Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

ISSN NO. 2320-5407

Article DOI: 10.21474/IJAR01/15172
DOI URL: http://dx.doi.org/10.21474/IJAR01/15172

RESEARCH ARTICLE

ELABORATION AND STUDY OF THE CAPACITIVE PROPERTIES OF POLYANILINE COMPOSITE FILMS – MIXED OXIDES, NICKEL-COBALT ($NI_{0.6}CO_{2.4}O_4$) ELECTROCHEMICALLY SYNTHESIZED ON A PLATINUM ELECTRODE

Mor Cissé, Mamadou Guèye, Modou Gningue Diop and Makhtar Guène
Organic Physical Chemistry and Environmental Analysis Laboratory, Department of Chemistry, Faculty of Science and Technology, Cheikh Anta Diop University, Dakar, Senegal.

……

Manuscript Info

Manuscript History
Received: 06 June 2022
Final Accepted: 10 July 2022
Published: August 2022

Key words:-
Polyaniline, $Ni_{0.6}Co_{2.4}O_4$, Pani, Composite Films, Mixed Oxides, Nickel-Cobalt., Chronoamperometry, Cyclic Voltammetry, Specific Capacity

Abstract

The design of electrode material for energy production and storage devices is becoming more and more timely in a world where energy is an essential pillar for development. This context urges us to develop and study the capacitive properties of polyaniline composite films – mixed oxide of $Ni_{0.6}Co_{2.4}O_4$ which can be used as electrode material.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. Polyaniline – $Ni_{0.6}Co_{2.4}O_4$ composite films deposited on a platinum substrate (Pt/PANI - $Ni_{0.6}Co_{2.4}O_4$) were prepared by incorporating mixed nickel and cobalt oxide particles into the matrix of polyaniline. This process was realized by chronoamperometry by electropolymerization of the aniline monomer dissolved in a 0.5M HCl electrolyte with different contents of $Ni_{0.6}Co_{2.4}O_4$ oxides (0.5 g/L, 1 g/L).Physical and electrochemical characterizations were made with scanning electron microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS), UV-visible spectroscopy,X-ray diffraction (XRD) and cyclic voltammetry.SEM, EDS, XRD and UV-visible analyzes confirmed the nature of the synthesized products and the incorporation of $Ni_{0.6}Co_{2.4}O_4$ in the composite films. The electrochemical performance measurements of the Pt/PANI-$Ni_{0.6}Co_{2.4}O_4$ film (1 g/L) give a specific capacity about 386.108 $F.g^{-1}$, which is much higher than that of the Pt/ PANI, 164.340 $F.g^{-1}$ at 5 mV/s.

……

Introduction:-

Electronically conductive polymers are highly preferred in electrochemical applications such as sensors, redox capacitors, catalysis and batteries **[1–4]** due to their chemical structure, characterized by alternating single and double bonds ($\pi - \sigma - \pi$) or another type of n-σ-π conjugation (alternating non-bonding doublet–single bond–double bond), energetically favorable to conduction and their high capacity **[5].** Among them, polyaniline occupies a prominent place owing to its conductivity which can reaches 104 $s.cm^{-1}$**[6],** its different oxidation states (leucoemeraldine, emeraldine base, emeraldine salt and pernigraniline) and its good specific capacity **[7, 8].**In order to increase the conductivity, stability and specific capacity of conductive polymers, reinforcements are added to the reaction medium during polymerization to obtain composites.A composite material is, by definition, the association

Corresponding Author:- Makhtar Guène
Address**:-** Organic Physical Chemistry and Environmental Analysis Laboratory, Department of Chemistry, Faculty of Science and Technology, Cheikh Anta Diop University, Dakar, Senegal.

of at least two components of different natures and structures. It makes it possible to obtain a more efficient material than these components taken separately. Composites are generally made up of two parts:

1. reinforcements, generally taking the form of particles or fibers, providing most of the mechanical properties of the composite;
2. a matrix, in which the reinforcements are imprisoned, ensuring the cohesion of the assembly and the transfer of forces as well as other properties.

In this study, we were interested in a new generation of composites based on a porous organic matrix in electronically conductive polymer (polyaniline) in which is incorporated a new phase of nanometric dimensions consisting of particles of mixed nickel and cobalt oxides prepared by the sol-gel method. These oxides offer significant catalytic and electrocatalytic properties, rich redox reactions from both nickel and cobalt cations**[9–12]**.The synthesis of our PANI-$Ni_{0.6}Co_{2.4}O_4$ composite films was carried out by electrochemical method which consists of adding directly $Ni_{0.6}Co_{2.4}O_4$ oxide particles at different concentrations (0.5 and 1g/L) in a 0.5 M HCl solution containing the aniline monomer. Thus, the incorporation of the particles and the electropolymerization of the monomer arise simultaneously. This technique has already been used to develop composites based on PANI or PPy containing different oxides such as PANI/$LiMnO_4$**[6],**PPy/Fe_3O_4**[13-15]**,PPy/MnO_2**[16],**PANI/RuO_2**[17]…**etc.for electrochemical applications. The structure and morphology of our products have been studied by scanning electron microscopy (SEM) coupled with energetic dispersion spectroscopy, visible ultraviolet spectroscopy. Capacitive properties were analyzed by cyclic voltammetry in a three cell electrodes.

Experimental Methods

Chemicals and devices:

Aniline (Aldrich product) $C_6H_5NH_2$is the monomer used for the electropolymerization of Pt / PANI and Pt / PANI - $Ni_{0.6}Co_{2.4}O_4$ films. Nitrate hexahydrate [$Co(NO_3)_2$, $6H_2O$] and nickel nitrate hexahydrate [$Ni(NO_3)_2$, $6H_2O$] are the precursors used to synthesize nickel-cobalt mixed oxides. 0.5M concentration hydrochloric acid was used for the electrochemical syntheses of the films, propionic acid and liquid nitrogen for the preparation of nickel-cobalt mixed oxides.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 aPotentiostat/Galvanostat μAutolab Type III + FRA 2 controlled by a computer equipped with software allowing selection of the electrochemical technique and the desired parameters (chronoamperometry, cyclic voltammetry, etc.) and data processing.The Pt / PANI and Pt / PANI - $Ni_{0.6}Co_{2.4}O_4$ (0.5 and 1g/L) films were characterized by various techniques: scanning electron microscopy coupled with energy dispersive spectroscopy using a Hitachi model S-520 device, UV-visible spectroscopy using a SAFAS 2000 type UV-visible spectrophotometer, X-ray diffraction with a Siemens D-500 type diffractometer configured in Bragg-Brentano mode.

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

The mixed oxides particles were elaborated by sol gel route via propionic acid. 0.435 g of $Ni(NO_3)_2.6H_2O$ and 1.74 g of $Co(NO_3)_2.6H_2O$ are mixed in an excess of propionic acid. To obtain the gel, the excess of propionic acid is evaporated by heating the mixture to 120°C in an oven. 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 to obtain the spinel phase of the mixed oxides.

Synthesis of Pt/PANI and Pt/PANI-$Ni_{0.6}Co_{2.4}O_4$ films by chronoamperometry:

The synthesis of the films was carried out using potentiostatic method (chronoamperometry), consisting of the deposit of polyaniline and polyaniline -$Ni_{0.6}Co_{2.4}O_4$ films on the working electrode (platinum disc) at a constant potential. In this study, a potential of 0.8 V was used for a bias time of 400 seconds. The bath (aniline + HCl + $Ni_{0.6}Co_{2.4}O_4$) is kept constantly stirred during the electropolymerization, using a magnetic stirrer. To avoid the dissolution of the nickel oxide in the hydrochloric acid, the electrolyte bath is slightly stirred and the electrosynthesis took place at room temperature. The synthesis was carried out in a three electrode system containing 0.1 M aniline, 0.5M hydrochloric acid and 0, 0.5 and 1g/L $Ni_{0.6}Co_{2.4}O_4$ mixed oxide.

Results And Discussions:-

Interpretation of chronoamperometric curves:

During the initial stage, the anodic current decreases this corresponds to the process of nucleation. It is also attributed to the formation of a uniform polyaniline film during the polymerization phase by radical coupling **[18].** In this step, the current is controlled by diffusion of the aniline.However, even after the initial step, the anode current continues to increase with the electrolysis time. This stage corresponds to two-dimensional growth progressive nucleation and one-dimensional growth of progressive nucleation**[18].**In addition, the current/time slope is greater in the presence of incorporated mixed oxide particles and increases with the mixed oxide content. This suggests that the polyaniline - $Ni_{0.6}Co_{2.4}O_4$ composite film has greater capacitance and conductivity than polyaniline alone. Similar curves were obtained by G. Zotti et al **[19]** and by A. Sayah **[5].**

Scanning Electron Microscopy and Energy Dispersive Spectroscopy:

Figure 2 shows the scanning electron microscopy (SEM) image of $Ni_{0.6}Co_{2.4}O_4$ oxide and the energy dispersion spectrum (EDS) obtained using a Hitachi model S-520 device under a voltage of 5.0 kV. The SEM microphotograph shows micronic aggregates of poorly dispersed sizes with absence of platelets. It reveals a good dispersion of the prepared mixed oxide powders.The EDS shows characteristic peaks of the main elements of the mixed oxide prepared according to increasing atomic number, namely oxygen, cobalt and nickel.Figures 3.a and 3.c show the morphology of our films. In both cases the structure of the films obtained is in the form of interconnected aggregates. Compared to pure PANI (Fig. 3.a), the composite PANI - $Ni_{0.6}Co_{2.4}O_4$ (Fig. 3.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 3.b and 3.d confirm the presence of cobalt and nickel mixed oxide particles in the polyaniline matrix. Characteristic peaks of polyaniline main elements as carbon and nitrogen are observed in figure 3.b and those of carbon, nitrogen, oxygen, nickel and cobalt characteristic of the composite PANI-$Ni_{0.6}Co_{2.4}O_4$ in figure 3.d.The chlorine represented appearing in the spectra is from the acid used during electrosynthesis.

