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RESEARCH ARTICLE

DEVELOPMENT AND CHARACTERIZATION OF A NANOCOMPOSITE BASED ON POLYANILINE MODIFIED BY THE INCORPORATION OF NANOPARTICLES OF MIXED OXIDE OF COBALT AND NICKEL ($NI_{0.6}CO_{2.4}O_4$) WITH A SPINEL STRUCTURE.

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ABSTRACT

The search for good electroactive materials for electrochemical applications is attracting increasing interest in the field of electrons chemistry. It is in this context that we have developed the nanocomposite PANI / Ni_{06} $Co_{2.4}O_4$ in order to reinforce the properties of polyaniline. We synthesized nickel and cobalt mixed oxides nanoparticles with spinel structure $Ni_{06}Co_{24}O_4$, films of polyaniline and polyaniline / $Ni_{0.6}$ Co_{24} O_4 nanocomposite. The mixed oxide nanoparticles were prepared by the sol-gel method via propionic acid route, the polyaniline and polyaniline / $Ni_{0.6}Co_{24}O_4$ nanocomposite films were prepared electrochemically via cyclic voltammetry. Physical and electrochemical characterizations were made by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), cyclic voltammetry and electrochemical impedance spectroscopy. XRD, FTIR and SEM confirmed the structure of the synthesized products and the incorporation of $Ni_{0.6}Co_{2.4}O_4$ in the nanocomposite films. Electrochemical analyzes of the films revealed a higher conductivity of PANI / $Ni_{0.6}$ Co_{24} O_4 nanocomposite films compared to the PANI films.

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INTRODUCTION

The world's electrical energy needs are largely met (80%) (1) by the use of non-renewable fossil fuels such as oil, coal, gas, etc. The rest is distributed between solar, hydroelectric, geothermal, wind energy sources... So, as the world population increases, energy needs increase and it now appears inevitable that this consumption will exhaust existing fossil resource. In addition, the use of these fossil fuels increases significantly greenhouse gases. In this context, the research of promising materials for energy production and storage systems is topical. Conductive polymers such as polyaniline, polypyrrole, polythiophene and their derivatives have already been explored as electrode materials due to their good conductivity (2). Among these conductive polymers, polyaniline (PANI) has been widely studied due to its mechanism of doping / dedoping by simple proton exchange, its intrinsic electrical conductivity, easy synthesis and environmental stability (3, 4). In addition, it is a suitable material as a composites matrix (5). Likewise, spinel oxides mixed with different transition metals have generated considerable interest in research due to their exceptional electrochemical properties, their rich redox reactions involving different ions, and their synergistic effects (6). Compared to simple metal oxides, mixed metal oxides exhibit high electrical resistance, good conductivity due to lower activation energy for electron transfer between cations(7). Among them, spinel mixed transition metal oxides of nickel and cobalt exhibit rich redox reaction from both nickel and cobalt cation. They are low cost, abundant and harmless to the environment (8). Zhu (9) has shown that the spinel $NiCo_2O_4$ prepared by the sol gel method has an ultra-high specific capacity. Despite the qualities of polyaniline, it exhibits poor cycling stability due to volumetric changes during the doping / dedoping process (10).

