni-POAP electrode is proposed to be the Ni-FGO-POAP enhances the electrochemical activity of Ni<sup>2+</sup>/Ni<sup>3+</sup> redox through fine dispersion of the particles into the conductive polymer matrix to result in a drastic increase in surface area.

After approving high activity of Ni-FGO-POAP respect to Ni-POAP, composite film has been used in electrocatalytic oxidation of ethanol in alkaline media. Fig. 4a shows cyclic voltammograms of Ni-FGO-POAP electrode in the presence of 1.2 M ethanol at a potential sweep rate of 10 mV s<sup>-1</sup>. The larger ethanol response at the Ni-FGO-POAP electrode is due to the composite material which enhances the catalytic properties of nickel oxide through fine dispersion of the catalyst particles into the conductive polymer matrix to results in a drastic increase in surface area.

Fig. 4b shows cyclic voltammograms of Ni-FGO-POAP electrode in 1 M NaOH solution in the presence of various concentrations of ethanol at a potential sweep rate of 10 mV s<sup>-1</sup>. At Ni-FGO-POAP electrode, oxidation of ethanol appeared as a typical electrocatalytic response. The anodic charge increased with respect to that observed for the modified surface in the absence of ethanol and it was followed by decreasing the cathodic charge upon increasing the concentration of ethanol in solution.

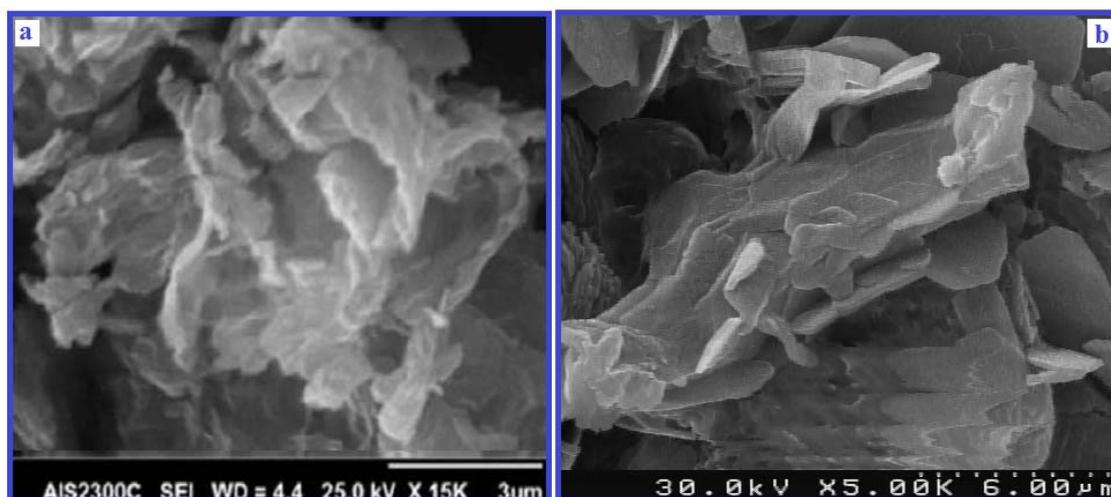
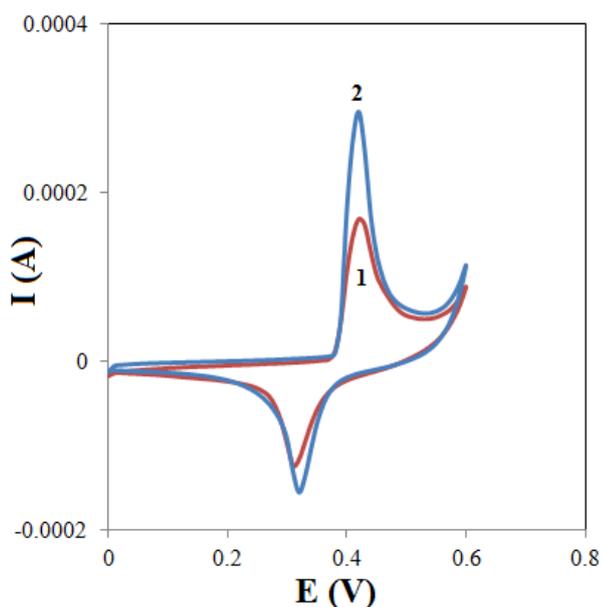
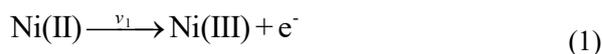