UV-visible spectral analyzes:

The spectrum of pure PANI shows two absorption bands at 380-420 nm and 680-900 nm (Figure 4.a) characteristic of the emeraldine salt form of PANI. The band between 380-420 nm is a combination of the π-π* transitions of the benzenoid rings (~350 nm) and the polaron band (~430 nm) and the absorption band observed between 780 - 900 nm is attributed to the bands π- polarons of doped PANI in its emeraldine salt form **[20 –22].**Similar bands were observed with a slight shift towards the highest wavelength in the case of the PANI-$Ni_{0.6}Co_{2.4}O_4$ composite film (figure 4.b) but the absorption intensity band in the visible domain of the composite film is greater than that of the pure PANI. This may be attributable to the strong interaction between the mixed oxide particles and the polymer chain which seems to promote conjugation within the composite film.

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 5, diagramm (5.a) shows a wide peak at plane 110 characteristic of PANI. The diffractogram (5.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 (5.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.

Electroactivity of Pt/PANI-$Ni_{0.6}Co_{2.4}O_4$ film:

The electrochemical response (electroactivity) of the film obtained was analyzed by cyclic voltammetry in an 0.5M HCl aqueous solution. The study was conducted in a potential range between -0.2 and 1 V/Ag/AgCl with scan rates of 5 mV/s, 10 mV/s, 15 mV/s, 20 mV/s, 25 mV/s and 30mV/s.The voltammograms obtained (figure 6) show that the synthesized film is electroactive in the aqueous medium (HCl, 0.5M). This is highlighted by the appearance of three peaks which reflect the oxidation and reduction of the different forms of polyaniline. They also allow to highlight a very interesting property of polyaniline, namely the doping and dedoping phenomenon which means its ability to pass from the reduced state to the oxidized state and vice versa during a voltammetry cycle. In our case, the films are doped with Cl^- chloride anions. One can see that the intensity of these peaks increases with the scanning rate. In fact; during rapid scanning stage, the diffusion layer cannot extend far from the surface of the electrode, thus facilitating a higher flow of electrolyte to the electrode and leading to a greater value of the electric current, unlike in the case of low sweep speeds where the large width of the diffusion layer reduces considerably the flow of electrolyte towards the working electrode and therefore a decrease in current **[23].**We also observe a shift of the anodic and cathodic peaks towards the increasing and decreasing potentials respectively with the increase in the scanning rate. This shifting of the peaks indicates an enhanced of the electrochemical bias at high scan rates **[24–26].**

Kinetics of electrochemical systems in the composite electrode:

To study the electrochemical kinetics of the electroactive system and its reversibility, the values of the peaks currents (Ip) and potentials (Ep) of the oxidation and reduction processes noted on the voltammograms of figure 6 have been plotted to obtain the curves Ip as a function of the square root of the scan rate ($v^{1/2}$) and as a function of the scan rate (v) (Figures 6 and 7). The current intensities of the peaks vary with the scanning rate (v) according to a the type relation$I_p = k.v^{1/2}$**[27, 28]**. The linearity of the curves $I_p = f(v^{1/2})$(Figure 7) and of$I_p = f(v)$ (Figure 8) indicates that the redox reactions proceed rapidly at the electrodes [**24, 28**] and reflects a prevalence of the diffusion phenomena on the absorption phenomena due to the correlation coefficients of the curves$I_p = f(v^{1/2})$ (0.99968 in oxidation and -0.99789 in reduction) are closer to 1 than those of the curves I_P = f(v) (0.9901 and -0.9976). That's mean the diffusion of electrolytic Cl^- ions is a rate-controlling process **[29 - 32].**A slope of absolute value 4.70 was found in reduction and a slope of 3.80 in oxidation. The ratio of the two slopes is equal to 1.2. This value, close to unity, shows a fairly good reversibility of the electrochemical system studied and the symmetrical nature of the redox peaks of the voltammograms taken at different scanning speeds confirms it **[24, 33, 34].**

Capacitive properties:

The characterization of the capacitive performance of the films obtained was analyzed by cyclic voltammetry in a 0.5M HCl aqueous medium and without any monomer and/or mixed oxide.Figures 9.a, 9.b and 9.c illustrate the cyclic voltammograms of Pt/PANI and Pt/PANI-$Ni_{0.6}Co_{2.4}O_4$ (0.5 and 1g.L^{-1}) composite films performed in a potential interval from -0.2 to 1V, relative to the Ag/AgCl electrode, and at different scanning rates (5, 10, 20, 25, 30 mVs^{-1}). The analysis of the cyclic voltammetry curves of the Pt/PANI-$Ni_{0.6}Co_{2.4}O_4$ films with those of Pt/PANI shows an increase in the charge and discharge curves surfaces of Pt/PANI-$Ni_{0.6}Co_{2.4}O_4$ compared to those of Pt/PANI. In addition, the curves surfaces increase with the content of incorporated nickel-cobalt mixed oxide nickel cobalt.An evolution of the anodic and cathodic currents is observed with the concentration of nickel and cobalt mixed oxide. And that the currents are higher in the composite PANI- $Ni_{0.6}Co_{2.4}O_4$ (1g.L^{-1}) where the mixed oxide content is higher. These observations show that the charges are much freer in the films of PANI-$Ni_{0.6}Co_{2.4}O_4$.This corroborates the results obtained by chronoamperometry. This improvement in conductivity is probably due to the contribution of cobalt and nickel ions from the mixed oxide.The values of the specific capacities of the synthesized films (Table 1) were obtained using equation 1.

$$\mathrm{SC} = \frac{\int_{E1}^{E2} i(E)dE}{2(E_2 - E_1)mV} \qquad (\mathrm{Eq.}\,1)$$

SC: specific capacity.
E_2-E_1: Potential window in cyclic voltammetry (CV).
$\int_{E1}^{E2} i(E)dE$: Voltammetric load obtained by integration of the CV curve.
m: mass of the film deposited on the working electrode.
V: sweep rate.

The results show that the specific capacities of the Pt/PANI film are lower than those of the Pt/PANI-$Ni_{0.6}Co_{2.4}O_4$ films. And that the capacity increases with the mixed oxide content, the values with 1 g.L^{-1} are higher than those with 0.5g.L^{-1}.At 5 mV/s, the specific capacitance of the Pt/PANI electrode is 164.340 F.g^{-1}, it increases to 386.108 F.g^{-1} following the incorporation of 1 g.L^{-1} of $Ni_{0.6}Co_{2.4}O_4$. A significant increase in the specific capacity is then noted. It can be deduced that the pseudo capacitance of the polyaniline and its porosity increase in the composite film. The porosity of the film facilitates the movement of charge carriers and the pseudocapacitive effect of polyaniline results from surface oxidation-reduction reactions.Mixed oxides of nickel and cobalt ($Ni_{0.6}Co_{2.4}O_4$) have exceptional electrochemical properties, due to their rich oxidation-reduction reactions involving nickel and cobalt ions and their synergistic effects **[32].**The immersion of these particles in the matrix of the polyaniline offers a more extensive contact interface between the polymer and the electrolyte **[35-38],** a larger active electrochemical surface, it is then obvious that the specific capacity increases with the film mixed oxide content. Similar results are reported in the literature, Sayah et al had a capacity increase from 176.29 F.g^{-1} to 305.57 F.g^{-1} by incorporating 3mg of grapheneinto the FTO/PANI film with a slew rate of 5 mV/s **[5].**J. H Shendkar et al found an average capacity of

215 $F.g^{-1}$ for the PANI /$Co(OH)_2$ composite with a scan rate of 10 mVs^{-1} in a 1M NaOH medium **[39].**N. Harfouche obtained a raise of significant capacitance with the PANI-$LiMn_2O_4$ film on a platinum substrate attributed to the contribution of Li^+ ions released by $LiMn_2O_4$**[6].**In figure 10, the specific capacities are represented according to the sweep rates speeds, all the capacities decrease with the increase of the sweep rate. Indeed, when with the scanning rate increases, the diffusion of Cl^- ions decreases. The ions can only reach the outer surface of the electrode thus the active material inside is not fully involved in the electrochemical process, so the decrease in capacity **[40].**Nevertheless, it should be noted that, among the three films, that of PANI–$Ni_{0.6}Co_{2.4}O_4$ (1g/L) offers the best specific capacities. This capacitance gain due to the presence of mixed oxide particles confirms that the latter allow a more efficient transport of electrons and ions within the surface of the composite electrode and improve the pseudo capacitance of the polyaniline.

Conclusion:-

The composite films of PANI-$Ni_{0.6}Co_{2.4}O_4$ were prepared by the electrochemical method via chronoamperometry on a platinum substrate. The characterization of the films by SEM, EDS, XRD and UV-vis allowed to verify the nature of our products. The UV-visible spectra show a more intense polaronic band of the composite film favoring electronic conduction compared to the pure polyaniline film.Tests to estimate the specific capacitance of Pt/PANI-$Ni_{0.6}$ $Co_{2.4}O_4$ films by cyclic voltammetry revealed that these films would be good materials for energy storage devices such as supercapacitors. Indeed, a significant increase in specific capacity is noted following the incorporation of $Ni_{0.6}Co_{2.4}O_4$ particles. The specific capacitances are worth 164.340 $F.g^{-1}$and 386.108 $F.g^{-1}$ respectively for Pt/PANI and Pt / PANI- $Ni_{0.6}Co_{2.4}O_4$ electrode ($1g.L^{-1}$).This is due to the beneficial contribution of the electronic conduction of the nickel and cobalt mixed oxide particles.