Nanoscale polyaniline films have been synthesized to resolve cycling degradation (11, 12). In addition, the use of nanometric inorganic fillers in the PANI matrix gives materials with complementary behavior between PANI and inorganic nanoparticles. Kanatzidis et al (13), ones of the pioneers in the study of nanocomposites based on polyaniline, synthesized chemically the PANI / V_2O_5 nanocomposite with good electrical behavior. Therefore, the development of nanocomposites have received considerable attention. Various metal oxides such as Fe_3O_4, TiO_2, MnO_2, NiO, ZnO and SnO_2 have been tested, to improve the conductivity of conductive polymers. Huo et al (14) studied the PANI - MnOx nanostructured 3D composite. Ternary polyaniline nanocomposites (CS - ZnO / PANI) were successfully synthesized by Pandiselvi K (15). PANI / RuO_2 and graphene / PANI / CNT (16, 17) films of good specific capacity were prepared by X. Li and X.J. Lu. $NiCo_2O_4$ / PANI and PANI / $NiCo_2O_4$ composites were chemically synthesized respectively by P. Tamilarasan (6) and by Hui Xu (18) while the PANI / $NiCo_2O_4$ nanocomposite electrochemically synthesized in an HCl solution is not yet reported to our knowledge. In this work, we synthesized PANI / $Ni_{0.6}Co_{2.4}O_4$ nanocomposites by electropolymerization of aniline via the cyclic voltammetry method in an HCl solution (1M) in the presence of $Ni_{0.6}Co_{2.4}O_4$ nanoparticles. The latter were prepared by sol-gel method via propionic acid route. The structure and morphology of our products has been studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The electrochemical properties of PANI and the PANI / $Ni_{0.6}Co_{2.4}O_4$ nanocomposite were studied by cyclic voltammetry and three-electrode electrochemical impedance spectroscopy.

Experimental methods

Chemicals and devices: Cobalt nitrate hexahydrate ($Co(NO_3)_2$, $6H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2$, $6H_2O$) are used in the synthesis $Ni_{0.6}Co_{2.4}O_4$ nanoparticles. Aniline (Aldrich product), also known as aminobenzene, phenylamine or benzeneamine, $C_6H_5NH_2$, is used for the polyaniline electropolymerization and PANI / $Ni_{0.6}Co_{2.4}O_4$ nanocomposite. Acidified water (hydrochloric acid at 1M concentration) is used for electrochemical syntheses, propionic acid and liquid nitrogen are used for the preparation of nickel and cobalt mixed oxides. All electrochemical measurements were carried out in a glass cell containing the electrolysis solution in which three electrodes are immersed (working electrode in platinum disc, reference electrode in silver (Ag / AgCl), and auxiliary electrode in platinum). The three electrodes cell is connected to a µAutolab Type III + FRA 2 Potentiostat / Galvanostat controlled by a computer equipped with software allowing the electrochemical technique and the desired parameters to be selected (cyclic voltammetry, impedance spectroscopy, etc.) and data processing.

Synthesis of $Ni_{0.6}Co_{2.4}O_4$: The mixed oxide samples were prepared in the form of powders by the sol gel route. The amounts of $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ in mass ratios of 10:40 mixed together are dissolved in an excess of propionic acid. The solution is then heated to 120 °C in an oven to evaporate the excess of propionic acid and form a gel. Liquid nitrogen is immediately added to obtain a mixed cobalt nickel propionate. The powder is heated to 140 °C to remove the excess of water and subsequently heat-treated at 350 °C to obtain the spinel phase of the mixed oxides.

The balance equation for the chemical reaction leading to the mixed oxide $Ni_{0.6}Co_{2.4}O_4$ is

$$3\,Ni(NO_3)_2.6H_2O + 12\,Co(NO_3)_2.6H_2O \rightarrow 5\,Ni_{0.6}Co_{2.4}O_4 + 10\,N_2O_5 + 10NO_2 + 90\,H_2O$$

The quantities (in masses) used are given in Table 1.

Synthesis of polyaniline: The electrochemical synthesis of polyaniline was carried out using the cyclic voltammetry method. The aniline monomer (0.1 M) is dissolved in the electrolyte solution (HCl 1 M). Then the synthesis is carried out at a scanning rate of 20 mV/s in a potential range between -0.2 and 1 V / Ag / AgCl at room temperature.