Fig. 2. SEM image of FGO (a) and FGO-POAP (b) composite film.



**Fig. 3.** cyclic voltammograms of Ni-POAP (1) and Ni-FGO-POAP (2) electrode in 1.0 M NaOH solution in the potential sweep rate of 10 mV s<sup>-1</sup>.

The anodic current in the positive sweep was proportional to the bulk concentration of ethanol and any increase in the concentration of ethanol caused an almost proportional linear enhancement of the anodic current. So, catalytic electrooxidation of ethanol on Ni-FGO-POAP seems to be certain. The following mechanism is proposed for the mediated electro-oxidation of ethanol. The redox transition of nickel species present in the film is:



and ethanol is oxidized on the modified surface via the following reaction

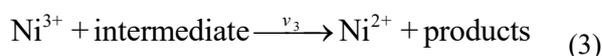


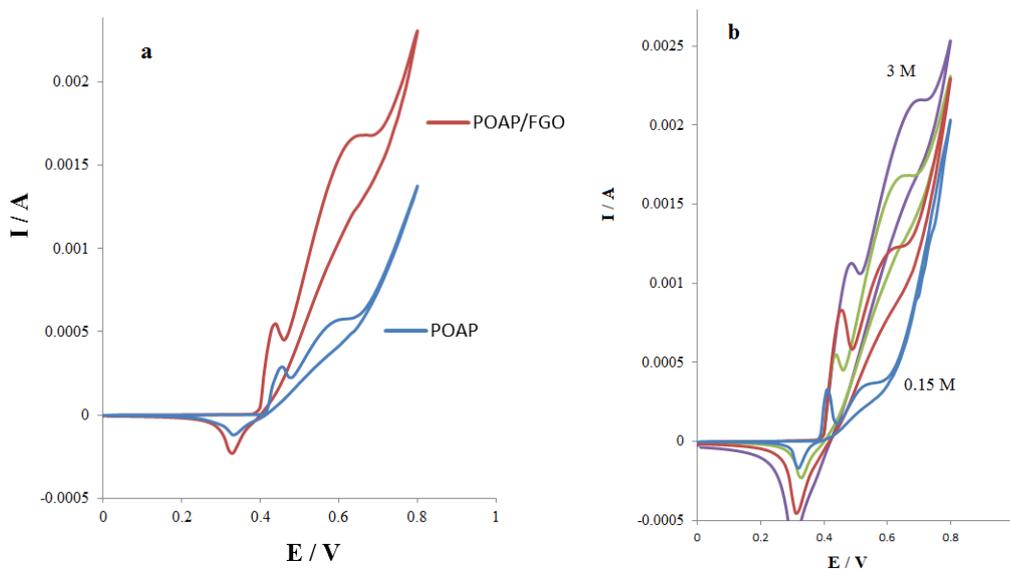
Fig. 5a and 5b shows double steps chronoamperograms for the Ni- POAP and Ni-FGO-POAP in presence of ethanol over a concentration range of 0.15-3.0 M with an applied potential steps of 480 and 220 mV, respectively. Plotting of net current with respect to the inverse of the square roots of time, after removing the background current presents a linear dependency (Fig. 5c). The dominance of a diffusion controlled process is evident. Using the slope of this line in Cottrell equation [28-31].