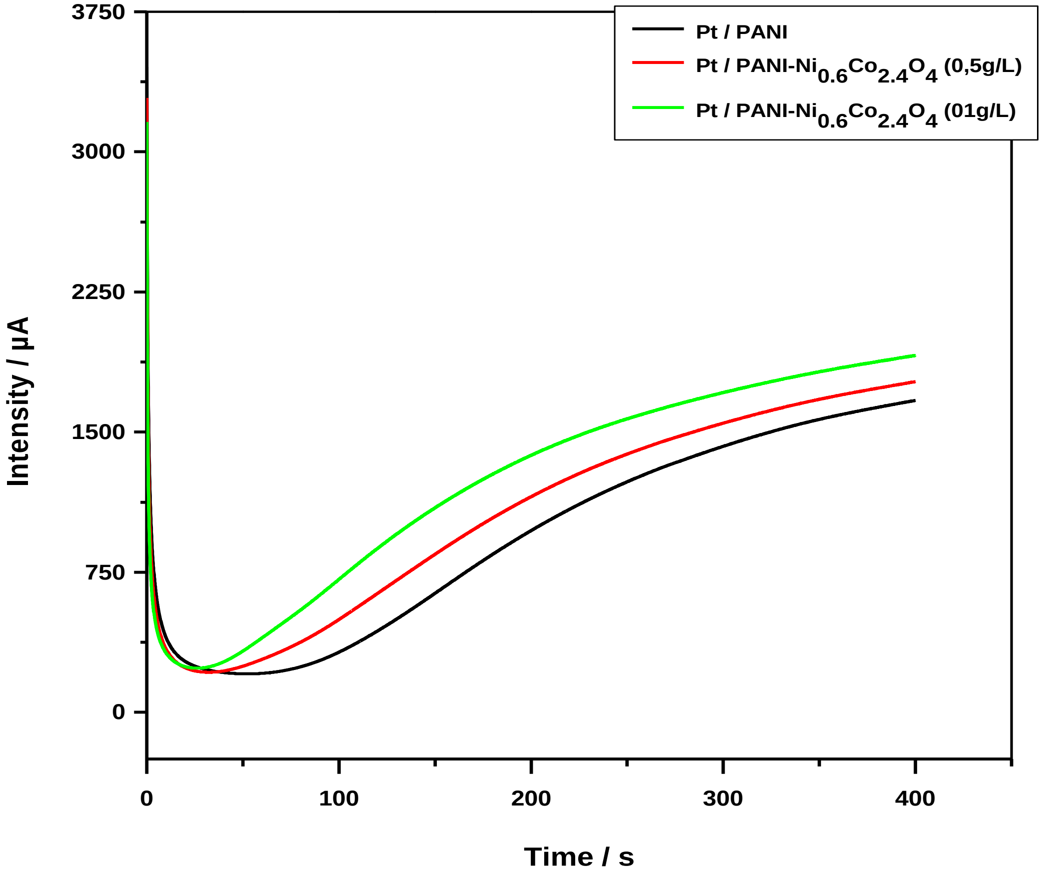

Figure 1:- Potentiostatic curves of Pt/PANI, Pt/PANI-$Ni_{0.6}$ $Co_{2.4}$ O_4 (0.5 and 1g/L) deposits at 0.8 V during 400 s.

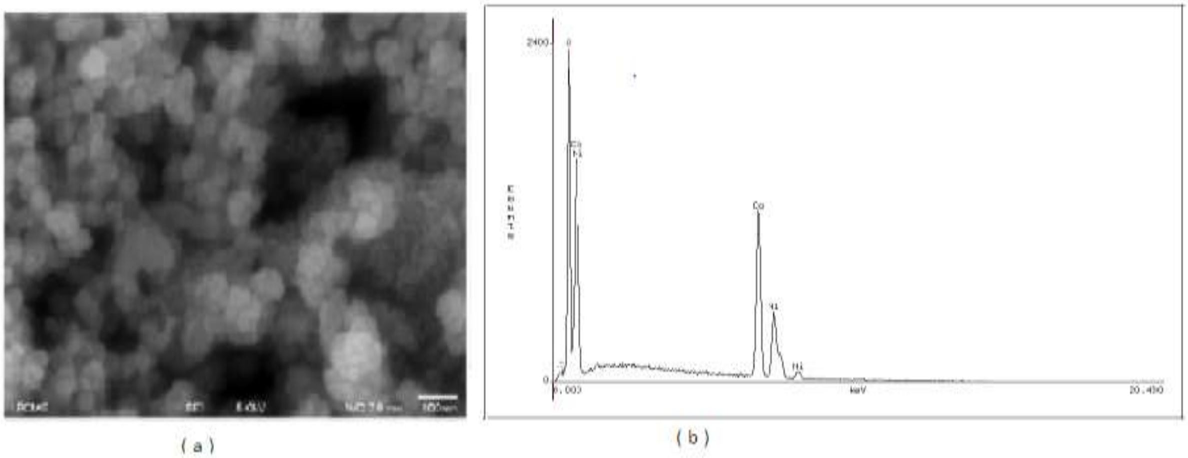

Figure 2:- SEM micrographs and EDS spectrum of $Ni_{0.6}Co_{2.4}O_4$ oxide.

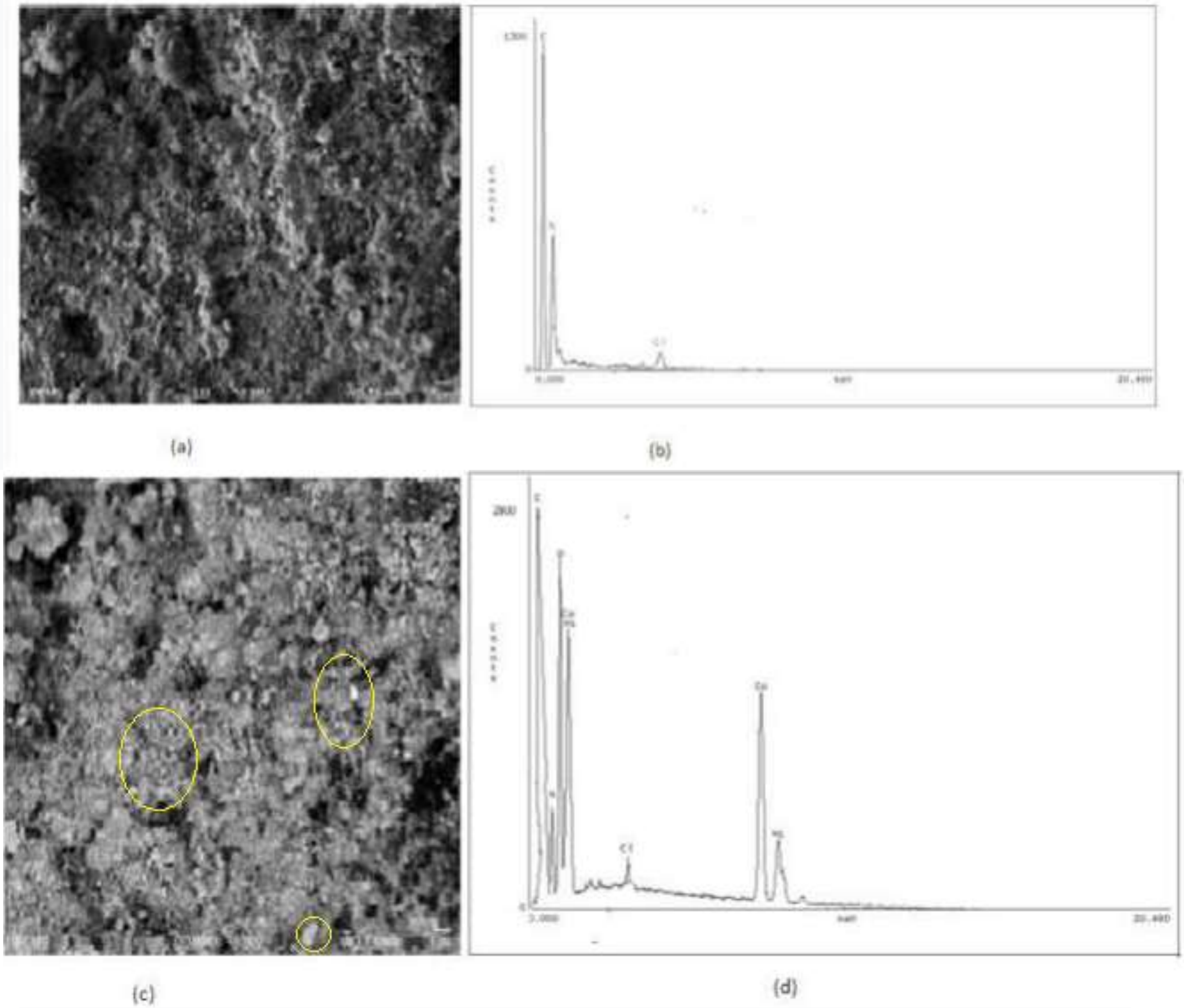

Figure 3:- SEM images of PANI (a) and PANI/$Ni_{0.6}Co_{2.4}O_4$ (c). EDS of PANI (b) and PANI / $Ni_{0.6}Co_{2.4}O_4$ (d).

