

# HYBRID ELECTRODE FORMED BY $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ NANOPARTICLES INCORPORATED INTO POLYPYRROLE: ELECTROCATALYSIS OF $\text{O}_2$ REDUCTION

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## ABSTRACT

A hybrid electrode was formed on glassy carbon (GC) electrode with polypyrrole (Ppy) and mixed valence  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  nanoparticles to study their behaviour towards the oxygen reduction reaction (ORR). The oxide nanoparticles were prepared by sol-gel route and characterized by XRD method.

The result showed that the desired oxide was obtained and the nanocrystallites exhibit a diameter about 13 nm. The hybrid electrode was then fabricated by the electropolymerization of pyrrole (Py) in the presence of  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  nanoparticles in KCl (0.15 mol/L) at room temperature and characterized by SEM and LSV methods.

Investigation of the hybrid electrode confirmed that  $\text{O}_2$  reduction mechanism changes by applying potential. Thus, at low overpotential the  $\text{O}_2$  reduction involves two electrons and provides  $\text{H}_2\text{O}_2$ , with cathodic transfer coefficients ( $\beta$ ) of 0.33 and an exchange current density ( $j_0$ ) of about  $8 \times 10^{-3}$  mA/cm<sup>2</sup>, while, at high overpotential  $\text{H}_2\text{O}_2$  is further reduced into  $\text{H}_2\text{O}$ . Also, the result shows that the sol-gel method led to the preparation of  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  nanoparticles having a spinel structure with a desired stoichiometry which exhibits a high electrocatalytic activity for reducing oxygen mostly to  $\text{H}_2\text{O}_2$ .

**Keywords:** *sol-gel, nanopowders, polypyrrole, oxygen reduction reaction, hybrid electrode*

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## NOMENCLATURE

### Symbols:

GC	glassy carbon
Py	pyrrole
Ppy	polypyrrole
ORR	oxygen reduction reaction
K-L	Koutecky-Levich
LSV	Linear sweep voltammetry
RDE	rotating disc electrode
$n$	transferred electrons number
$J_0$	exchange current density
$\beta$	cathodic transfer coefficients

### Greek symbols:

$\omega$	electrode rotational speed, rad
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## 1. INTRODUCTION

Over the last years, electrocatalyst particles dispersion throughout the matrix of an electronically conductive polymer (ECP) as electrocatalytic systems for various reactions were widely explored [1]. Thus, the obtained composite exhibits a three-dimensional distribution of accessible active sites and provides a better charge transport conditions through the polymer film.

Among ECP, polypyrrole (Ppy) has attracted a great attention in recent years due to its non-toxicity, easy fabrication by electropolymerization (which promotes application of aqueous and organic solvents and using chemical and electrochemical methods), high conductivity, thermal and environmental stability. Several recent studies were focused on the development of a composite electrode for oxygen reduction reaction (ORR) catalysis and production of  $H_2O_2$ , which can be used as an oxidizer of organic pollutants and bleaching or sterilizing agent in chemical or pharmaceutical industry. The spinel  $Ni_xCo_{3-x}O_4$  ( $0 \leq x \leq 1$ ) nanoparticles seem to be very promising electrocatalyst. Thus, Chartier et al. [2] reported that the nanoparticles with  $x = 0.3$ , synthesized by thermal decomposition of nitrates, had the average size of 35 nm and maximum  $O_2$  reduction activity producing high amount of  $H_2O_2$ , with an exchange current density ( $j_0$ ) of  $2 \times 10^{-3}$  mA/cm<sup>2</sup>.

Many authors claimed that when the catalysts dimensions are reduced, the materials properties might be remarkably changed. It was noticed that the preparation route influences the oxide physicochemical properties, including its size [3]. Among different synthesis methods, sol-gel is considered as a low-temperature soft chemical route frequently used to produce nanosized oxide powders having a strong catalytic activity and relatively high stability [4].