$$I = nFAD^{1/2}C \times \pi^{1/2}t^{-1/2}$$

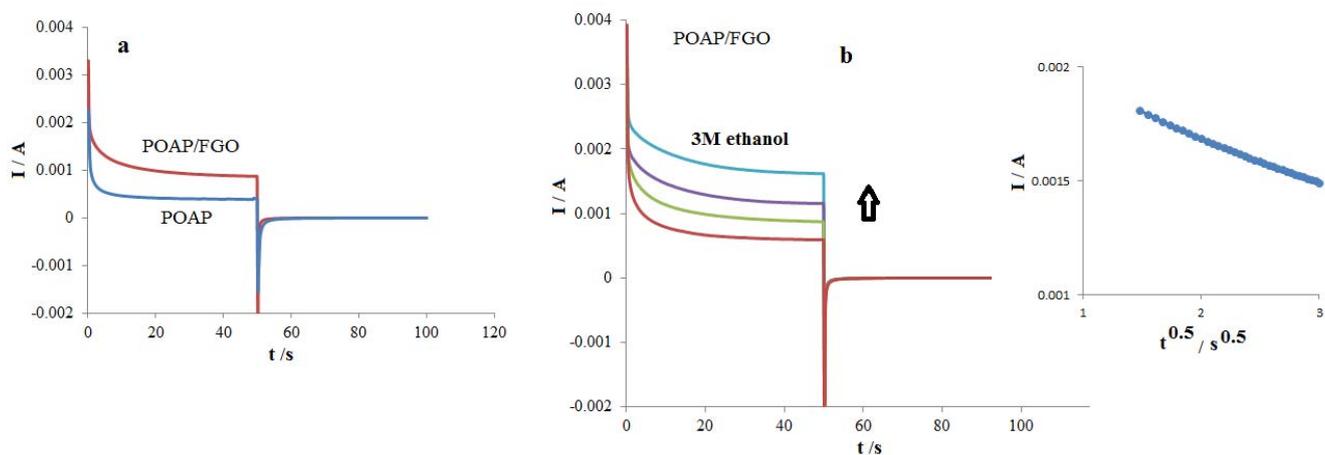
The diffusion coefficient of ethanol has been obtained to be 3.78×10<sup>-4</sup> cm<sup>2</sup> s<sup>-1</sup> in agreement with the cyclic voltammetric result.

#### 4. Conclusion

A simple and general strategy, namely in situ electropolymerization has been used for electrosynthesis of POAP/FGO film. The FGO has an obvious improvement effect, which makes the composites have more active sites for faradic reaction and larger electrocatalytic activity than pure POAP.



**Fig. 4.** (a) Cyclic voltammograms of Ni-POAP and Ni-FGO-POAP (in the presence of the SDS in monomer solution in electropolymerization process) electrode in 1 M NaOH solution in the presence of 1.2 M ethanol at a potential sweep rate of 10 mV s<sup>-1</sup> and (b) Cyclic voltammograms of Ni-FGO-POAP electrode in the presence of (0.15-3.0) M of ethanol.



**Fig. 5.** (a) compared chronoamperograms of Ni-POAP and Ni-FGO-POAP electrodes in 1.2 M ethanol, (b) Double steps chronoamperogram of Ni-FGO-POAP electrode in 1 M NaOH solution with absence and different concentrations of ethanol (0.15-3.0)M. Potential steps were 480 mV and 220 mV, respectively and (c) dependency of transient current on  $t^{1/2}$  for chronoamperogram of Ni-FGO-POAP electrode.

Also, it results in enhanced electric conductivity, lower the resistance, and facilitate the charge-transfer of the composites. In comparison with a Ni- POAP, a Ni-FGO-POAP electrode shows a better catalytic performance for the electrocatalytic oxidation of ethanol. From the Chronoamperometry results the diffusion coefficient of ethanol has been obtained to be  $3.78 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ .

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