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Research Article

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Composite PANI@$Ni_{0.6}Co_{2.4}O_4$, active material for energy storage systems such as supercapacitor

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Abstract

In the present study, the mixed oxides of $Ni_{0.6}Co_{2.4}O_4$ were synthesized by the sol gel method via propionic acid. The composite films of PANI@$Ni_{0.6}Co_{2.4}O_4$ deposited on a platinum substrate (PANI@$Ni_{0.6}Co_{2.4}O_4$/Pt) were prepared by incorporating particles of mixed oxides of nickel and cobalt into the matrix of polyaniline during electropolymerization with stirring of the HCl electrolyte (0.5M) containing the aniline monomer and the different contents of oxides $Ni_{0.6}Co_{2.4}O_4$(0.5g.L^{-1}, 1 g.L^{-1}) via cyclic voltammetry. Physical and electrochemical characterizations were made with scanning electron microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS), X-ray diffraction (XRD), cyclic voltammetry (VC) and chronopotentiometry. The analyzes by SEM, EDS and DRX confirmed the nature of the synthesized products and the incorporation of $Ni_{0.6}Co_{2.4}O_4$ in the composite films. It has been observed that the electrochemical performance measurements show an improvement in the storage capacity of polyaniline in the presence of nickel cobaltite nanoparticles in the film, an energy density around 10.3 Wh.kg^{-1} for PANI@$Ni_{0.6}Co_{2.4}O_4$ /Pt, higher than that of PANI/Pt, 6.25Wh.kg^{-1}. That is a 65% increase in energy autonomy.

Keywords: $Ni_{0.6}Co_{2.4}O_4$, Polyaniline, PANI@$Ni_{0.6}Co_{2.4}O_4$, cyclic voltammetry, chronopotentiometry, energy density.

Introduction

The design of electrode material for energy storage devices is attracting growing interest in a world where the question of energy is a major economic and societal issue. Conductive polymers such as polyaniline, polypyrrole are frequently used due to their good conductivity in the doped state. In the case of polyaniline, its conductivity which can reach 10^4 S.cm^{-1} [1] and its different oxidation states (leucoemeraldine, emeraldine base, emeraldine salt and pernigraniline) contributing to its good specific capacity [2, 3] make it a good candidate for energy storage devices such as supercapacitors. The latter are intermediate electrical energy storage systems between the batteries and the dielectric capacitors.

In order to increase the stability and storage capacity of conductive polymers, reinforcements are added to the reaction medium during polymerization to form composites. In this context, we added nanoparticles of nickel and cobalt oxide ($Ni_{0.6}Co_{2.4}O_4$) in the electrolyte containing aniline to electrochemically synthesize the composite PANI@$Ni_{0.6}Co_{2.4}O_4$.

Mixed oxides offer significant catalytic and electrocatalytic properties, rich redox reactions from both nickel and cobalt cations and their synergistic effects [4]. Compared to simple metal oxides, mixed metal oxides exhibit high mechanical strength, good conductivity due to lower activation energy for electron transfer between cations [5].

It is in the same vein that N. Harfouche synthesized the PANI/$LiMnO_4$ composite [1], N. IDIRI prepared the Ppy/$Ni_{0.3}Co_{2.7}O_4$composite [6] and many other polymer-based composites driver have been prepared in recent years.

The development of our PANI@$Ni_{0.6}Co_{2.4}O_4$composite films was carried out by cyclic voltammetry which consists of directly adding the $Ni_{0.6}Co_{2.4}O_4$oxide particles at different levels (0.5 and 1g/L) in the solution of HCl (0.5M) containing the aniline monomer. Thus the incorporation of the particles and the electropolymerization of the monomer are done simultaneously.

The structure and morphology of our products have been studied by scanning electron microscopy (SEM) coupled with energetic dispersion spectroscopy, X-ray diffraction (XRD). The energy and power densities were made by the galvanostatic charge and discharge method in a three-electrode cell.

Experimental methods

Chemicals and devices

Aniline (Aldrich product) is the monomer used for the electrosynthesis of PANI/Pt and PANI@$Ni_{0.6}Co_{2.4}O_4$/Pt films. The products used for the synthesis of nickel cobaltite particles are cobalt nitrate hexahydrate [$Co(NO_3)_2$, $6H_2O$] and nickel nitrate hexahydrate [$Ni(NO_3)_2$, $6H_2O$].

