Preparation and Characterization of the Cobalt Doped Polyaniline/MWCNT Nanocomposites for Supercapacitor Application

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Abstract

Transition metal ion doped poly-aniline (PANI)/ multiwall carbon nanotube (MWCNT) composite was successfully prepared by *in-situ* oxidative polymerization of aniline monomer for supercapacitor application. The Co-doped PANI/MWCNTs composite showed improved capacitive behavior and lower electrical resistance compared to HCl doped PANI (DPANI)/MWCNT composite. By using carbon nano tube with conducting polymer offer exceptional power andhigh performance by supplying high surface area, high conductivity and high retention of mechanical strength under charge-discharge cycle. All the materials were characterized by Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM). The electrochemical capacitive performance of the asymmetric supercapacitor was tested by cyclic voltammetry (CV), impedance spectroscopy (EIS) and cyclic charge-discharge (CCD) test in a three-electrode system. The highest specific capacitance value (576 F/g) was obtained at a scan rate of 2 mV/s in 1 (M) KOH electrolyte for Co-PANI/MWCNTs composite.

Keywords: cobalt doped PANI, in-situ polymerization, carbon nanotubes, polymeric composites, electrochemical characterization, supercapacitor

1. Introduction

In recent years, supercapacitors have attracted great attention due to their application in the field of charge storage devices. A typical supercapacitor which is employed in a light weight vehicle or a telecommunications device requires to be made of a material characterized by moderately high energy density, high power density, small size, low initial cost and prolonged life cycle. Supercapacitor forms the bridge between batteries and conventional capacitors with covering several orders of magnitude both in energy (moderately) and in power density (high). Supercapacitors are of two types: electric double layer and pseudocapacitor capacitor and they differ from each other in terms of mechanism followed for charge storage. The first one charge store by forming electrical double layer on electrode/electrolyte interfacewith electrostatic attractionbut latter one charge store completely different mechanismwith redox reaction i.e. faradic reaction process (Gupta et al., 2006). For the preparation of supercapacitor electrode material, we have used multiwall carbon nanotubes. It is more advantageous to use carbon nanotubes than using other carbonaceous materials since carbon nanotubes tend to entangle with each other to from a durable and porous material (Chunsheng, Ning et al., 2007). Polyaniline (PANI) is used as conducting polymer since it has good environmental stability; it is relatively less expensive, exhibits high conduction with protonic acid (Chiang & Macdiarmid, 1986). It consist of two units namely, benzoid and quinonid. Each tetramer consists of two amine and two imine nitrogen atoms which can be doped to obtain the conducting polymer emerilidine salt-PANI. When protonic acid was added to the insulatingemeraldine base (EB) form of PANI, it can be converted to the conducting formandresulting in an increase of conductivity by more than 10 fold in magnitude (Zengin et al., 2002). It can also bind with carbon nano tube via Pi-Pi stacking or electron acceptance from carbon nanotube. Many researchers have investigated transition metal doped conducting polymer and have found higher conductivity with increase in doping level of transition metal. $IrCl_3$ polypyrrole gives enhanced capacitance for electrochemical energy storage device (Chang & Chien, 2000), $RuCl_3$ doped polypyrrole gives higher capacitance in $NaNO_3$ electrolyte solution (Ben et al., 2004), $MnCl_2$ doped Polyaniline was also used for electrochemical supercapacitor application and gives 474 F/g with highest doping

level (Patil et al., 2011), Using transition metal (Co^{2+}), charge accumulation property increasing with increasing doping level due to HSAB principle, hard acids (border line Co^{2+}) prefer to bind to hard bases (PANI). Another reason to take Cobalt (II) has vacant d-orbital to bind up with nitrogen lone pair & Cobalt cation can follow the two step redox mechanism with PANI where as first metal ionoxidized the polymer unit and get reduced, this reduced metal ion again bind with imine nitrogen from quinoide ring of PANI and get oxidized. This phenomena leads to the formation of radical cation segments and therefore corresponding metal ions (Celly et al., 2009; Li et al., 2009).

