

Morphology and electrocatalytical activity of the composite electrode (GC/Ppy(Ni_{0.3}Co_{2.7}O₄)) synthesized by galvanostatic and cyclic voltammetry methods

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Abstract: The Polypyrrole (Ppy) and mixed valence Ni_{0.3}Co_{2.7}O₄ nanoparticles were used essentially to elaborate the composite electrode (GC/Ppy(Ni_{0.3}Co_{2.7}O₄)) by galvanostatic and cyclic voltammetry (CV) methods. Electrololymerization of Pyrrole (Py) in the absence and in the presence of the oxide was performed on glassy carbon (GC) electrode in KCl (0.15 mol/L). The obtained materials morphologies and behavior towards the oxygen reduction reaction (ORR) were then checked. The result reveals that the Ppy film electrodeposition signal and its surface morphology were affected by the oxide presence in the synthesis medium and the formed hybrid materials exhibit electrocatalytical properties whatever, the processing route used. Both cyclic voltammetry and galvanostatic methods lead to potential decrease. Furthermore, the incorporation of oxide into polymeric matrix increases its porosity allowing easier charges transfer and higher accessible active sites. Moreover, the SEM photographs reveal a porous film containing inhomogenously dispersed nanoparticles when galvanostatic method is used. However GC/Ppy(Ni_{0.3}Co_{2.7}O₄) obtained by CV, are porous and a sponge-like structure with Ni_{0.3}Co_{2.7}O₄ particles uniformly distributed in the film surface with few areas appearing agglomeration.

Keywords: Cyclic voltammetry, composite material, galvanostatic, oxygen reduction reaction,

1. Introduction

Nowadays polymer nanocomposites (PNCs) prepared by dispersing oxide nanoparticles (NPs) into an electronic conducting polymer (ECP) are proposed to have wide applications because of their many advantages, such as low cost, environmental stability, light weight, and unique properties [1-4]. Among diverse conducting polymers, polypyrrole (Ppy) has attracted great attention due to its tunable conductivity by various doping ways, easy preparation under different conditions, thermal and environmental stability [5-6]. As reported in our preliminary paper [7], the spinel nanoparticles Ni_{0.3}Co_{2.7}O₄ oxide synthesized by sol-gel route and 3D incorporated by

galvanostatic method in Ppy matrix exhibit a very good electrocatalytic activity toward the oxygen reduction reaction (ORR).

The properties of the (PNCs) and (ECP) obtained electrochemically are dependent on the choice of electrochemical polymerization techniques [8-9]. Electrochemical synthesis can be generally carried out using the galvanostatic technique, for its simplicity, practicability application. Where as the potentiostatic and potentiodynamic methods are seldom used [10-12]. The last technique even rarely used, it produces films with better morphology, conductivity and structural integrity than potentiostatic deposition[13], besides, it is useful for elucidating PNCs interface.

The effect of electrochemical synthesis route on Ppy films and Ppy/(Ni_{0.3}Co_{2.7}O₄) morphology and the electrochemical signal has not been reported yet in the literature. Here, we prospect to use the cyclic voltammetry (CV) as complementary of our previous study [7] to

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prepare the Ppy films embedded with the spinel oxide and to compare the results between these two synthesis methods.

2. Experimental

A three electrode electrochemical cell was used to prepare Ppy films with and without $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ nanopowders. The electropolymerization of Pyrrole (Aldrich) was carried out at room temperature by either galvanostatically with a current density (j) of 3 mA during 150 s or potentiodynamically (scanning the potential between +1.3 and -0.8 V versus Ag/AgCl, scan rate 500 mV/s until reaching 25 cycles), using 0.1M of freshly distilled Pyrrole in a solution of KCl (0.15M). The counter electrode is a platinum plate of 1cm^2 area, a saturated Ag/AgCl electrode was used as the reference throughout this work, and the working electrode is a glassy carbon (GC) rotating disk. Potentiostat/Galvanostat Autolab PGSTAT 30 driven by FRA 4.9 Software, controlled by a PC was used. Prior every trial, the solution was deoxygenated by nitrogen bubbling for 30 min and maintained under it during the acquisition. The synthesized electrodes were characterized by scanning electron microscopy (SEM) and their electrocatalytic activity toward the (ORR) was checked by linear sweep voltammetry (LSV) by scanning potential from 0.2 V to -0.8 V with a rate of $5\text{ mV}\cdot\text{s}^{-1}$, in deaerated, and oxygen saturated solutions.