The solutions used during the syntheses are acidified water (hydrochloric acid of 0.5M concentrations) for the electrochemical syntheses of the films, propionic acid and liquid nitrogen for the preparation of the mixed oxides of nickel and cobalt.

The PANI/Pt and PANI@$Ni_{0.6}Co_{2.4}O_4$(0.5 and 1g/L)/Pt films were characterized by various techniques: scanning electron microscopy coupled with energy dispersive spectroscopy using a Hitachi model S-520 apparatus, X-ray diffraction using a Siemens D-500 type diffractometer.

The electrochemical tests were carried out at room temperature in a glass cell containing the electrolysis solution in which three electrodes are immersed (platinum disk working electrode, silver reference electrode (Ag/AgCl), the auxiliary electrode in platinum). This three-electrode cell is connected to a Potentiostat/Galvanostat µAutolab Type III + FRA 2 controlled by a computer equipped with software allowing selection of the electrochemical technique and the desired parameters (cyclic voltammetry, chronopotentiometry, etc.) and data processing.

Synthesis of $Ni_{0.6}Co_{2.4}O_4$

The nickel cobaltite $Ni_{0.6}Co_{2.4}O_4$was produced by the sol-gel process by mixing 0.435 g of $Ni(NO_3)_2$•$6H_2O$ and 1.74 g of $Co(NO_3)_2$.$6H_2O$ in an excess of propionic acid. This mixture is heated to 120°C in an oven to obtain the gel. Liquid nitrogen is added to the gel to obtain a mixed propionate of cobalt and nickel in powder form. The latter is heated to 140°C to dehydrate it and, subsequently, heat-treated at 350°C for 4 hours to obtain the spinel phase of the mixed oxides [7].

Synthesis of PANI/Pt and PANI @$Ni_{0.6}Co_{2.4}O_4$/Pt films by cyclic voltammetry

For the electrosynthesis of polyaniline on the platinum electrode (figure 1): the aniline

monomer (10^{-1} M) is dissolved in the electrolytic solution H_2O/HCl 0.5 M then the synthesis is carried out at a scanning speed equal to 20mV/s in a potential range between – 0.2 and 1V/ Ag/AgCl at room temperature [8, 9].

The electropolymerization of the PANI@$Ni_{0.6}Co_{2.4}O_4$ (0.5 and 1g/L)/Pt composite films (figures 2.a and b) was carried out in the same electrochemical cell using the same optimal conditions with levels of different $Ni_{0.6}Co_{2.4}O_4$ oxides (0.5g/L, 1g/L)incorporated into the electrolyte. Before each synthesis, the bath (aniline + HCl + $Ni_{0.6}Co_{2.4}O_4$) is stirred under ultrasound and is kept under magnetic stirring with a low frequency during electrosynthesis.

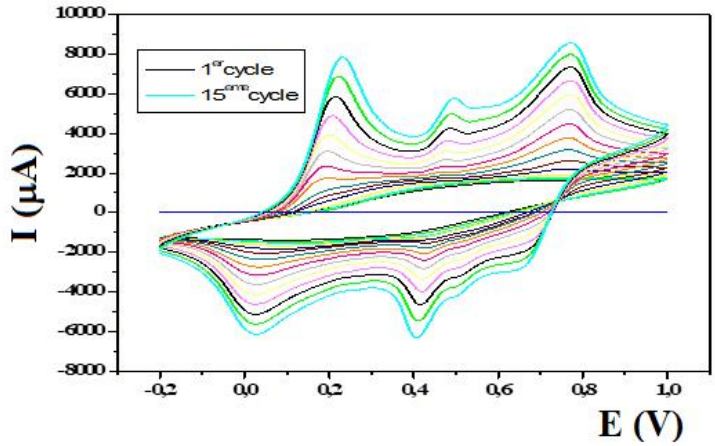

Figure 1: Voltammograms of polyaniline electrosynthesis: 0.1M aniline in 0.5M HCl at a rate of 20mV/s