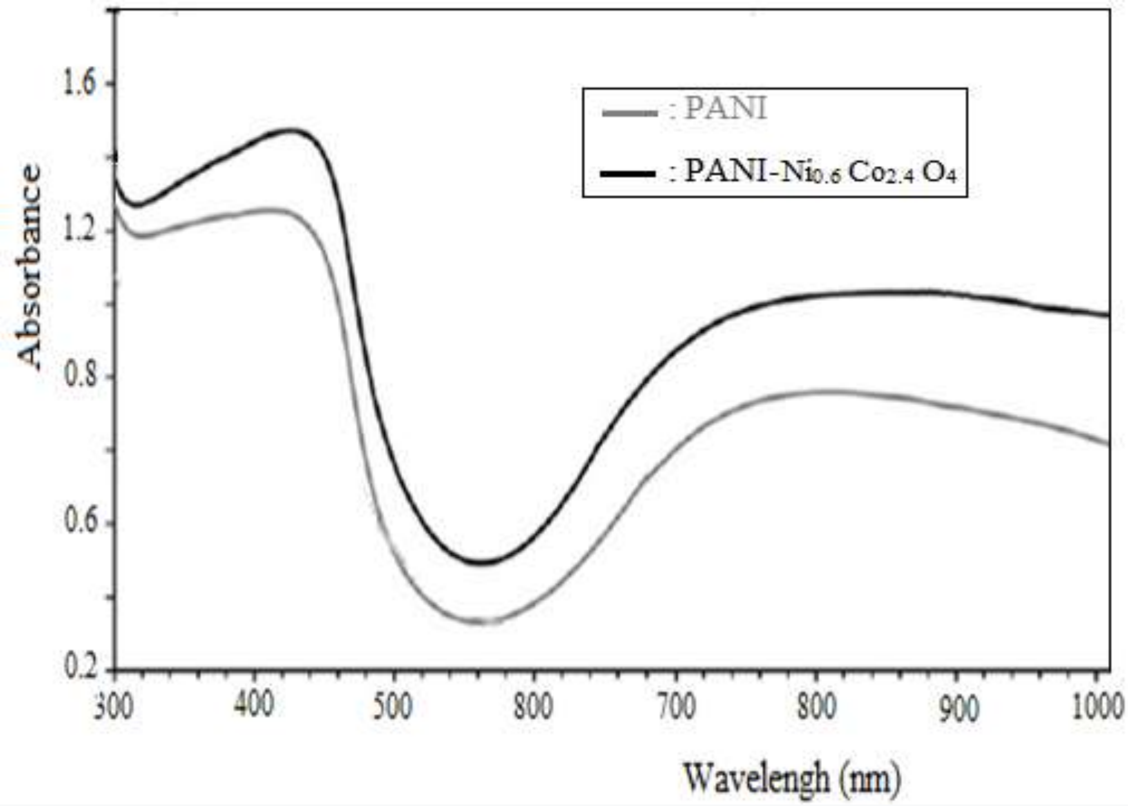

Figure 4:- UV spectra of polyaniline and polyaniline - $Ni_{0.6}Co_{2.4}O_4$.

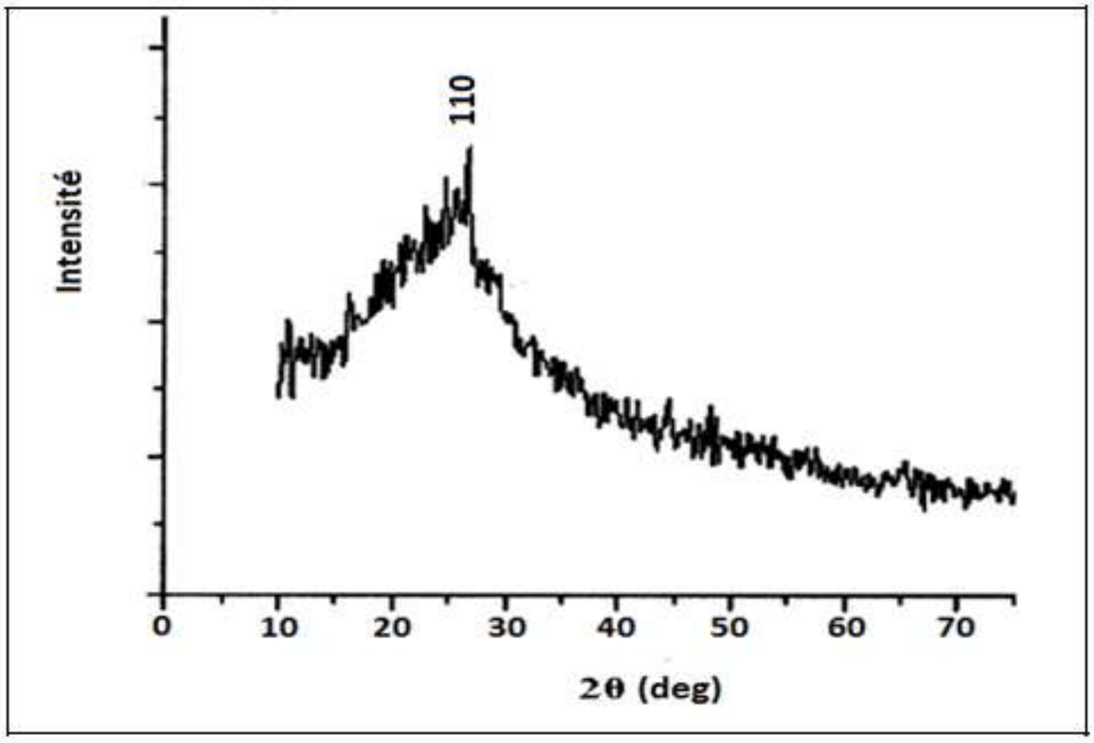

Figure 5.a:- X ray diffractograms of polyaniline.