In this study  $Ni_{0.3}Co_{2.7}O_4$  powders were prepared by sol-gel method using the citric acid as chelating agents and calcined at 300°C. The electrocatalytic activity of the embedded oxide particles in Ppy film (being part of the hybrid electrode Ppy( $Ni_{0.3}Co_{2.7}O_4$ )) has been studied. The hybrid electrode was synthesized by chronopotentiometry and characterized by linear sweep voltammetry (LSV) using rotating disc electrode (RDE). The data were exploited by Koutecky-Levich (K-L) equation to evaluate ORR kinetic parameters that allow us to check out the electrocatalytic performances.

## 2. RESULTS

### 2.1 Powder characterization

X-ray diffraction spectra, presented in Fig. 1, confirmed the crystalline nature of the prepared  $Ni_{0.3}Co_{2.7}O_4$  nanoparticles. The characteristic *hkl* lines are: 111, 220, 311, 400, 422, 511 and 440, indicated on the pure cubic spinel structure. The estimated crystallites cell parameter *a* is about  $8.11 \pm 0.015$  Å. The crystallites average size  $d_{p(XRD)}$  was estimated by Scherrer formula and it was about 13 nm.

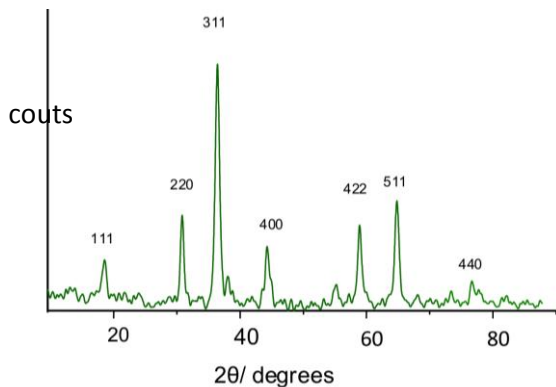


FIGURE 1. X-ray diffractograms of  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  powders prepared with citric acids and calcined at  $300\text{ }^\circ\text{C}$

## 2.2 Characterization of composite electrode

Figure 2 shows the chronopotentiogram of the electropolymerization of Py in KCl solution, under nitrogen bubbling with  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  particles. An increasing electrode potential characterizes the initiation stage. This could indicate that the presence of the nanoparticles could facilitate the Ppy formation.

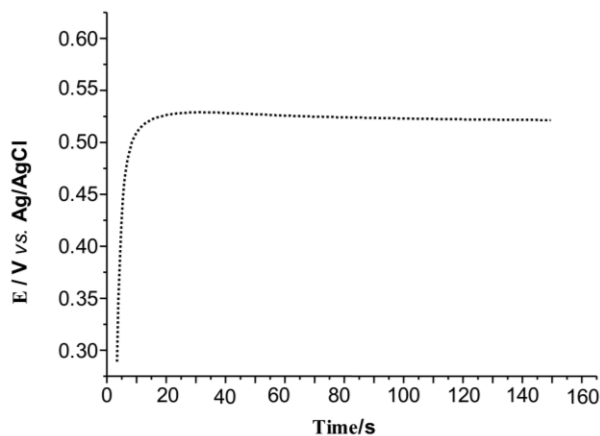


FIGURE 2. Chronopotentiograms recorded during  $\text{Ppy}(\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4)$  preparation

The morphology of the hybrid composite films was investigated by SEM (Figure 3). SEM images of the Ppy film (Figure 3a) and nanocomposite film ( $\text{Ppy}(\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4)$ ) (Figure 3b) show a typical, so called “cauliflower” structure as reported in literature [5]. It can be seen that  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  nanoparticles aggregates are inhomogeneously dispersed on the surface of the latter film (Figure 3b).