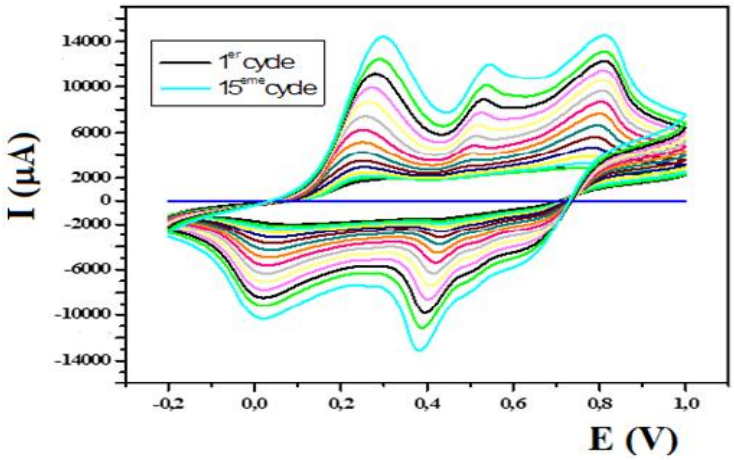

Figure 2. a : Voltammograms of *PANI@$Ni_{0.6}Co_{2.4}O_4$* polyaniline electrosynthesis: 0.1M aniline. *$Ni_{0.6}Co_{2.4}O_4$ (0,5 g/L)* in 0.5M HCl at a rate of 20 mV/s

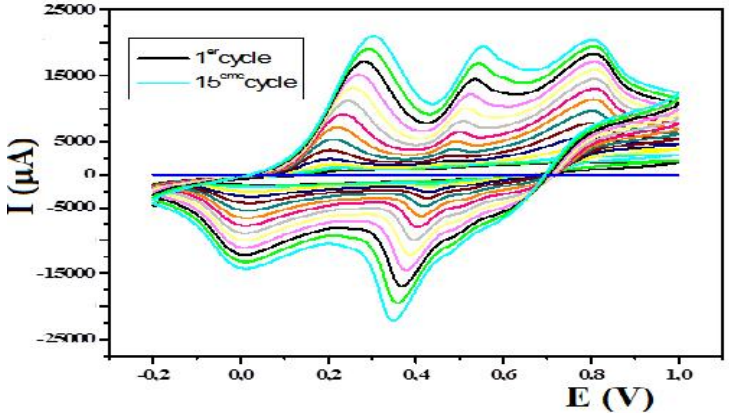

Figure 2.b : : Voltammograms of *PANI@$Ni_{0.6}Co_{2.4}O_4$* polyaniline electrosynthesis: 0.1M aniline. *$Ni_{0.6}Co_{2.4}O_4$ (01 g/L)* in 0.5M HCl at a rate of 20 mV/s

Results and Discussions

X-ray diffractograms of $Ni_{0.6}Co_{2.4}O_4$, PANI, and PANI@$Ni_{0.6}Co_{2.4}O_4$

X-ray diffraction was used to examine the crystallinity of our products and verifie the insertion of the particles during the polymerization of polyaniline. It was done using a Siemens D-500 type diffractometer configured in Bragg-Brentano mode.

The diffractograms are represented in Figure 3, the diagram (a) presents peaks corresponding to the reflections of the planes 111, 220, 222, 311, 400, 422 and 440. These diffraction lines are characteristic of a crystallized phase of the spinel type in accordance withthe file (JCPDS No. 73-1702). The diffractogram (b) shows a broad peak at the 110 plane characteristic of PANI. The diffractogram (c) shows characteristic peaks of polyaniline (plane 110) and nanoparticles of $Ni_{0.6}Co_{2.4}O_4$of spinel structure (planes 111, 220, 311, 222, 400, 422 and 440) confirming the insertion of the nanoparticles nickel cobaltite in polyaniline.