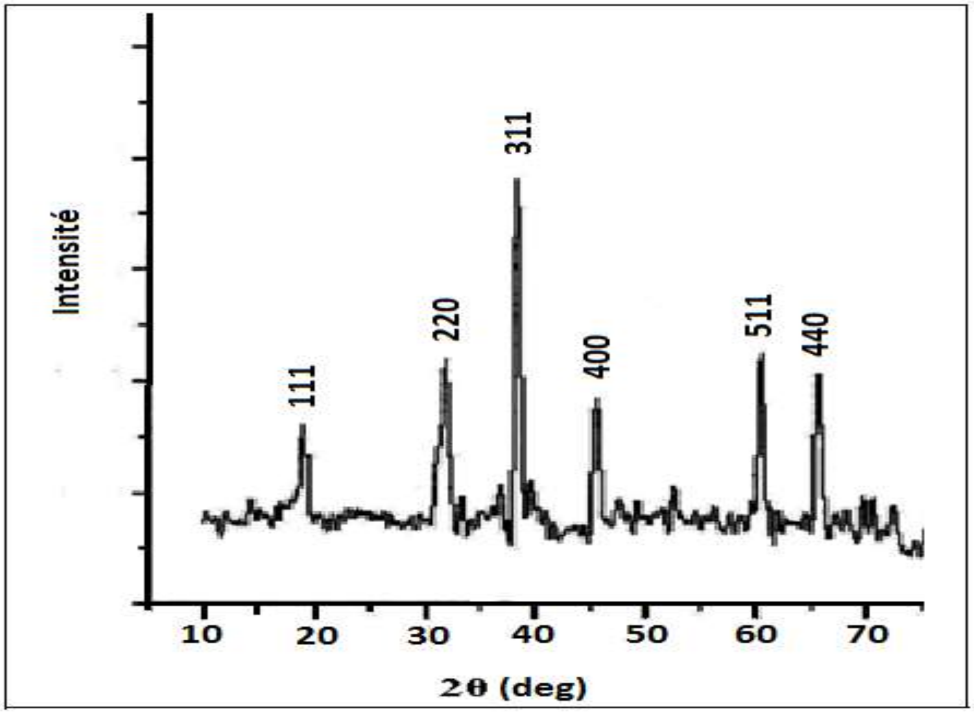

Figure 5.b : **X ray diffractograms of $Ni_{0.6}Co_{2.4}O_4$**

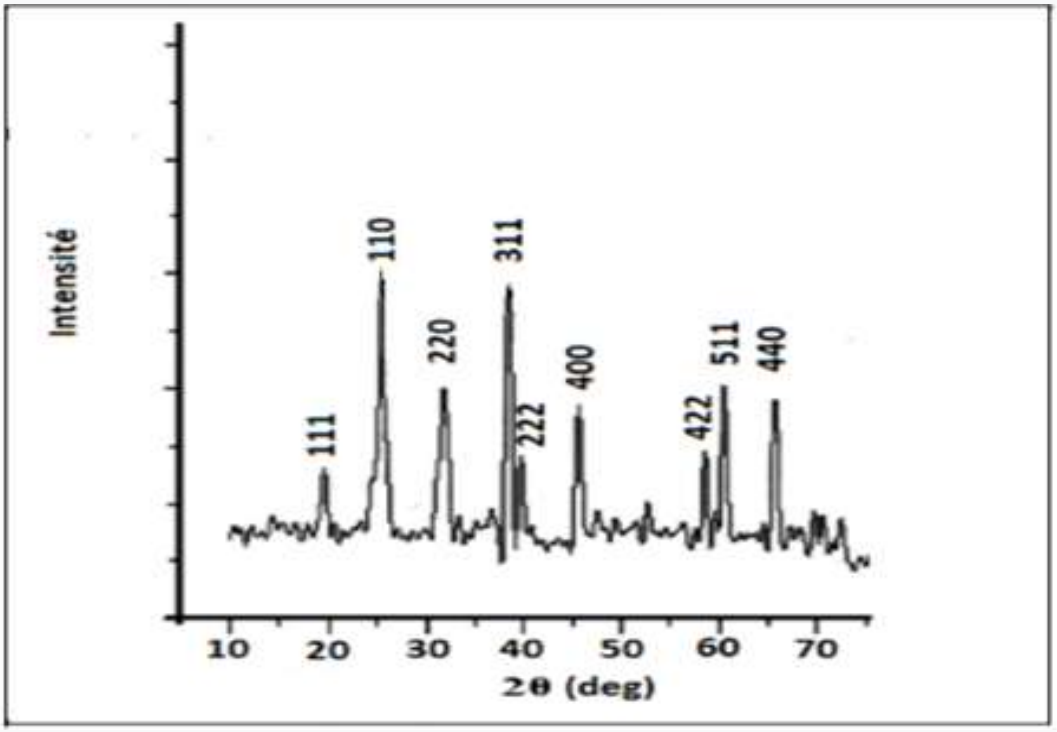

Figure 5.c:- X ray diffractograms of PANI-$Ni_{0.6}Co_{2.4}O_4$.

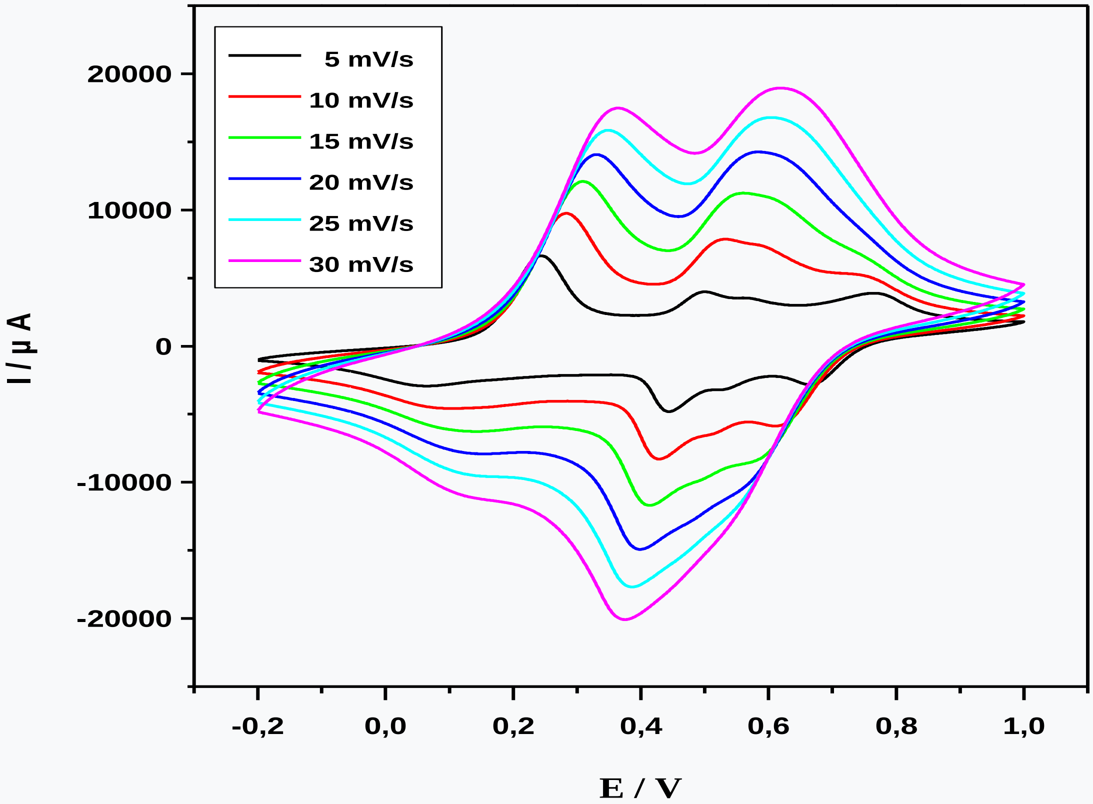

Figure 6:- Electroactivity of the PANI/$Ni_{0.6}Co_{2.4}O_4$ composite obtained by cyclic voltammetry in a 0.5M hydrochloric acid medium.

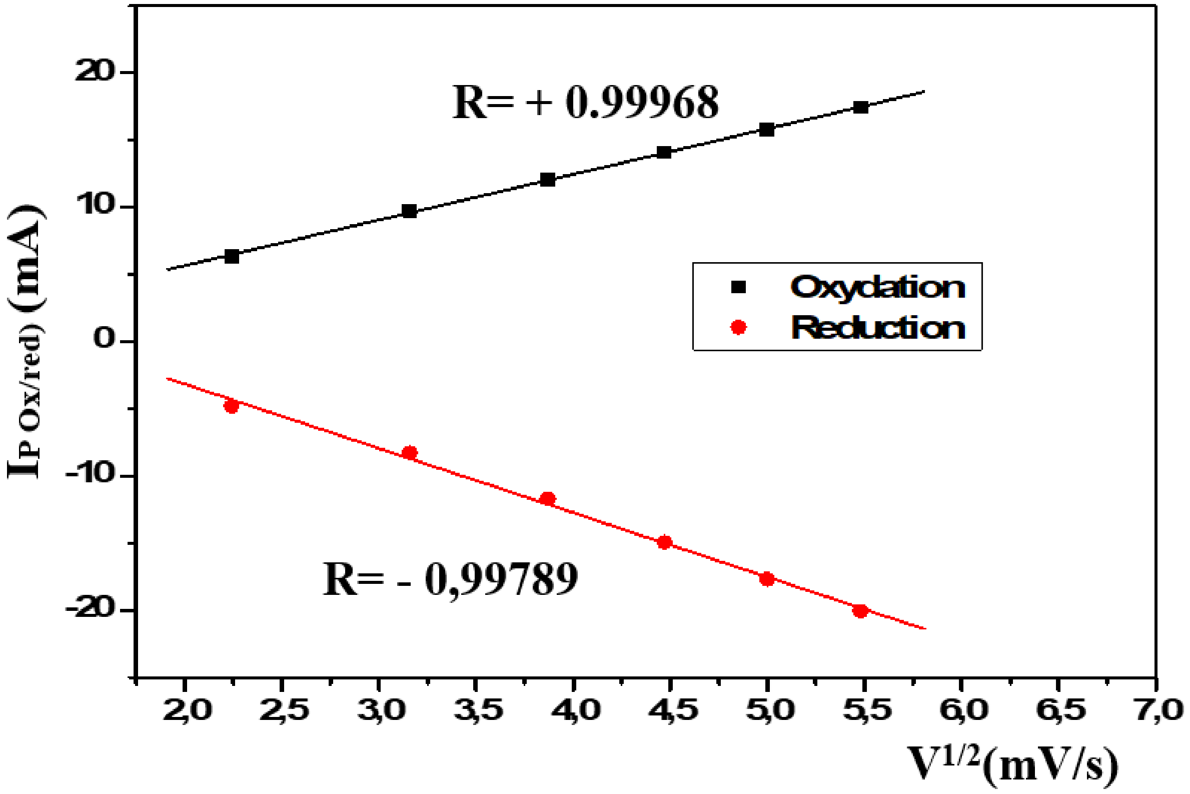

Figure 7:- Current intensity peaks (Ip) as a function of square root of slew rate.

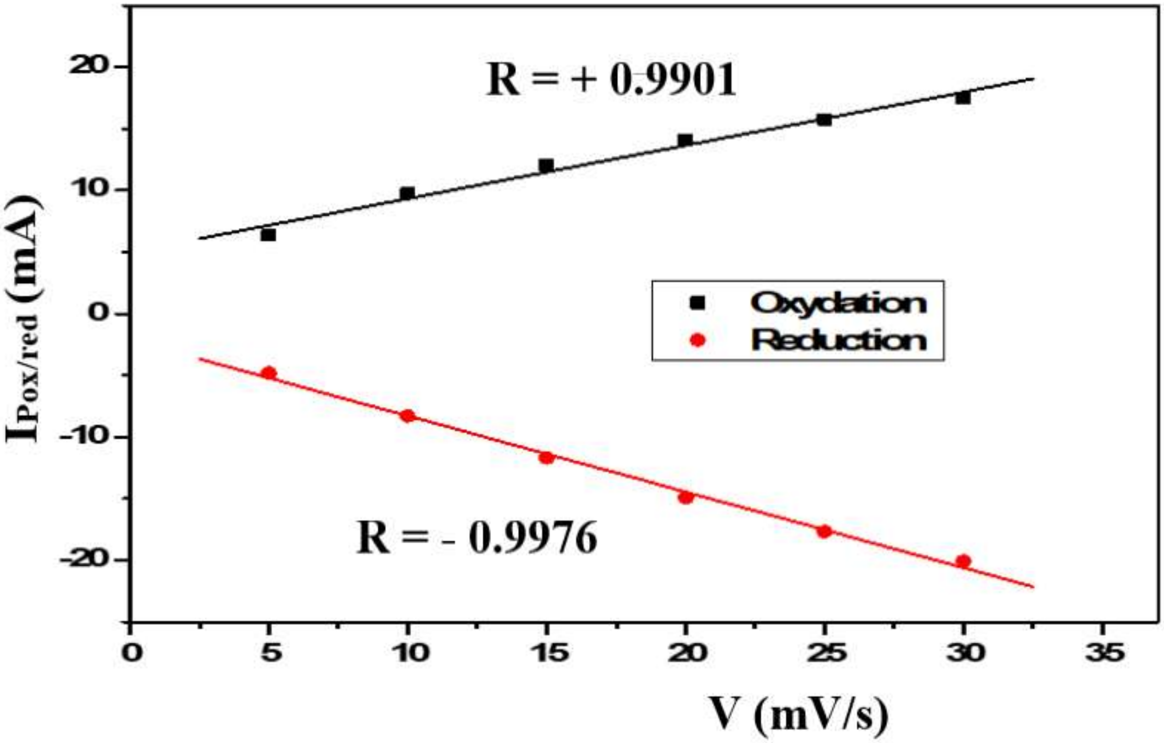

Figure 8: Current intensity peaks (Ip) as a function of sweep speed.