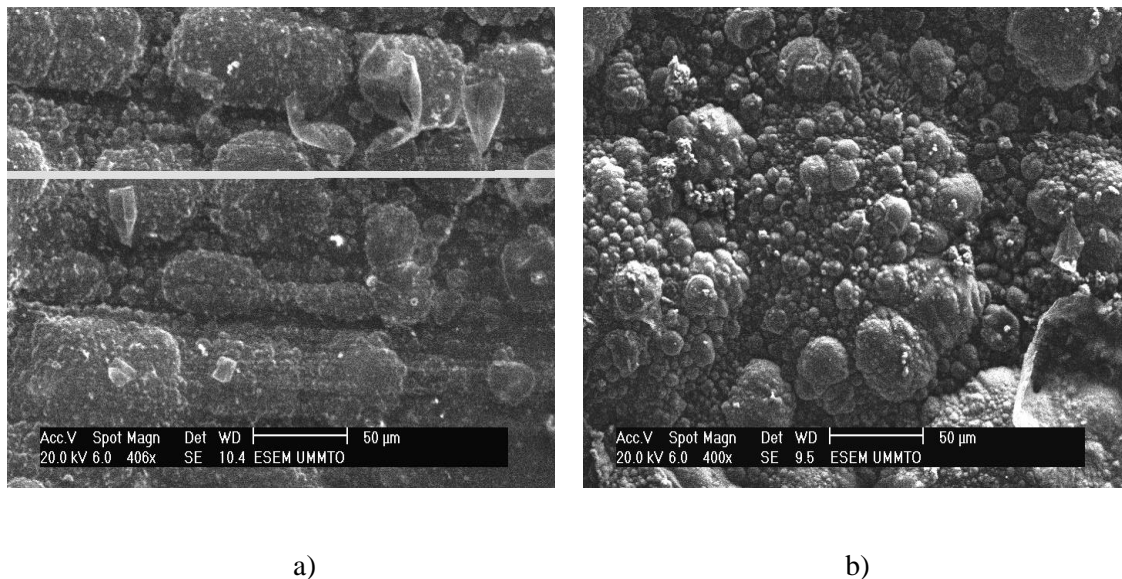


FIGURE 3. SEM micrographs of GC/Ppy (a) and hybrid electrode Ppy(Ni<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub>) (b)

### 2.3 Oxygen reduction reaction on the composite electrode

The obtained LSV results for the hybrid GC/Ppy(Ni<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub>) electrode at different rotational speeds of the rotating disk electrode were presented in Figure 4. As expected, the current densities are rising with the increasing of the rotational speed.

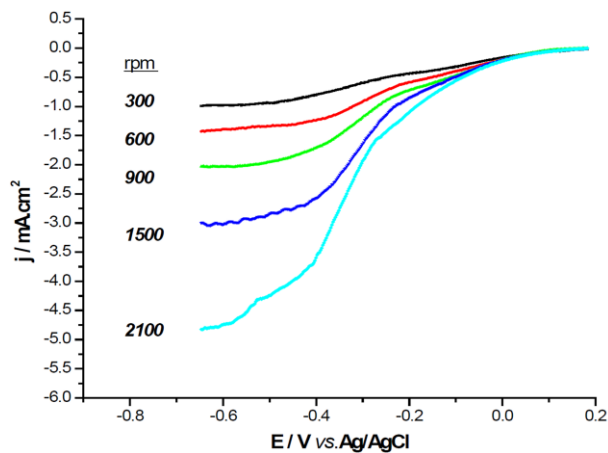


FIGURE 4. Polarization curves for O<sub>2</sub> reduction at 5 mV/s on GC/Ppy(Ni<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub>) electrode for different rotational speeds in KCl (0.15 mol/L) O<sub>2</sub> saturated solution

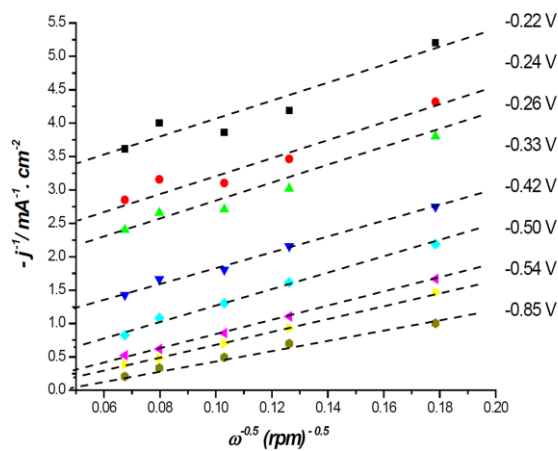


FIGURE 5. Koutecky-Levich ( $j^{-1}$  vs.  $\omega^{-1/2}$ ) plots at different potentials ( $E$ )

The total current density  $j^{-1}$  is plotted in function of  $\omega^{-1/2}$  at different potentials (Figure 5). The straight lines for each electrode potential indicate the first order reaction against dissolved oxygen.