Synthesis of the polyaniline / $Ni_{0.6}Co_{2.4}O_4$ nanocomposite: The electrochemical synthesis of PANI / $Ni_{0.6}$ $Co_{2.4}$ O_4 nanocomposite films was carried out in the same electrochemical cell using the optimal conditions previously studied: Different oxide contents of $Ni_{0.6}Co_{2.4}O_4$ (0.1 g/L, 0.5 g/L, 1 g/L) were added to the electrolyte. Before each synthesis, the solution (aniline + HCl + $Ni_{0.6}Co_{2.4}O_4$) is stirred under ultrasound. During the electropolymerization process, mechanical stirring is used in order to maintain $Ni_{0.6}Co_{2.4}O_4$ particles in permanent contact with the platinum electrode where the film is deposited.

RESULTS AND DISCUSSION

X-ray diffract grams of PANI, $Ni_{0.6}Co_{2.4}O_4$ and PANI / $Ni_{0.6}Co_{2.4}O_4$: The crystallinity of our products and the confirmation of particle insertion during the polymerization of polyaniline were examined by X-ray diffraction with a Siemens D-500 type diffractometer configured in Bragg-Brentano mode. Diffract grams are shown in Figure 3, diagramm (3.a) shows a wide peak at plane 110 characteristic of PANI. The diffractogram (3.b) shows 7 peaks corresponding to the reflections of planes 111, 220, 222, 311, 400, 422 and 440. These diffraction lines are characteristic of a crystallized phase of spinel type according to the file (JCPDS No. 73-1702). The diffractogram (3.c) shows peaks which reveal the presence of polyaniline (plane 110) and $Ni_{0.6}Co_{2.4}O_4$ nanoparticles of spinel structure (planes 111, 220, 311, 222, 400, 422 and 440) in the analyzed product.

Table 1. Masses of nickel and cobalt nitrates used as precursors

Reagents	Mass in grams
$Ni(NO_3)_2.6H_2O$	0.870
$Co(NO_3)_2.6H_2O$	3.480

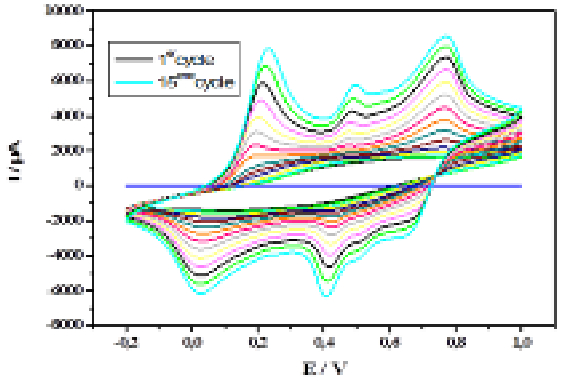

Figure 1. Voltammograms of the electopolymerization of 0.1M aniline electrode in 1M HCl ET scan rate of 20m V/s

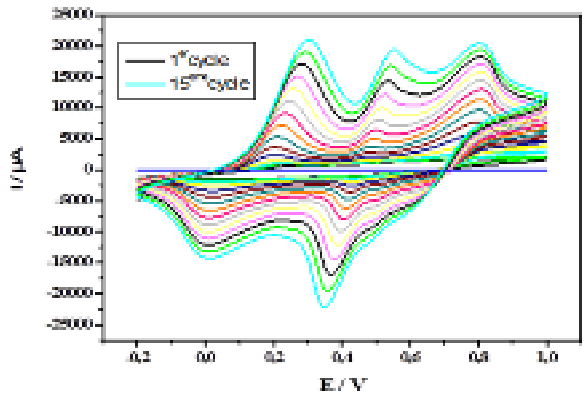

Figure 2. Voltammogram of the electropolymerization of the 0.1M aniline composite electrode, Ni06 $Co_{24}O_4$ (01 g/L) in 1MHCl at a rate of 20 mV/s