Our aim is to develop the super capacitor performance and increase the cyclic stability of supercapacitor electrode material. For this purpose we have used carbon nano tube which has high surface area, low resistance, high electron donor and acceptor properties and high stability indicates that it can be used to improve the supercapacitive performances and stability of the supercapacitor electrode materials.

2. Experimental

Multiwall carbon nanotubes were obtained from Iljin Nano Technology, Korea, (95% purity and 20-40 nm diameter). 1.24 g of CTAB (cetyltrimethyl ammonium bromide) (Lobachemie Pvt. Ltd.) was added in 150 ml 1 (M) HCl in a beaker.

Subsequently, 60 mg of MWCNT was added and sonicated for 30 minutes at room temperature. In another beaker, 2 ml of aniline monomer in 50 ml of 1 (M) HCl was taken and 4 wt % of $CoCl_2$ (99.99% Aldrich) was added by stirring to achieve a well dispersed suspension. The solutions contained in both the beakers were mixed with each other and sonicated for 10 minutes. Subsequently, 60 ml of HCl containing 2.04 g of ammonium persulphate (APS) (Lobachemiepvt.Ltd, India) was added drop by drop to the above solution and sonicated for another 10 minutes. The reaction mixture was maintained at 1~5 ^{o}C for 24 hrs. The resulting precipitate was filtered and washed with distilled water and ethanol several times and dried at 100°C for 12 hrs.

MWCNT/PANI also has been prepared by above procedure without adding metal salt.

3. Characterizations

3.1 FT-IR Spectroscopy

FT-IR was studied by NEXUS 870 FTIR (Thermo Nicolet) instrument. In dry condition samples were prepared by mixing KBr and samples with weight ratio of 1:10 andpellet were made to perform this test.

3.2 Morphology

FESEM analysis was investigated on gold coated samples in Carl Zeiss-SUPRATM 40 FESEM instrument. HRTEM and EDX observations were performed on JEOL 2100 HRTEM by dispersing the sample by sonication in acetone. A drop of the well dispersed mixture was taken in a copper mesh type grid and fully dried in air for TEM analysis.

3.3 Electrode Preparation and Electrochemical Analysis

Cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), constant current charging/discharging (CCD) measurementsof the materials were carried out on GAMRY reference 3000 instrument using a three electrode system where platinum and standard calomel electrode (SCE) were used as counter and reference electrode. For working electrode preparation, 2 mg sample was dispersed in 200 µlnafion binder (1wt % ethanol solution) by 30 min sonication (Saswat et. al., 2011). This sample solution has been cast on glassy carbon electrode with a diameter of 3 mm and dried fully over vacuum before electrochemical test. 1 (M) KOH solution was used as electrolyte solution for electrochemical measurement. CV were performed with potential window -8 V to +8 V vs SCE.

4. Result and Discussion

4.1 FT-IR Measurement

The bond vibration frequency of cobalt doped poly-aniline with MWCNT was characterized by FT-IR and the plot is shown in figure 1. The FT-IR spectrum of 1560 cm^{-1} and 1490 cm^{-1} are characteristic peak of the stretching vibration of the N=Q=N ring and N-B-N respectively (where B refers to the benzenoic-type rings and Q refers to the quinonic-type rings (Tanga et al., 2009). The characteristic peak appeared at 1300 cm^{-1} corresponds to C-N bond vibration. The characteristic peaks at 1109 and 800 cm^{-1} are attributed to the characteristic of B-NH-Q or B-NH-B bonds, and out-of-plane bending vibration of C-H on the 1, 4-disubstituted aromatic ring. Figure 1 shows that band appeared at 1300 cm^{-1} assigned to C-N stretching vibration shifts to 1236 cm^{-1} when Co^{2+} is added in the reaction system, which indicates that the Co^{2+} can interact with the nitrogen