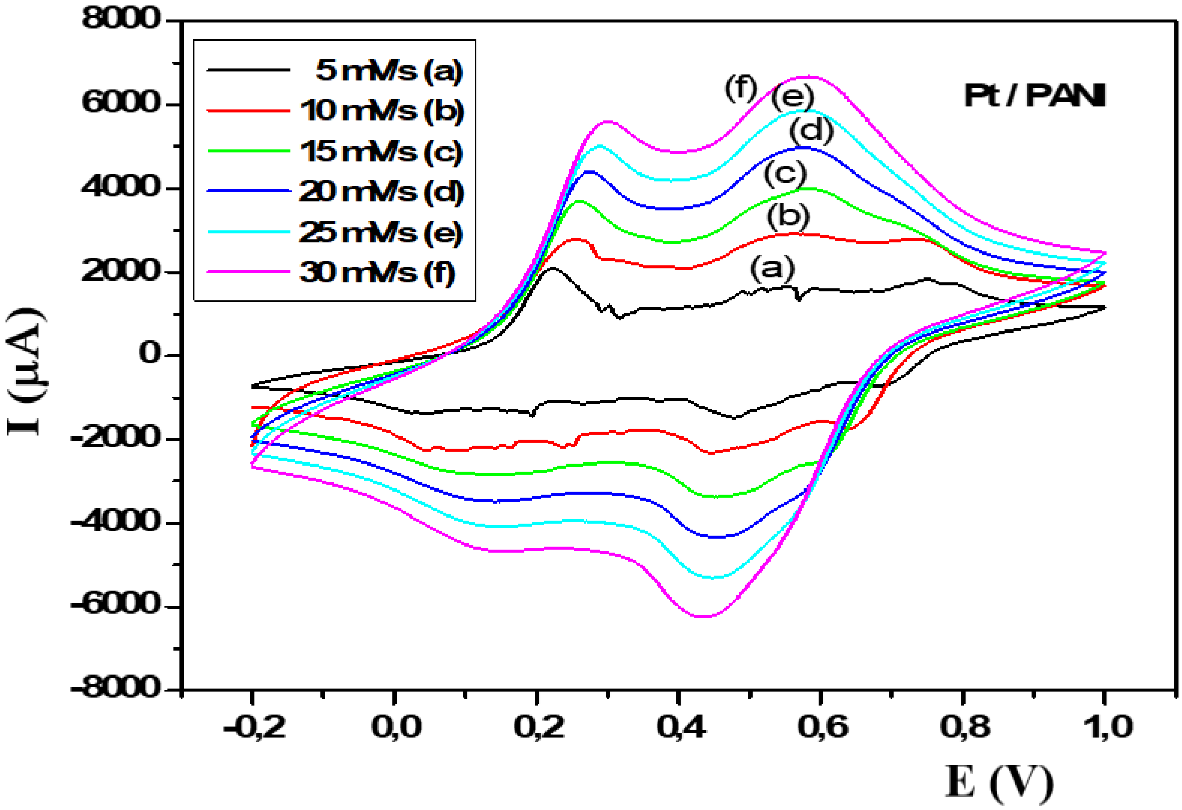

Figure 9.a:- Cyclic voltammogram of Pt/PANI film in a 0.5 M HCl solution at different scanning speeds.

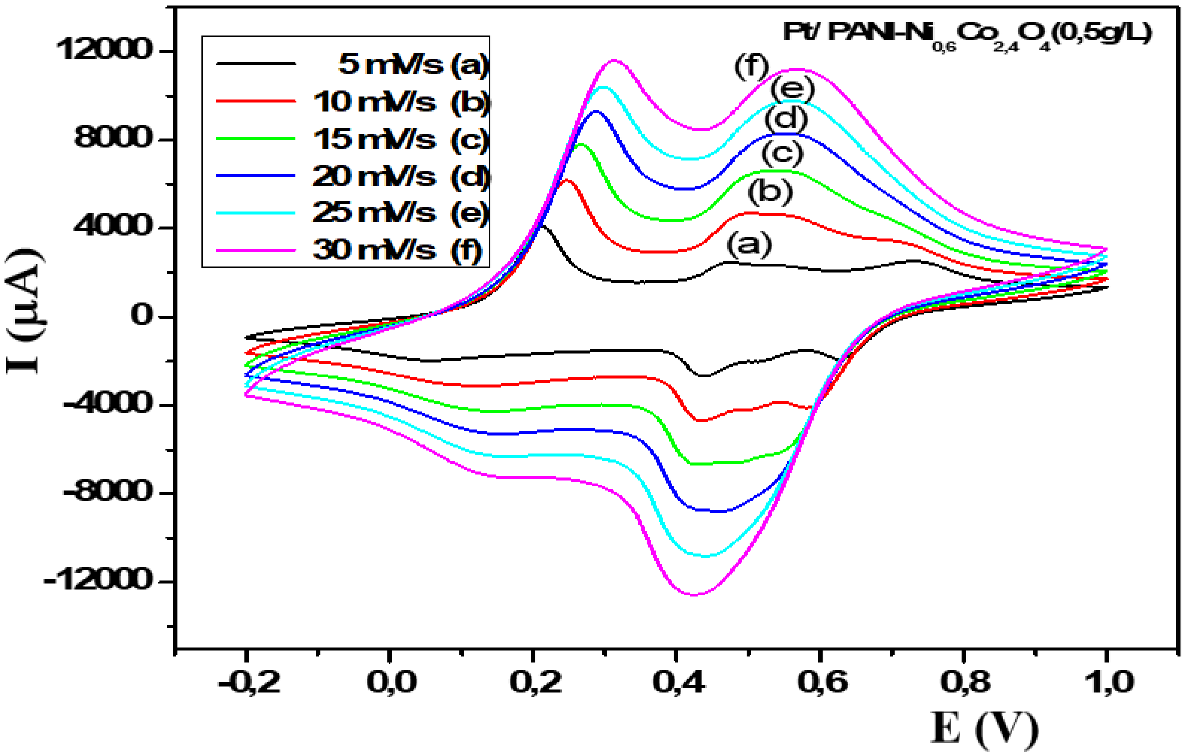

Figure 9.b:- Cyclic voltammogram of Pt/PANI-Ni$_{0.6}$ Co$_{2.4}$O$_4$ film (0.5g.L^{-1}) in a 0.5 M HCl solution at different scanning speeds.

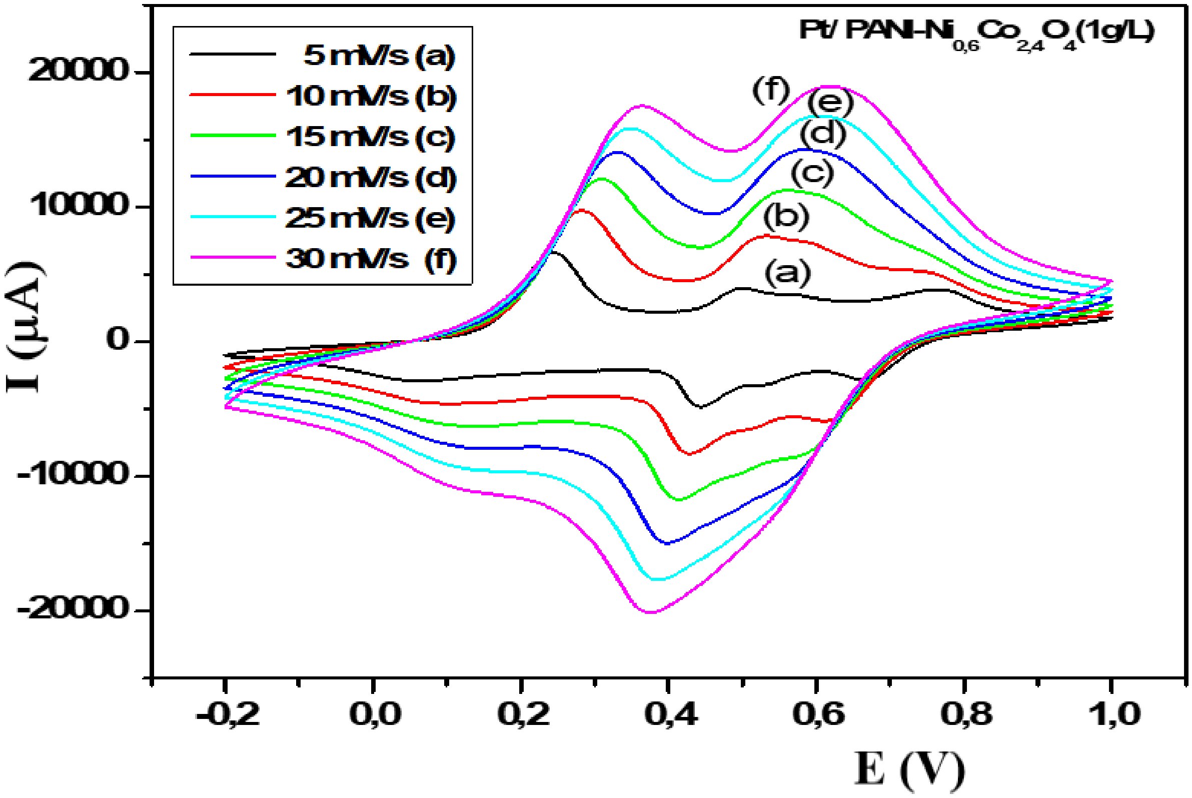

Figure 9.c:- Cyclic voltammogram of Pt/PANI-Ni$_{0.6}$ Co$_{2.4}$ O$_4$ (1g.L^{-1}) film in a solution 0.5 M HCl at different scan rates.