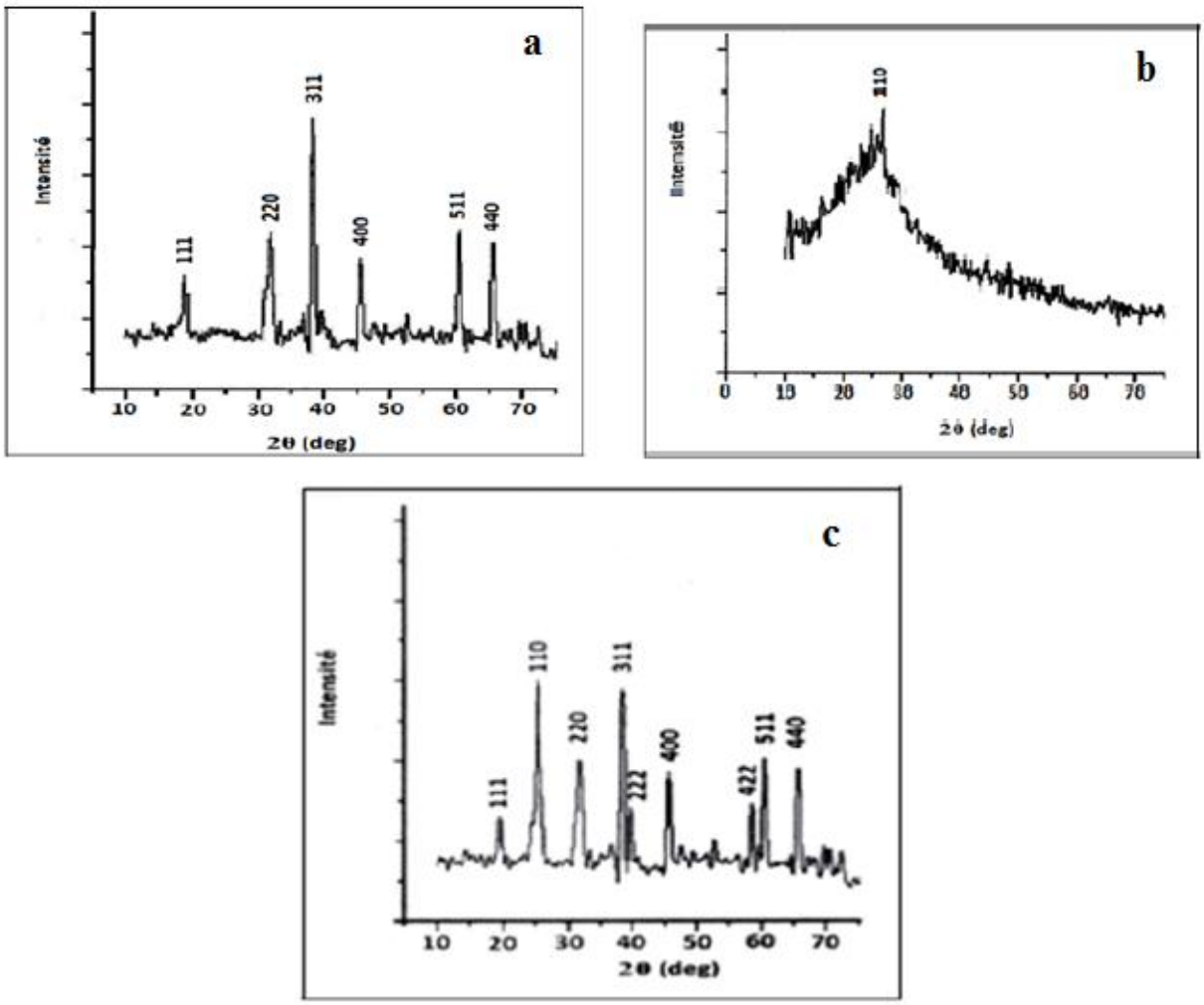

Figure 3 *: X-ray diffractograms of $Ni_{0.6}Co_{2.4}O_4$ (a), polyaniline (b) and PANI @$Ni_{0.6}Co_{2.4}O_4$ (c)*

Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Figure 4 shows scanning electron microscopy (SEM) images of $Ni_{0.6}Co_{2.4}O_4$oxide associated with energy dispersion spectra (EDS). In micrograph 4.a one can note the form of micronic aggregates of poorly dispersed sizes, and the absence of platelets. It reveals a good dispersion of the prepared mixed oxide powders. The associated EDS shows characteristic peaks of the main elements of the mixed oxide prepared according to increasing atomic number, namely oxygen, cobalt and nickel. Figures 4.b and 4.c images show the morphology of our films, in both cases, the structure of the films synthesized is in the form of interconnected aggregates. Compared to pure PANI (Fig.4.b), the PANI@$Ni_{0.6}Co_{2.4}O_4$composite (Fig.4.c) appears to exhibit a coarser structure. This observed change shows that the cobalt and nickel oxide particles have been integrated into the PANI via adequate interconnections. The EDS spectra in Figures 4.b and 4.c confirm the presence of cobalt and nickel oxide particles in the polyaniline matrix. Indeed, we observe peaks characteristic of the main elements of polyaniline, namely carbon and nitrogen in Figure 4.b and peaks of the elements carbon, nitrogen, oxygen, nickel and cobalt characteristic of the composite PANI@$Ni_{0.6}Co_{2.4}O_4$in Figure 4.c. The element chlorine represented in the spectra is a constituent of the acid used during electrosynthesis.