atoms in the PANI chains. The π-bonded surface of CNT interacts strongly with the conjugated structure of PANI, especially through quinonoid rings (Zengin et al., 2002). Then carbon nanotube can donate the π electron to the vacant d-orbital of Co^{2+} and simultaneously π- π stacking also observed between DPANI and CNT which is shown in scheme-1.
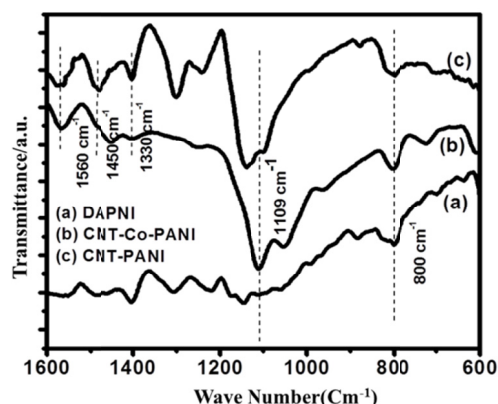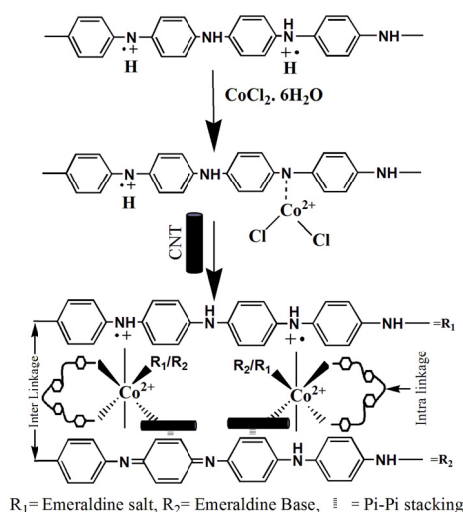

Figure 1. FT-IR spectra of (a) HCl doped PANI (DPANI),(b) Cobalt doped PANI/Carbon nano tube (CNT/Co/PANI), (c) CNT-PANI

Scheme1. Mechanism of the Cobalt doped PANI/MWCNT nanocomposite formation

4.2 Raman Measurements

Raman spectroscopy is a well-liked technique for successfully used in the micro-structural characterization of carbon based materials. The Raman spectrum of diamond has a single Raman active mode at 1332 cm^{-1} (Ashish et al., 2009). It is apparent that the Raman spectra present two broad bands centred at around 1330 and 1590 cm^{-1} wavenumbers, which attributes to the D and G bands of graphite. The G and D mode is related with the ordered graphite in CNT and disordered graphitic carbon respectively (Krishna et al., 2009). The Raman spectrum taken at an excitation wavelength of 633 nm for the samples is shown in figure 2. The spectrum shows peaks, which can be associated with characteristic bands of the quinone and semi-quinone structures in the undoped and doped samples, respectively. The band at 1160 cm^{-1} corresponds to the β_{C-H} vibration of the quinoid ring, 1217 cm^{-1} corresponds to ν_{C-N}, 1470 cm^{-1} Corresponds to $\nu_{C=N}$ and 1590 cm^{-1} corresponds to $\nu_{C=C}$. All these bands are characteristic of quinone segments. For all the metal-doped samples, there is a decrease in the intensity of the band at 1470 cm^{-1}, corresponding to quinone segments, when compared with EB. A new band associated with ν_{C-N+} appears around 1330 cm^{-1}, corresponding to semi-quinone segments (Celly-Izumi et al., 2000) The decrease in the intensity for quinone bands and the appearance of bands corresponding to semi-quinone segments