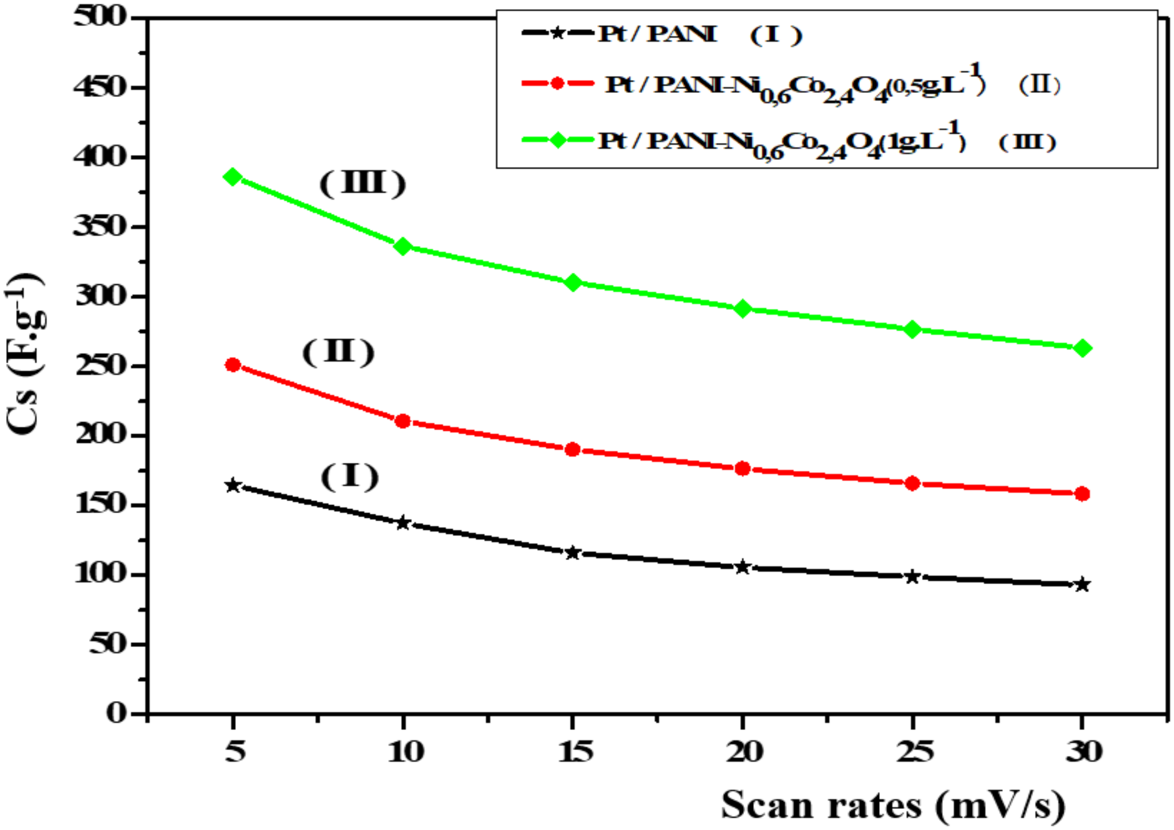

Figure 10:- Specific capacity of Pt /PANI (I), Pt / PANI - $Ni_{0.6}$ $Co_{2.4}O_4$ (0.5g/L) (II), Pt / PANI - $Ni_{0.6}$ $Co_{2.4}$ O_4 ($1g.L^{-1}$) (III) , at different sweep speeds.

Table 1:- Specific capacity of Pt/PANI and Pt/PANI-$Ni_{0.6}$ $Co_{2.4}O_4$ films (0.5 and $1g.L^{-1}$) with different scanning speeds.

	Pt / PANI	Pt / PANI-$Ni_{0,6}Co_{2,4}O_4$ ($0,5g.L^{-1}$)	Pt / PANI- $Ni_{0,6}Co_{2,4}O_4$ ($1g.L^{-1}$)
5 $mV.s^{-1}$	**164,340 $F.g^{-1}$**	**250,978 $F.g^{-1}$**	**386,108 $F.g^{-1}$**
10 $mV.s^{-1}$	**137,165 $F.g^{-1}$**	**210,508 $F.g^{-1}$**	**336,347 $F.g^{-1}$**
15 $mV.s^{-1}$	**115,829 $F.g^{-1}$**	**190,206 $F.g^{-1}$**	**310,118 $F.g^{-1}$**
20 $mV.s^{-1}$	**105,704 $F.g^{-1}$**	**176,299 $F.g^{-1}$**	**291,765 $F.g^{-1}$**
25 $mV.s^{-1}$	**98,489 $F.g^{-1}$**	**165,945 $F.g^{-1}$**	**276,567 $F.g^{-1}$**
30 $mV.s^{-1}$	**93,026 $F.g^{-1}$**	**158,280 $F.g^{-1}$**	**263,453 $F.g^{-1}$**

There is no conflict of interest
Funding
No funder.
Our work is self-funded.

References:-

[1] A. Bahloul, B. Nessark, E. Briot, H. Groult, A. Mauger, K. Zaghib, C.M. Julien, "Polypyrrole-covered MnO_2 as electrode material for supercapacitor", J. Power Sources 240 (2013): 267–272.https://doi.org/10.1016/j.jpowsour.2013.04.013

[2] H. Mi, F. Li, Ch. He, X. Chai, Q. Zhang, Y. Li, J. Liu, "Three-dimensional network structure of silicon-graphene-polyaniline composites as high performance anodes for Lithium-ion batteries", Electrochim. Acta 190 (2016): 1032–1040.https://doi.org/10.1016/j.electacta.2015.12.182

[3] H.T. Hie, H.T. Giang, T. Trung, C.V. Tuan,"Enhancement of biosensing performance using a polyaniline/multiwalled carbon nanotubes nanocomposite", J. Mater. Sci. 52 (2017) :1694 –1703. https://doi.org/10.1007/s10853-016-0461-z

[4] L. Gu, J. Wang, R. Qi, X. Wang, P. Xu, X.A. Han, "Novel incorporating style of polyaniline/TiO2 composites as effective visible photocatalysts"J. Mol. Catal. A Chem. 357 (2012): 19 – 25.https://doi.org/10.1016/j.molcata.2012.01.012

[5] A. Sayaha , F. Habelhamesa , A. Bahloula, , B. Nessarka , Y. Bonnassieuxb , D. Tendelierb , M. El Jouadc "Electrochemical synthesis of polyaniline-exfoliated graphene composite films and their capacitance properties", J. of Electroana. Chem. 818 (2018) : 26-34.
https://doi.org/10.1016/j.jelechem.2018.04.016

[6] N. Harfouche, B. Nessark, F. X. Perrin "Electrochemical and surface characterization of composite Polyaniline / $LiMn_2O_4$";J. of Electroanalytical Chemistry756 (2015): 179 - 185.
https://doi.org/10.1016/j.jelechem.2015.08.031

[7] D. S Patil, J. S. Shaikh, D. S. Dalavi, M.M. Karanjkar, R. S. Devan, Y.R. Ma, P. S. Patil,"An Mn Doped Polyaniline Electrode for Electrochemical Supercapacitor". J. Electrochem. Soc., 158 (2011): A653–A657.

[8] M. Sawangphruk, T. Kaewsongpol,"Direct Electrodeposition and Superior Pseudocapacitive Property of Ultrahigh Porous Silver-Incorporated Polyaniline Films". Mater. Lett., 87 (2012): 142–145.https://doi.org/10.1016/j.matlet.2012.07.103

[9]M. Guéye, M. Guène, "Synthesis of $Ni_{0.9}Co_{2.1}O4$ mixed oxides powders prepared by sol-gel method via propionic acid and characterization by X-ray, ICP, FTIR and XPS analysis", J. Soc. Ouest-Afr. Chim 041 (2016): 35 - 40.