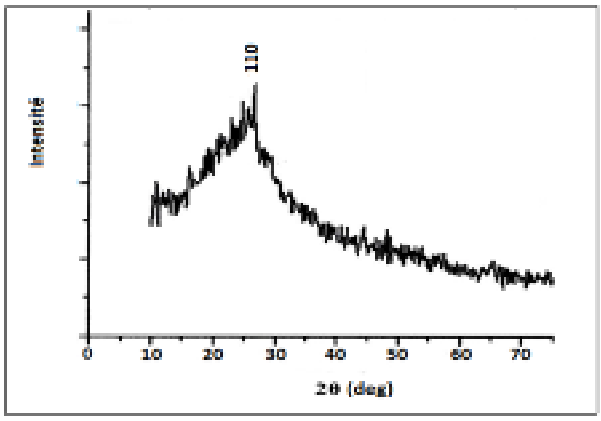

Figure 3. a. X ray diffractograms of poluaniline

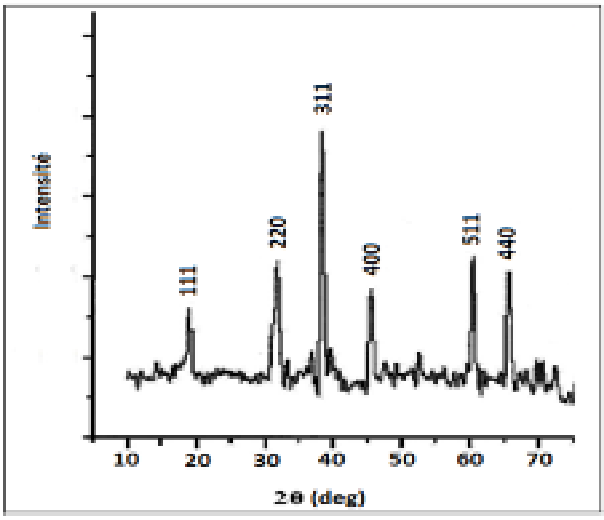

Figure 3. b. X-ray diffractograms of Ni 0.6 $CO_{2\cdot}{}_4O_4$

Optical characterization by infrared (IR): The IR spectra analysis of polyaniline and that of the polyaniline / $N_{i0.6}$ $Co_{2.4}$ O_4 nanocomposite reveals the characteristic bands of polyaniline and mixed oxide indicating the coexistence of the two phases (19 - 23). In Figure 4, a band appears around 3400 cm^{-1}, this band is attributed to the antisymmetric stretching of the NH_2 group (19). The wide band between 2400 and 3000 cm^{-1} is attributed to the symmetrical and antisymmetric O - H vibrations modes of the adsorbed water molecules and the hydroxyl groups on the surface of the polyaniline (20). The peaks between 1500 and 1600 cm^{-1} are associated with the stretching of the aromatic rings.