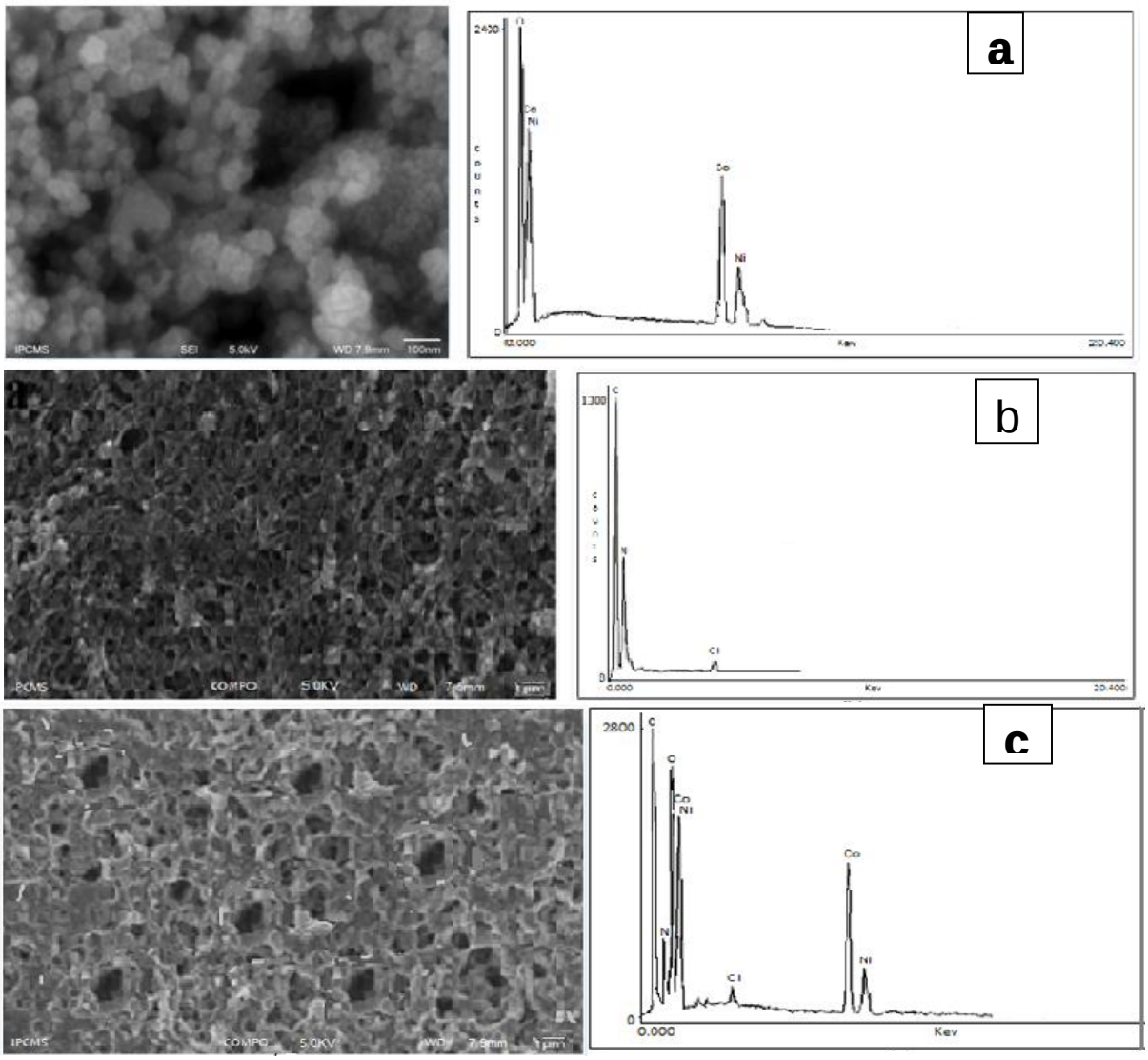

Figure 4: *SEM and EDS of$Ni_{0.6}Co_{2.4}O_4$ (a), PANI (b) and PANI@$Ni_{0.6}Co_{2.4}O_4$ (c).*

Characterization of films by cyclic voltammetry

Cyclic voltammetry has the particularity of being able to both develop a material and then characterize it [10].