Thus, for each scatter straight line, the total number of electrons  $n$  was calculated and the resulting values are reported versus electrode potentials (Figure 6).

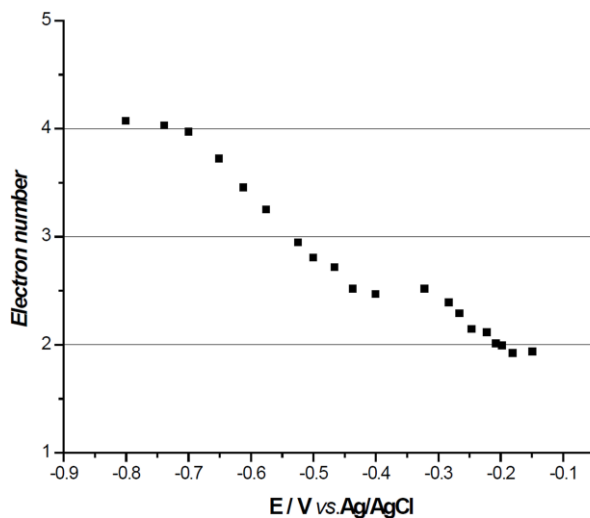


FIGURE 6. Variation of the total number of electrons  $n$  vs. electrode potential ( $E$ )

For the small applied potential (i.e. small overpotential), the total number of electrons was found to be close to  $n = 2$ , which indicates the  $O_2$  reduction into  $H_2O_2$ . By decreasing the applied potential (i.e. high overpotential), the total number of electrons is gradually increased up to  $n = 4$ . So,  $H_2O_2$  is further reduced into  $H_2O$ .

This behaviour based on potential was also reported by Chartier *et al.* [6] and attributed to a change in the mechanism with potential, which is a characteristic of the ORR on mixed valency spinel oxides.

From the K-L plot (Figure 5), the parameters  $j_0$  and  $\beta$  are deduced and summarized in Table 1.

$j_0$ [mA/cm <sup>2</sup> ]	$\beta$
$8.18 \times 10^{-3}$	0.33

TABLE 1 .Kinetic parameters of ORR on GC/Ppy(Ni<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub>)

### 3. DISCUSSION

The  $j_0$  value is 4 times higher than that reported by Chartier *et al.* [2] for the  $Ni_xCo_{3-x}O_4$  having particle size of about 35 nm and obtained by thermal decomposition method. So, it seems that the sol-gel nanoparticles, due to their smaller size, exhibit a better electrocatalytic activity toward ORR.

As the electrocatalysis depends on both geometrical and electronic factors previously exposed, the former are those related to the extension of the actual surface area or actual site density. The latter one is that related to the surface electrical conductivity. Thus, the enhanced catalytic activity observed in our study may be ascribed, at least in part, to the  $Ni_{0.3}Co_{2.7}O_4$  particle size which is smaller (higher surface area), or to its conductivity improvement.

#### 4. CONCLUSION

In the present study, the spinel  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  nanoparticles were successfully synthesized by the sol-gel route using the citric chelating and calcined at  $300^\circ\text{C}$ . The characteristic XRD peaks confirmed the formation of the pure spinel  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  structure having a size about 13 nm.

Investigation of the hybrid electrode ( $\text{Ppy}(\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4)$ ) confirmed that  $\text{O}_2$  reduction mechanism changes by applying potential. Indeed, ORR involves two electrons to form  $\text{H}_2\text{O}_2$ , with a cathodic transfer coefficient equals 0.33 and an exchange current density of about  $0.8 \times 10^{-3} \text{ mA cm}^{-2}$  at small overpotentials. Therefore, compared to thermal decomposition, sol-gel method is considered as an interesting and a promoting method as it enabled us to obtain finer nanoparticles, with larger specific surface area and higher electrocatalytic activity by producing a larger amount of  $\text{H}_2\text{O}_2$  making it more promising for many environmental applications, including electrochemical treatment involving oxygen reduction reaction .

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