[10] C. Belkessam, S. Bencherif, M. Mechouet, N. Idiri,"The Effect of Heteroatom Doping on Nickel Cobalt Oxide Electrocatalysts for Oxygen Evolution and Reduction Reactions" , J. Centering of chem, 85 (2020) : 1710-1718.https://doi.org/10.1002/cplu.202000436

[11] R. N. Singh, J. F. Koenig, G. Poillerat, P. Chartier, "Thin films of CO_3O_4 and $NiCo_2O_4$ prepared by the method of chemical spray pyrolysis for electrocatalysis: Part IV. The electrocatalysis of oxygen reduction",J. Electroanal. Chem 314 (1991): 241- 457. https://doi.org/10.1016/0022-0728(91)85440-Z

[12] I. Nikolov, R. Darkaoui, E. Zecheva, R. Stoyanova, N. Dimitrov, T. Vitanov. "Electrocatalytic activity of spinel related cobalties $M_xCo_{3-x}O_4$ (M = Li, Ni, Cu) in the oxygen evolution reaction", J. Electroanal. Chem, 429 (1997) :157-168. https://doi.org/10.1016/S0022-0728(96)05013-9

[13] A. Pailleret, N.T.L. Hien, D.T.M. Tranh, C. Deslouis, "Surface reactivity of polypyrrol / iron-oxide nanoparticules : electrochemicla and CS-AFM investigations",J. Solid State. Electrochem. 11 (2007): 1013-1021.https://doi.org/10.1007/s10008-007-0262-z

[14] B. Garcia, A. Lamzoudi, F. Pillier, H. Nguyen Thi Le, C. Deslouis,"Oxide/Polypyrrole Composite Films for Corrosion Protection of Iron". J. Electrochem. Soc., 149 (2002): B560-B566

[15] P. Montoya, F. Jaramillo, J. Calderón, S.I. Córdoba de Torresi, R.M. Torresi, "Evidence of redox interactions between polypyrrole and Fe_3O_4 in polypyrrole–Fe_3O_4 composite films",Electrochim. Acta 55 (2010) :6116-6122.https://doi.org/10.1016/j.electacta.2009.09.042

[16] K.Q. Ding, F.M. Cheng, "Cyclic voltammetrically prepared MnO_2–PPy composite material and its electrocatalysis towards oxygen reduction reaction (ORR)", Synt. Met. 159 (2009): 2122-2127.
https://doi.org/10.1016/j.synthmet.2009.08.005

[17] X. Li, W. Gan, F. Zheng, L. Li, N. Zhu, X. Huang. "Preparation and electrochemical properties of RuO_2/polyaniline electrodes for supercapacitors", Synth Met 162 (2012) :953-957.
https://doi.org/10.1016/j.synthmet.2012.04.002

[18] K. Sasaki, M. Kaya, J. Yano, A. Kitani, A. Kunai, "Growth mechanism in the electropolymerization of aniline and **p**-aminodiphenylamine"J. Electroanal. Chem. 215 (1986): 401-407. https://doi.org/10.1016/0022-0728(86)87033-4

[19] G. Zotti, S. Cattarin, N. Comisso,"Electrodeposition of polythiophene, polypyrrole and polyaniline by the cyclic potential sweep method", J. Electroanal. Chem. 235 (1987) 259.-273.
https://doi.org/10.1016/0022-0728(87)85212-9

[20] Y. Cao, P. Smith, A.J. Heeger."Spectroscopic Studies of Polyaniline in Solution and in Spin-Cast Films", Synth. Met. 32 (1989): 263–281.https://doi.org/10.1016/0379-6779(89)90770-4

[21] S. Ito, K. Murata, S. Teshima, R. Aizawa,Y. Asako, K. Takahashi, B. M. Hoffman. "Simple Synthesis of Water-Soluble Conducting Polyaniline",Synth. Met. 96 (1998): 161–163.
https://doi.org/10.1016/S0379-6779(98)00074-5

[22] J. Huang, M. Wan, "Polyaniline Doped with Different Sulfonic Acids by in Situ Doping Polymerization", J. Polym. Sci. Part Polym. Chem. 37 (1999) :1277–1284.https://doi.org/10.1002/(SICI)1099-0518(19990501)37:9%3C1277::AID-POLA7%3E3.0.CO;2-A

[23] A. K. Singh, Sarkar D., Khan G. G., Mandal K.,"Designing one dimensional Co-Ni/Co_3O_4-NiO core/shell nano-heterostructure electrodes for high-performance pseudocapacitor ", Appl. Phys. Lett. 104 (2014): 133904-133909.https://doi.org/10.1063/1.4870628

[24] A. N. Naveen, S. Selladurai, "Novel low temperature synthesis and electrochemical characterization of mesoporous nickel cobaltite-reduced graphene oxide (RGO) composite for supercapacitor application",Electrochimica Acta, 173 (2015): 290–301.
https://doi.org/10.1016/j.electacta.2015.05.072

[25] E. R. Ezeigwe, P. S. Khiew, C. W. Siong, Tan M. T. T., "Solvothermal synthesis of $NiCo_2O_4$ nanocomposites on liquid-phase exfoliated graphene as an electrode material for electrochemical capacitors", J. Alloys Compounds. 693 (2017): 1133-1142.
https://doi.org/10.1016/j.jallcom.2016.09.244

[26] S. Yang, X. Wu, C. Chen, H. Dong, W. Hu, X. Wang,"Spherical α-Ni $(OH)_2$ nanoarchitecture grown on graphene as advanced electrochemical pseudocapacitor materials" , Chem. Commun. (Camb). 48 2012): 2773-2775.https://doi.org/10.1039/C2CC16565A

[27] M. Diagne, "Contribution to the characterization by electrochemical impedance spectroscopy of conductive organic polymers and application of polyaniline to energy storage", Doctoral thesis Dakar University (2007): 70-72.

[28] M. Fall, J. J. Aaron, M. M. Dieng, S. Aeiyach, P. C. Lacaze, "Role of surfactants in the electrosynthesis and the electrochemical and spectroscopic characteristics of poly (3-methoxythiophene) films in aqueous micellar media", Synth. Met. 118 (2001) :149-155
https://doi.org/10.1016/S0379-6779(00)00402-1

[29] E. Laviron. "Surface linear potential sweep voltammetry: Equation of the peaks for a reversible reaction when interactions between the adsorbed molecules are taken into account", J. Electroanal. Chem. 52 (1974): 395- 402. https://doi.org/10.1016/S0022-0728(74)80449-3

[30] P. Simon, Y. Gogotsi, B. Dunn, "Where Do Batteries End and Supercapacitors Begin",
Science Magazine, 343 (2014): 1210–1211.

[31]X.Zhang, J.Xiao, X.Zhang, Y. Meng, D. Xiao, "Three-Dimensional Co_3O_4 Nanowires@Amorphous $Ni(OH)_2$ Ultrathin Nanosheets Hierarchical Structure for Electrochemical Energy Storage",Electrochim. Acta, 191 (2016) :758-766.
https://doi.org/10.1016/j.electacta.2016.01.159

[32] M. Guéye, P. C. H. Mandiamy, M. Guène, and A. A. Diagne "Nanostructured $Ni_{0.9}Co_{2.1}O_4$ spinel oxide: electrochemical, spectroscopic and morphological investigation ",Int. J. Adv. Res. 5(2017): 816 - 823.http://dx.doi.org/10.21474/IJAR01/5124

[33] X. Tian, C. Cheng, L. Qian, B. Zheng, H. Yuan, S. Xie, D. Xiao, and Choi M. M. F.,"Microwave-assisted non-aqueous homogenous precipitation of nanoball-like mesoporous α-$Ni(OH)_2$ as a precursor for NiO_x and its application as a pseudocapacitor", J. Mater. Chem. 22 (2012) :8029.
https://doi.org/10.1039/C2JM16057A

[34] J. H. Kim, K. Zhu, Y. Yan, C. L Perkins, and A. J. Frank, "Microstructure and pseudocapacitive properties of electrodes constructed of oriented NiO-TiO2 nanotube arrays",Nano Lett. 10 (2010): 4099 – 4104. https://doi.org/10.1021/nl102203s

[35] P. Tamilarasan, K. Rajasekar and E. Muthusankar."Synthesis of NiCo2O4/PANI electrodes for Supercapacitors Using Nanocomposites",April 9-11, (2015) 548-555

[36] D.W. Wang, F. Li, J.P. Zhao, W.C. Ren, Z.G. Chen, J. Tan, Z.Sh. Wu, I. Gentle,
G.Q. Lu, H.M. Cheng, "Fabrication of graphene/polyaniline composite paper via in situ anodic electropolymerization for high-performance flexible electrode", ACS Nano 3 (2009): 1745–1752,
https://doi.org/10.1021/nn900297m

[37] Q. Wu, Y.X. Xu, Z.Y. Yao, A.R. Liu, G.Q. Shi, "Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films", ACS. Nano. 4 (2010): 1963 -1970.
https://doi.org/10.1021/nn1000035

[38] H. Zhang, G. Cao, Z. Wang, Y. Yang, Z. Shi, Z. Gu,"Tube-covering-tube nanostructured polyaniline/carbon nanotube array composite electrode with high capacitance and superior rate performance as well as good cycling stability ", J. Electrochem. Commun. 10 (2008) :1056 -1059.
https://doi.org/10.1016/j.elecom.2008.05.007

[39] JH. Shendkar, M. Zate, K. Tehare, VV. Jadhav"Polyaniline - cobalt hydroxide hybrid nanostructures and their supercapacitor studies",Materials Chemistry and Physics 180 (2016) : 226-236.https://doi.org/10.1016/j.matchemphys.2016.05.070

[40] R.K. Sharma, H. Oh, Y. Shul, H. Kim,"Growth and characterization of carbon supported MnO_2 nanorods for supercapacitor electrode",Physica B 403 (2008): 1763 -1769.
https://doi.org/10.1016/j.physb.2007.10.007.