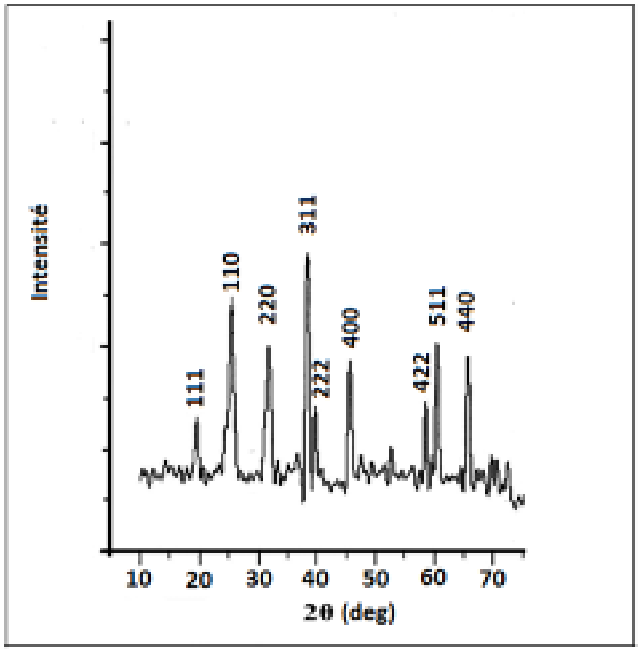

Figure 3. C. X-ray diffractograms of PANI/ Ni0.6 $C0_{2\cdot4}O_4$

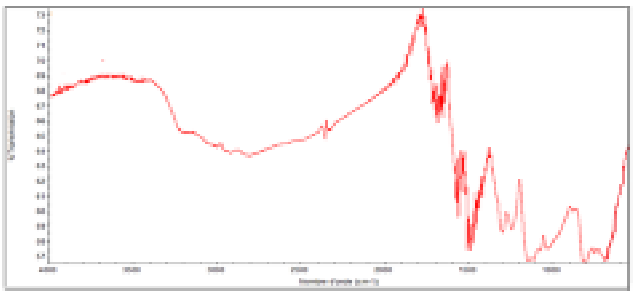

Figure 4. IRTF spectrum of polyaniline

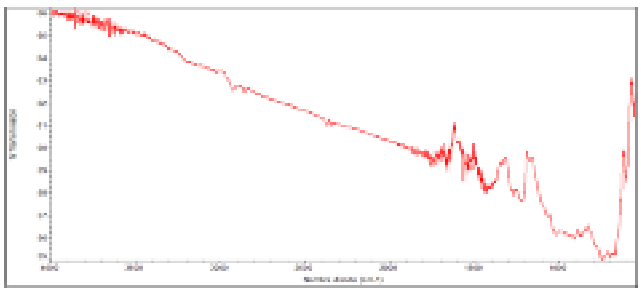

Figure 5. IRTF spectrum of polyaniline/ Ni0.6 $C0_{2\cdot4}O_4$

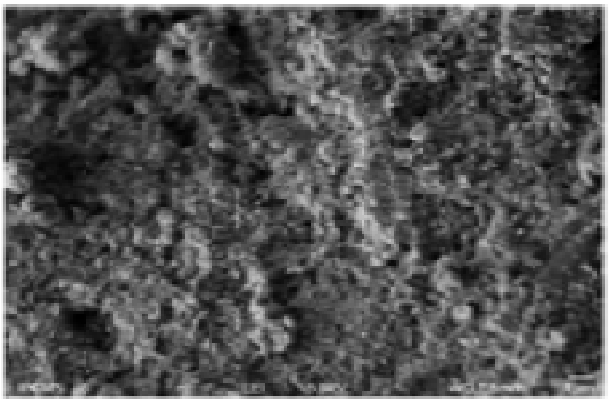

Figure 6.a SEM images of PANI

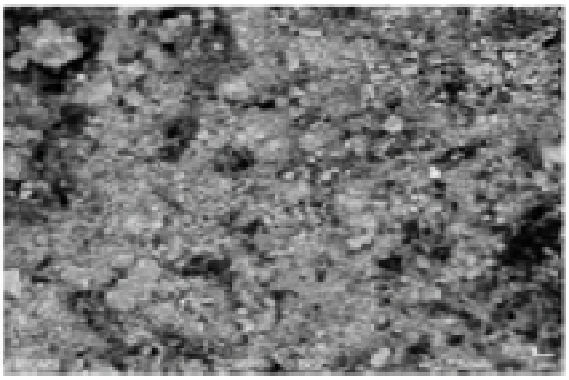

Figure 6. b. SEM images of PANI/ Ni0.6 $C0_{2\cdot4}O_4$

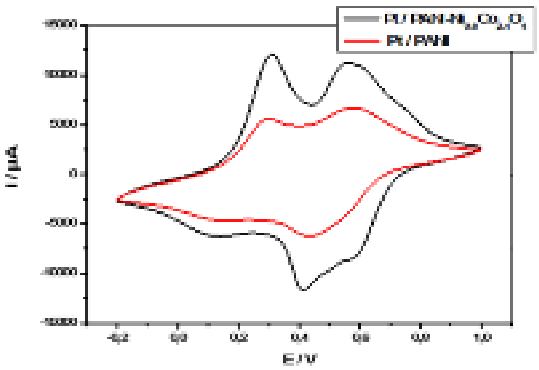

Figure 7. Electroactivity of PANI and PANI/ Ni0.6 $C0_{2\cdot4}O_4$ (lg/L) in HCl (1M) with a speed of 20mV/s