The voltammograms in figures 5 and 6 all show the successive appearance of three oxidation peaks and three reduction peaks which correspond to the different forms of PANI: leucoemeraldine, emeraldine and pernigraniline, described in the literature. Hao et al obtained these three forms of PANI in HCl medium [11].

♣ The first anodic peaks obtained around, E = 0.18 V/Ag/Ag/Cl show the oxidation of the reduced form of PANI in the form of radical-cation,
♣ The second peaks, towards E = 0.42 V/Ag/Ag/Cl illustrate the oxidation of intermediate compounds or that of secondary products,
♣ The third peaks obtained around E = 0.8 V/Ag/Ag/Cl would explain the oxidation of the PANI, deposited on the platinum plate by aniline [12-16].

In addition, we note that the presence of the nanoparticles of $Ni_{0.6}Co_{2.4}O_4$ did not affect the usual progress of the process of electropolymerization of the polyaniline since no reaction relating to the mixed oxide was noted in this area of potential. However, their presence increased the oxidation and reduction current intensities, which suggests an enhancement of the electroactivity of polyaniline [17]. The increase in electrical charges reflects an improvement in the storage capacity of polyaniline in the presence of nickel cobaltite nanoparticles during electrosynthesis.

Characterization of films by galvanostatic charge-discharge

Energy density and power are key criteria to get an idea of the efficiency and performance of the materials used in the energy storage device.

The study of the galvanostatic charge / discharge, in order to know the values of the energy and power densities of the PANI/Pt and PANI@$Ni_{0.6}Co_{2.4}O_4$ /Pt films, is therefore imperative. Using the potentiostat, we imposed a constant current density (0.1A/g) and varied the potential between two predefined values (0 and 0.75V). The curves obtained are shown in Figure 5.

From the data collected on the curves, we calculated the specific capacities, the energy densities and the powers using equations (1), (2) and (3).

$$C_s = \frac{I_m \Delta t}{\Delta V} \text{(Eq.1)}; E = \frac{C_s \Delta V^2}{2} \text{(Eq.2)}; \quad P = \frac{E}{\Delta t} \text{(Eq.3)}$$

Cs: Specific capacity (F/g); Im: Discharge current (A/g); Δt: discharge duration (hour); ΔV: Potential window; E: Energy density (Wh / Kg); P: Power (W/Kg)

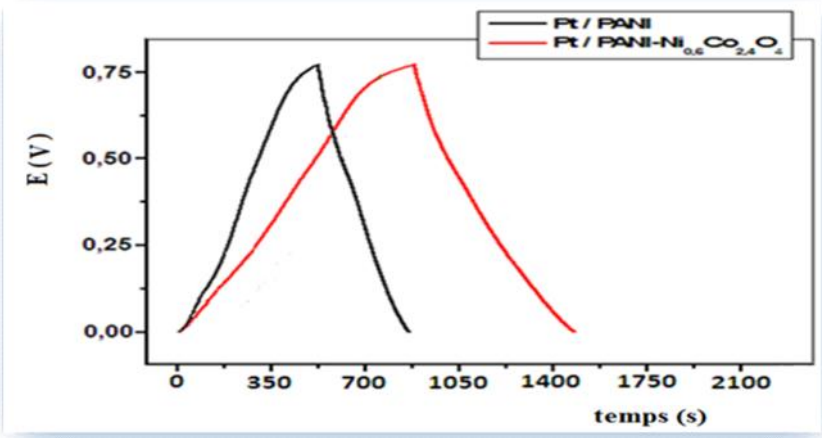

Figure 5: *Galvanostatic charge-discharge curves of PANI/Pt, PANI@$Ni_{0.6}Co_{2.4}O_4$.(1g/L)/Pt at a current density of 0.1A. g^{-1} in 0.5M HCl.*