indicates the doping of EB with metal ions. The bands at 1162 cm^{-1} (ν_{C-H}) and 1219 cm^{-1} (ν_{C-N}) are assigned to reduced amine benzene ring (Krishna et al., 2009).
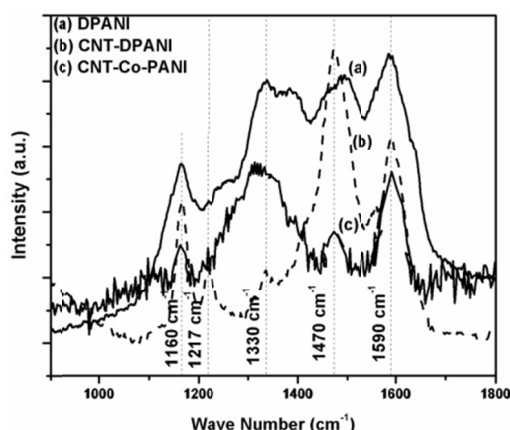

Figure 2. Raman spectra of (a) HCl doped PANI (DPANI), (b) Cobalt doped PANI/CNT (CNT-Co-PANI), (c) CNT-PANI

4.3 FESEM and TEM Studies

Surface morphologies of the composites were analyzed by FESEM and the images are presented in figure 3. It was found that the surface of MWCNT was coated by cobalt doped PANI. Figure 4 (a) shows the TEM image of MWCNT coated with cobalt doped PANI (figure 4b for PANI) which is shows the successful coating of the cobalt doped PANI. Cobalt is shown with PANI which is confirmed by EDX figure 4 (d) analysis.
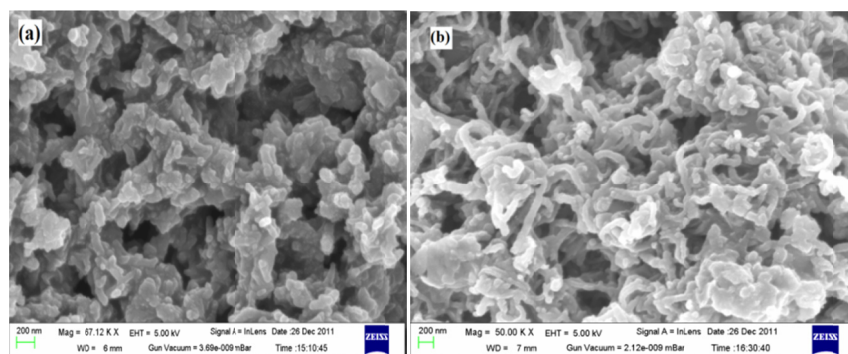

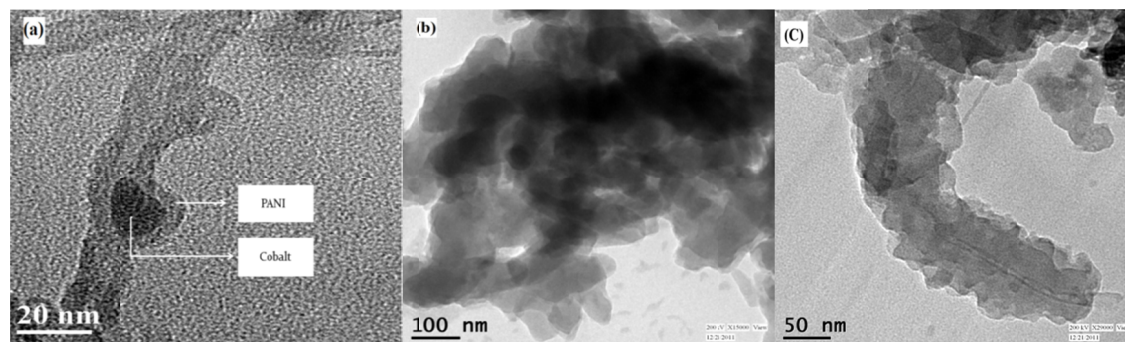Figure 3. FESEM images of (a) PANI (b) CNT-Co-PANI