3. Results and discussions

3.1. Electropolymerization of Py in the absence and in the presence of $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$

a. Galvanostatic method

The chronopotentiograms of the electropolymerization of Py/ $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ are presented in Fig.1

The chronopotentiometric curve of Py/ $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ is characterized by 3 steps: the initiation stage (step A) is characterized by an increasing electrode potential. This could indicate that the presence of nanoparticles could facilitate Ppy formation [14], then the potential decreases in the second step (B) during which the electrode is covered with a Ppy layer. The succeeding plateau (step C) refers to further polymerization on already formed polymer [15].

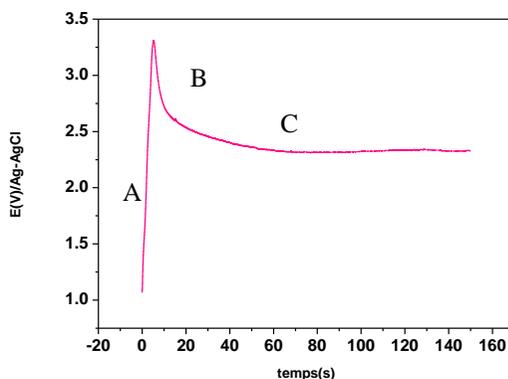


Fig.1 Chronopotentiograms recorded during the preparation of Py/ $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ in KCl (0.15M), (j) = 3 mA during 150 s

b. CV method

Fig.2 shows the cyclic voltammograms recorded during the formation of Ppy and Ppy /($\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$). The registered voltammograms shape and Ppy electropolymerization process are not inhibited by the addition of $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ nanopowders to the synthesis medium. So the Ppy doping and dedoping process remains reversible even in the NPs presence.

The Ppy/ NPs oxidation peak (doping) is observed at a lower potential, while its reduction peak (dedoping) is registered at higher potential, this potential decrease is also observed when Ppy /($\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$) is prepared by galvanostatic route. This could indicate that the NPs oxide incorporation into Ppy matrix reduces the required energy for polymer film formation, as reported by Montoya *et al.* [16].

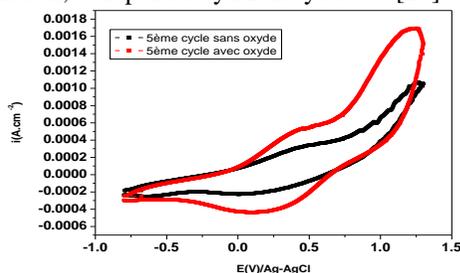


Fig.2 the 5th Electropolymerization cycle of Py alone and in the oxide presence at $500\text{ mV}\cdot\text{s}^{-1}$ from 1.3V to -0.8

3.2 Morphology

Scanning electron microscopy (SEM) was used to reveal the morphology of the obtained electrodes. The corresponding SEM images are showed in Fig.3.

The Ppy films alone (Figs. 3a, c) exhibit a typical, so called “cauliflower” structure as generally reported in literature [17] whether it is prepared by galvanostatic or CV routes .

On the other hand, it was found that the galvanostatic method produced a porous, globular surface containing nanoparticles aggregates inhomogeneously dispersed on Ppy surface, while the CV method generated a porous and a sponge-like structure with uniformly NPs distribution and few areas appearing agglomeration.

This behavior, regarding the synthesis method, was also reported by S. Patra *et al.*[18] in a study comparing PEDOT synthesized using the three electrochemical methods, it was found that the potentiostatic and galvanostatic routes produced a porous, globular surface, while the

potentiodynamic method generated a rod-like, fibrous morphology

3.3 Electrocatalytical activity

To check the electrocatalytic activity toward the ORR of GC/Ppy($\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$) prepared by CV and galvanostatic route, polarization curves were recorded and reported in (Fig.4). The hybrid materials formed by both methods exhibit no significant current densities under deoxygenated medium. However, by increasing oxygen concentration, growing reduction wave was observed [7]. This confirms powder electrocatalytic activity toward ORR [19].