Table 1: Values of the energy and power densities of the PANI/Pt and PANI@$Ni_{0.6}Co_{2.4}O_4$ ($1g.L^{-1}$)/Pt composite films at a current density of 0.1 $A.g^{-1}$

Film	E ($Wh.Kg^{-1}$)	P ($W.Kg^{-1}$)
PANI/Pt	6,25	36,8
PANI@$Ni_{0,6}Co_{2,4}O_4$($1g.L^{-1}$)/Pt	10,3	37,2

For the PANI/Pt electrode, the energy density and the power are respectively 6.25$Wh.kg^{-1}$ and 36.8 W.kg. Following the addition of $1g.L^{-1}$of $Ni_{0.6}Co_{2.4}O_4$ in the composite electrode, the values move to10.3 $Wh.kg^{-1}$ for the energy and 37.2 $W.kg^{-1}$ for the power. This considerable increase in energy density of 65% resulting from the addition of mixed oxide particles proves that the latter have increased the active surface of the electrode [18].

For the reproducibility of single-current charge/discharge cycles, we observe triangular-shaped curves (Figure 6) recorded with a current density of 0.1 A/g in the same environment. The curves reveal satisfactory behavior in cycling, the calculation of the capacity during the discharge phases shows a slight decrease in value which goes from 133.2 $F.g^{-1}$ to 129.15 $F.g^{-1}$ after about fifty cycles (Figure 6). This attests that the PANI@$Ni_{0.6}Co_{2.4}O_4$/Pt electrode has good cycling stability. The drop in capacitance during cycling is usually caused by an increase in resistance due to degradation of the active materials.

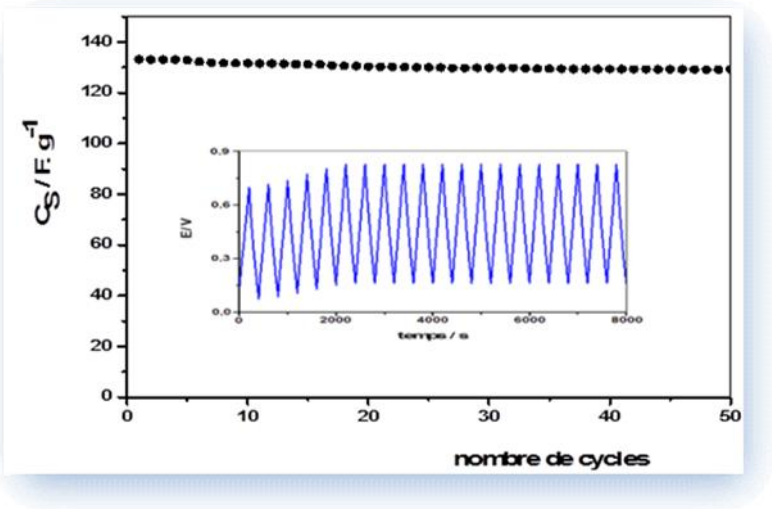

Figure 6: *Variation of the specific capacitance of the PANI@$Ni_{0.6}Co_{2.4}O_4$ /Pt electrode with the number of charge/discharge cycles.*

Conclusion

PANI and PANI@$Ni_{0.6}Co_{2.4}O_4$films were synthesized on a platinum substrate by cyclic voltammetry. Physical characterization, by conventional methods (X-ray, SEM, EDS), confirmed the nature of the synthesized products. It was observed that the presence of the nanoparticles of cobalt and nickel oxide during the electropolymerization of aniline gave rise to a film of coarser and more porous morphology than that of the PANI film, which can be also favorable to charge transfer by providing more active sites for faradic reactions. The electrochemical properties were compared and the composite films showed better performance. The composite PANI@$Ni_{0.6}Co_{2.4}O_4$having the highest concentration of $Ni_{0.6}Co_{2.4}O_4$ ($1g.L^{-1}$) gave the best energy and power densities due to the presence of $Ni_{0.6}Co_{2.4}O_4$ which acts as an ion conductor. This new composite material is therefore promising for electrochemical

applications, such as use as an electrode material for supercapacitors with reference to the Ragone diagram.

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