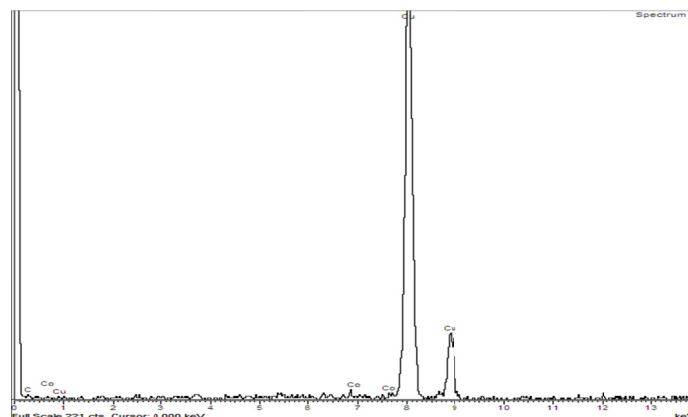Figure 4. TEM images of (a) CNT-Co-PANI (b) PANI (c) CNT-PANI

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Figure 4. (d) EDX analysis of cobalt doped PANI with CNT

4.4 Cyclic Voltammetry Studies

Cyclic voltammetry is a suitable tool to prove the capacitive behavior of electrode materials. For the preparation of electrode materials, we have used glassy carbon (GC) electrode as working electrode where nano composite samples are adhered to the GC surface by nafion binder (Saswat et al., 2011) and 1 (M) KOH has been used for electrolyte. Platinum electrode and calomel electrode were used as counter electrode and reference electrode respectively.
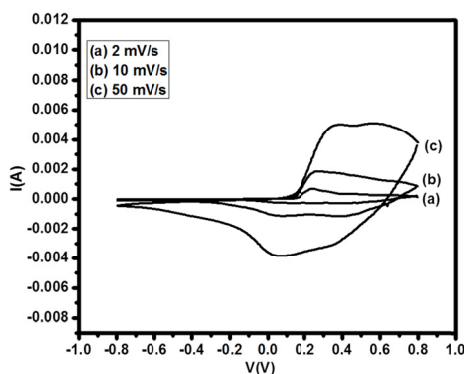

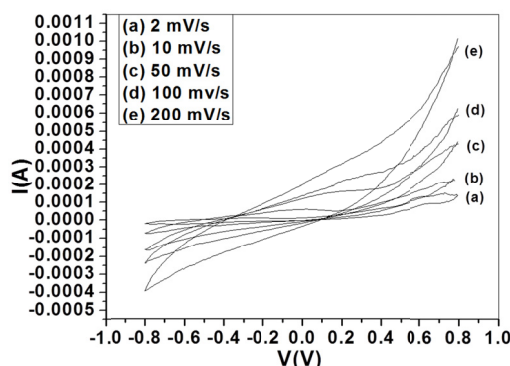Figure 5. Cyclic Voltammetry curve of CNT-PANI   Figure 6. Cyclic Voltammetry curve of CNT-Co-PANI

For CV method, overall specific capacitance (C_s) is obtained from (Zhuangjun et al., 2011; Jun et al., 2010):

$$C_s = C/m = \frac{\bar{i}}{vm} = \frac{\int_{V_1}^{V_2} i(V)dV}{(V_2 - V_1)vm}$$

Here, $\bar{i}(V)$ is the instantaneous current in cyclic voltammograms and dV/dt (V s^{-1}) is the scanning rate v (V s^{-1}). $\int_{V_2}^{V_1} i(V)dV$ is the area of the I-V curve & m is the mass of the electrode. Here, V_1 and V_2 are the switching potential in cyclic voltammetry. So, using the above equation, we have found from the CV curve figure 6 that the values of specific capacitance of cobalt doped PANI with MWCNT are 576 (for PANI/MWCNT 211 F/g shown in figure 5.) 384, 256, 186, 116 F/g at 2 mV/s, 10 mV/s, 50 mV/s, 100 mV/s, 200 mV/s respectively in 1 (M) KOH under the potential range -0.8 to + 0.8 V. The doping process can be achieved by two ways one is pseudo protonation and another one is two step redox process. While in first case, the Co (II) ions coordinate to imine nitrogen of EB-PANI and then because of an internal redox reaction in the polymeric chain, ES-PANI is obtained. And this happens without direct electron transfer between Co (II) ions and EB-PANI. Whereas if we look at the latter, the two-step redox process, Co (II) ions oxidize the amine segments resulting in PB-PANI