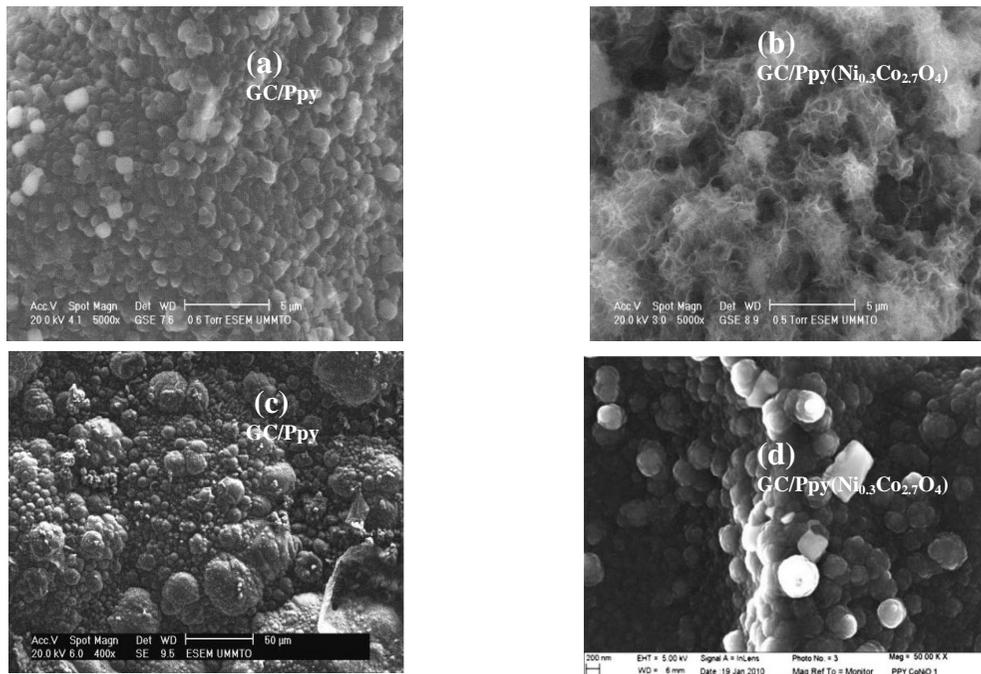


Fig.3 The SEM micrographs of GC/Ppy and GC/Ppy($\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$) prepared by CV(a,b) and galvanostatic (c,d) methods

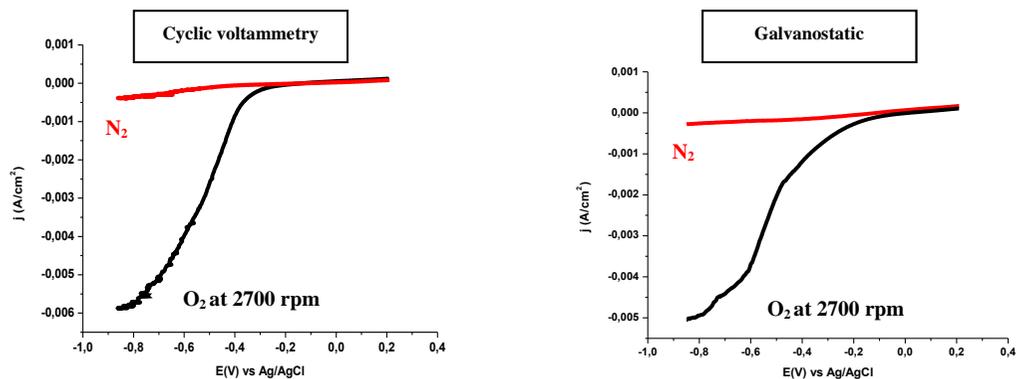


Fig.4 Polarization curves for O_2 reduction at 5 mV/s on GC/Ppy($\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$) Prepared by CV and galvanostatic method at 2700 rpm in N_2 and O_2 saturated solution

4. Discussion

The current intensity recorded for the RRO on the hybrid materials synthesized by CV method is higher than that obtained by galvanostatic route. This behavior can be at least explained by the different morphologies of the materials. Indeed, the CV method leads to spongy porous films having a larger surface area, which provide an excellent path for the charge transfer [20].

5. Conclusion

Comparing to the galvanostatic method, it seems that the cyclic voltammetry can be an advantageous electrochemical synthesis route allowing to Ppy / Ni_{0.3}Co_{2.7}O₄, having a reversible redox process and three-dimensional NPs distribution, a better accessibility to active sites. In addition, hybrid electrode keeps its electrocatalytic performance toward the ORR. For a relevant comparison, it is necessary to study the ORR on hybrid electrode prepared by CV route and to evaluate the kinetic parameters, compare them to those obtained by galvanostatic route. Finally, the use of CV synthesis method could enhance the performance of applications that are based on the electrochemical properties of the Ppy/NPs.

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