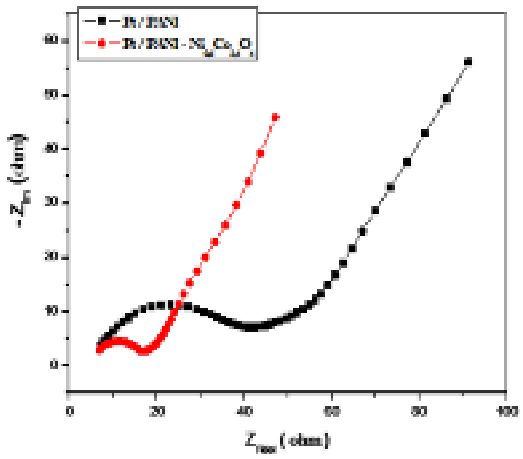

Figure 8. Nyquist plane impedance diagram of PANI/ Ni0.6 $C0_{2\cdot4}O_4$ (lg/L) ($lg.L^{-1}$) in aqueous medium containing 1MHCL

They are attributed to C = N and C = C the quinoid and benzoid units of polyaniline stretching modes (21). Peaks between 1200 and 1300 cm^{-1} are assigned to the C - N stretching mode of the benzene ring (22). The peak around 1200 cm^{-1} is characteristic of the conductive form of polyaniline (22).We notice that the characteristical benzene peak rings is greater than that of the quinoid rings, which confirms that it is the emeraldine salt that is synthesized (24). The bands observed between 1150 and 800 cm^{-1} are attributed to the deformation vibrations of C-H in the quinoid rings (N = Q = N) and out of the plane of the quinoid and benzoid rings (19). Figure 5 shows characteristic peaks of PANI located at 1570, 1490 and 1300, 1240, 1140 cm^{-1} and 880 cm^{-1}. These peaks correspond to the benzoid rings (NH-B-NH), the stretching of C = C benzene rings, the stretching mode of C - N, the out-of-plane deformation of aromatic CH, and the quinoid ring (NH - Q - NH) (19 - 22). The two bands between 550 and 650 cm^{-1} are attributed to the vibrations of the metal-oxygen bonds, confirming the presence of nickel and cobalt oxide nanoparticles in the obtained nanocomposite (19, 23).

Scanning electron microscopy: To study the surface morphology of PANI and PANI / $Ni_{0.6}Co_{2.4}O_4$ powders, the films were observed under a scanning electron microscope with a Hitachi model S-520 apparatus at a voltage of 5.0 kV. Figure 6 shows the surface morphologies of the samples. In both cases, the structure of the obtained films is in the form of interconnected aggregates. Compared to pure PANI (figure 6.a), the PANI / $Ni_{0.6}$ $Co_{2.4}O_4$ nanocomposite (figure 6.b) appears to have a coarser structure. From the observation of these images, we can clearly perceive a change in the structure of the polyaniline figure (6.a) compared to the polyaniline / $Ni_{0.6}Co_{2.4}O_4$ film. From the observed change, one can deduce that the nanoparticles of nickel cobaltite oxide were integrated uniformly into the polyaniline matrix.