moieties and Co (I) ions. So, this type of redox reaction in cobalt doped polyaniline in presence of MWCNT it gets greater accumulation of charge with increment of doping level. Hence, we get the high capacitance for doping composite (Tanga et al., 2009). From these specific capacitances we have also calculated the energy density and power density was calculated using the following equation (Zhuangjun et al., 2011; Jun et al., 2010):

$$E = \frac{1}{2}\, C_s V^2, \qquad P = E/t.$$

Where P (W/kg) and E (Wh/kg) are the power density and the energy density respectively, t is time in seconds. The energy density served by this composite is 41.24, 66.1, 91,136.52, 204Wh/Kg & Power density values of 5400, 3031, 1485,1674,1044 W/kg have been obtained at varying scan rates of 200 mV/s, 100 mV/s, 50 mV/s, 10 mV/s and 2 mV/s.

4.6 Electrochemical Impedance Spectroscopy

The electrical impedance has also been studied which is shown in figure 7 and 8. Here R_s is the solution resistance, R_{ct} is the charge transfer resistance, Y_0 is the constant phase element and a = n is the frequency power which indicates the ideal capacitor behavior of CPE. The impedance spectrum is shown for PANI /MWCNT (Figure 8) and Co-doped PANI/MWCNT (figure 7) and corresponding values have been evaluated by fitting with suitable circuit (figure 9) which are R_s = 1.87 x 10^{-3} ohms, CPE, $Y_0(Sxs^n)$ = 11.23 x 10^{-6}, freq. power (0<n<1) = 0.810 (0.5 for PANI/MWCNT), electrode resistance = 6.67 ohms, Warburg resistance (W_d) = 21.83x10^{-6}, double layer capacitance (F) C_{dl}=21.23 x 10^{-3}. This increased value of n leads to the more capacitive behavior of cobalt doped PANI/MWCNT composites.
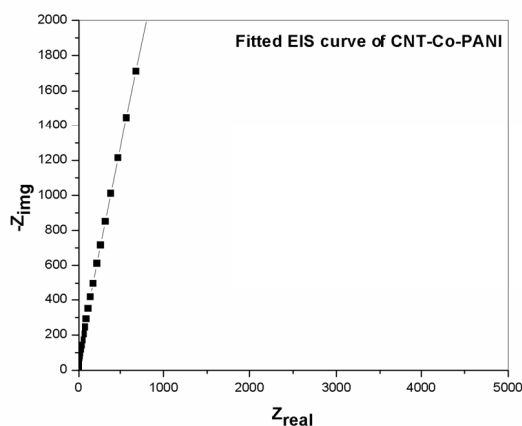

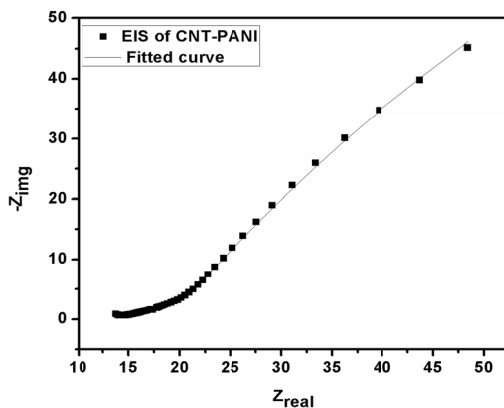Figure 7. Electrochemical Impedance Spectroscopy (EIS) of CNT-Co-PANI