Characterization by cyclic voltammetry: Cyclic voltammetry has the particularity of being able to both develop a material and then characterize it (25). The study by cyclic voltammetry showed that the presence of nanoparticles of $Ni_{0.6}Co_{2.4}O_4$ did not affect the usual course of the electropolymerization process of aniline and that no reaction relating to the mixed oxide has been noted in this potential(figure 7). However, their presence increased the oxidation and reduction currents, suggesting that mixed oxide particles offer more active sites favorable to charge transfer for faradic reactions. The $Ni_{0.6}Co_{2.4}O_4$ nanoparticles then increase the conductivity of the polyaniline.

Electrochemical impedance: The electrochemical characteristics of films via electrochemical impedance spectroscopy are studied in this part of the work. Aqueous medium containing HCl (1 M) was used. The frequency range was varied from 0.1 Hz to 10 kHz. The Nyquist diagrams of the Pt / PANI and Pt / PANI / $Ni_{0.6}Co_{2.4}$ O_4 (1 $g.L^{-1}$) films obtained at the potential (0.2 V) are shown in Figure 8. The impedance curves both have two parts: a semicircle in the high frequency region and a straight line in the low frequency region, which are characteristic of charge transfer and mass transfer processes, respectively. All the arcs have the same origin point. That's means the resistance of the electrolyte remains unchanged. However, the diameter of the PANI / $Ni_{0.6}Co_{2.4}O_4$ film semicircle is smaller. Since the diameter of the high frequency loop is directly related to the resistance of the film, one can see that the PANI / $Ni_{0.6}Co_{2.4}O_4$ film is significantly less resistant than the PANI film. At low frequency, the steeper slope close to 90° of the PANI/ $Ni_{0.6}Co_{2.4}O_4$ nanocomposite compared to that of the polyaniline, indicates the more capacitive behavior of the nanocomposite. This certifies that the latter could be used in capacitor electrodes as an active material (26). The shape of the Nyquist diagrams obtained are the same for the two films. This suggests that the phenomena which govern the kinetics are not affected by the presence of $Ni_{0.6}Co_{2.4}O_4$ particles. Using the software (FRA), certain properties such as the resistance of the solution, the load transfer resistance from the EIS spectra have been analyzed: The resistance of the solution is 6.25 Ω for the two films, the load transfer resistance is 37.5 Ω for PANI with a double layer capacitance of 0.71 mFagainst 11.75 Ω and 4.83 mF for PANI / $Ni_{0.6}Co_{2.4}O_4$. These observations show that the charges are much freer in PANI /

$Ni_{0.6}Co_{2.4}O_4$ films. This corroborates the results obtained by cyclic voltammetry. This improvement in conductivity is probably due to the contribution of cobalt and nickel ions from the mixed oxide. These results are in agreement with those found in the literature, for example Zhenyu Luo et al have shown that the insertion of SnO_2 particles into the polyaniline matrix increases the conductivity of the latter (27), N. Harfouche discovered that the PANI / $LiMn_2O_4$ nanocomposite is more conductive than polyaniline (28),he attributed this increase in conductivity to the contribution of Li^+ ions released by $LiMn_2O_4$(29).

CONCLUSION

PANI and PANI / $Ni_{0.6}Co_{2.4}O_4$ films were synthesized by an electropolymerization method on platinum substrates. X-ray diffraction, infrared spectroscopy and scanning electron microcopy confirmed the structure of the products obtained and the incorporation of $Ni_{0.6}Co_{2.4}O_4$ nanoparticles into the polyaniline matrix. The study of the electrochemical properties (cyclic voltammetry and electrochemical impedance) has shown that the PANI / $Ni_{0.6}Co_{2.4}O_4$ nanocomposite has a better performance compared to polyaniline alone. The nanoparticles of mixed oxides of nickel and cobalt then reinforce the qualities of PANI, whereby the latter exhibits better electrochemical behavior in the presence of $Ni_{0.6}Co_{2.4}O_4$. The PANI / $Ni_{0.6}Co_{2.4}O_4$ nanocomposite is therefore a promising material for electrochemical applications.

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