Figure 8. Electrochemical Impedance Spectroscopy curve (EIS) curve of CNT-PANI

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CPE is defined by (Hanlu et al., 2009):

$$Z_{cpe} = T_{cpe}(j\omega)_{cpe}^{-n}$$

Where T and n can be considered as frequency-independent constants and ω is called the angular frequency. The roughness of electrode surfaces is related with correction factor n. The minimum values for n is 0 and maximum value is 1. When n = 1, the electrode material behaves like an ideal capacitor but n=0 represents a resistor, while 0.5 denotes a Warburg behavior. The n value of the above data indicates the porous and highly capacitive behavior of the electrode.
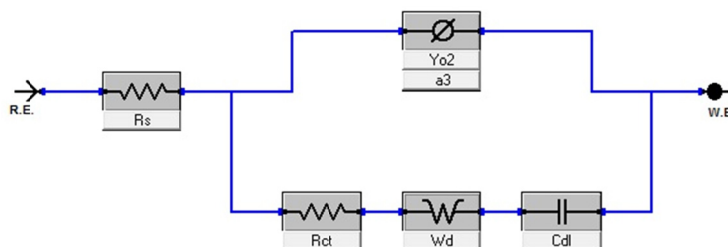

Figure 9. Circuit of the EIS fitting

4.7 Cyclic Charge-discharge Test

The specific capacitance of the composite is also calculated from the cyclic charge discharge curve (CCD) (figure 10) by the following equation (Alireza et al., 2007):

$$C_s = \frac{i \times \Delta t}{\Delta v \times m}$$

Where *i* is the constant current, Δt is the discharge time, ΔV denotes the potential range and m is the mass of the sample. Charge-discharge test also has been carried out at current density of 1.5 A/g. The charge-discharge curve with hump indicates the redox behavior of the composite, and proves the feasibility of the electrode material. From charge -discharge curve, we have found that the specific capacitance of the composite is 573 F/g.
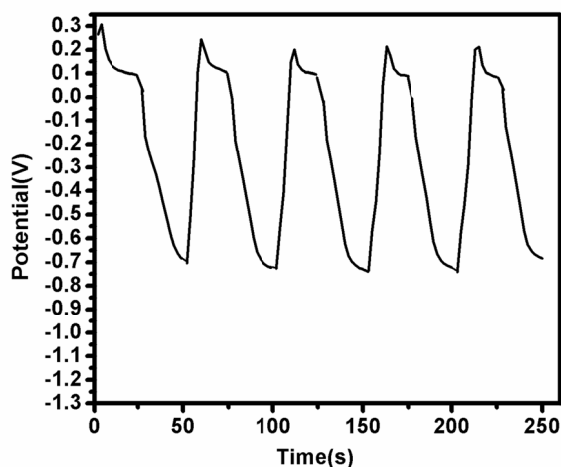

Figure 10. Cyclic Charge-Discharge (CCD) Curve of CNT/Co/PANI

So, the above experimental data shows that the specific capacitance increases due to the doping of PANI with transition metal in presence of carbon nano tube. The enhancement of specific capacitance of Co-doped PANI/MWCNT nanocomposite compared to HCl doped PANI because transition metal co-ordinate with PANI leads to the pseudo-protonation and simultaneously cobalt ion can bind with MWCNT by which charge

accumulation property increases. This type of work will help developing the better supercapacitor having high capacitance value and enhanced cyclic charging discharging capabilities.

5. Conclusion

Cobalt doped polyaniline/MWCNT composites were prepared successfully by the in situ polymerization process. The composite exhibits greater electrical conductivity because of transition metal doping. The FT-IR and Raman spectroscopy reveal that MWCNTs were coated with cobalt doped polyaniline. Morphological study (FESEM and TEM) also confirmed multiple doping sites of the Co^{2+} in polymer chain due to rough surface of the composite. The area under cyclic voltammetry and charge-discharge test indicate higher charge accumulation on surface of the composite which generates higher specific capacitance. The more research is required in this particular field specially by changing the doping method and the element in order to develop the better supercapacitor.

Acknowledgements

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