

Synthesis of Cd doped Polyaniline for supercapacitor

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Abstract:- Polyaniline (PANI) is an important conducting polymer because of its high conductivity in doped state. Also it exhibits electronic, optical, magnetic properties which lead to its applications in a wide range of areas like photovoltaic cells, light emitting diode, biosensors, electronic sensors, electromagnetic radiation absorbers and electromagnetic shields. In this study Cd was doped in polyaniline (PANI) by chemical oxidation method. Specific capacitance measured by cyclic voltametry was found to be increased due to doping of Cd in PANI.

Keywords:- Polyaniline, chemical oxidation, specific capacitance.

I. INTRODUCTION

Supercapacitor is dynamic field of research to develop next generation cost effective and energy efficient for variety of everyday applications [1, 2]. Two types of supercapacitor with different energy storage mechanism are: electric double layer capacitor (EDLC) and the redox supercapacitors. The basic principle for EDLC is separation of electronic and ionic charges at the interface between high specific areas of electrodes in an aqueous or organic electrolyte and for redox supercapacitor is Faradic charge transfer taking place at the electrode material.

A lot of efforts are made to develop a suitable material which having large surface area, hence, high specific capacitance. Today carbon nano tubes and graphene [3-5] are attractive materials because of their high surface area and showing high specific capacitance in range 200 to 375 F/g but their difficult methods of preparation is more cost effective. Polyaniline, polypyrrole, polythiophene and their derivatives are now attractive materials for supercapacitors because of their easy methods and less cost effective. Polyaniline (PANI) can be synthesized by chemically and electrochemically oxidative polymerization [6]. It is used as electrode materials for supercapacitor due to its high conductivity (10^3 - 10^4 Scm⁻¹) and four oxidation states (Leucoemeraldine, Emeraldine base, Emeraldine salt and Pemigraniline) which contributes to its high specific capacitance. But to develop high performance supercapacitor it is needed to improve its electronic conductivity. Hence, extensive research work has been focused on enhancement of electronic conduction by metal doping [7-9].

In doped state, Polyaniline (PANI) is an important conducting polymer because of its high conductivity. Also it exhibits electronic, optical, magnetic properties which lead to its applications in a wide range of areas like photovoltaic cells, light emitting diode, biosensors, electronic sensors, electromagnetic radiation absorbers and electromagnetic shields [10].

II. EXPERIMENTAL

2.1. Materials and Methods

The chemicals required for synthesis viz., aniline, ammonium per sulfate, CdCl₂ of analytical grade (AR) were purchased from commercial sources (S D Fine or SRL). Electronic spectra were recorded in methanol on a Jasco UV-Vis spectrometer model V-630 PC. IR spectra were recorded on a JASCO FT IR-6100 spectrometer. Cyclic voltametric studies were performed on Gamry Ref. 3000 Potentiostat/Galvanostat instrument in an aqueous electrolyte KOH of 6M concentration. Specific capacitance was measured by cyclic voltametry.

2.2. Synthesis

Synthesis of PANI

PANI was synthesized at lower temperatures (0-5 °C). Aniline (4.9 ml, 5.0 g, 0.054 mol) was dissolved in 70 ml of HCl (1 M solution). This solution was kept in ice bath maintaining the temperature between 0-5 °C. To this pre cooled (0-5 °C) solution, ammonium peroxydisulfate [(NH₄)₂S₂O₈] (12.35 g, 0.054 mol) dissolved in 70 ml of HCl (1 M solution) was added slowly with stirring. As the reaction proceeds within 2-3 minutes the intense blue green suspension appeared. The reaction mixture was stirred at room temperature for 2 hours. After

2 hours the precipitate was filtered over Buchner funnel and washed with deionized water until the colorless filtrate was observed. Later the precipitate was dried under suction to remove the solvent water substantially to get cracked cake. The black precipitate obtained was dried in vacuum at 70 °C for 1 hour to obtain black colored powder.

Synthesis of PANI doped with Cd

CdCl₂ (3.018 g, 0.0272 mol) was dissolved in 300 ml of HCl (1 M solution) and cooled at 0 °C which is treated as solution S₁. 150 ml of solution S₁ was mixed with pre cooled solution (at 0 °C) of aniline (20 ml, 20.4 g, 0.219 mol). This solution is treated as solution S₂. Ammonium peroxydisulfate [(NH₄)₂S₂O₈] (49.2 g, 0.216 mol) was added slowly with stirring to remaining solution S₁ (150 ml). This solution is treated as solution S₃. The solution S₃ is added to solution S₂. The reaction mixture was stirred for 2 hours and kept for 24 hours at 0 °C. It leads to formation of an intense blue green colored suspension. Later on the suspension was filtered by a Buchner funnel. The obtained precipitate was washed with deionized water till the filtrate become colorless. The precipitate was dried under suction to get the cracked cake. Then it was dried again completely *in vacuo* at 70 °C for 1 hour to give dark green compound.

2.3 Activation of PANI and PANI doped with Cd

The obtained material were finely powdered and then soaked in activating agent, 60% ZnCl₂ for 24 hours. The material was filter out and washed with deionized water to remove excess activating agent until the pH of water obtained between 6-7. The material was dried at 40 °C for 48 hours.

III. RESULTS AND DISCUSSIONS

3.1. Synthesis

These polymers exhibited poor solubility in dichloromethane (CH₂Cl₂), chloroform (CHCl₃) and moderate solubility in dimethylsulfoxide (DMSO) solvents. They exhibit thermal stability and an amorphous nature. The peaks superimposed in XRD pattern confirm Cd doping.

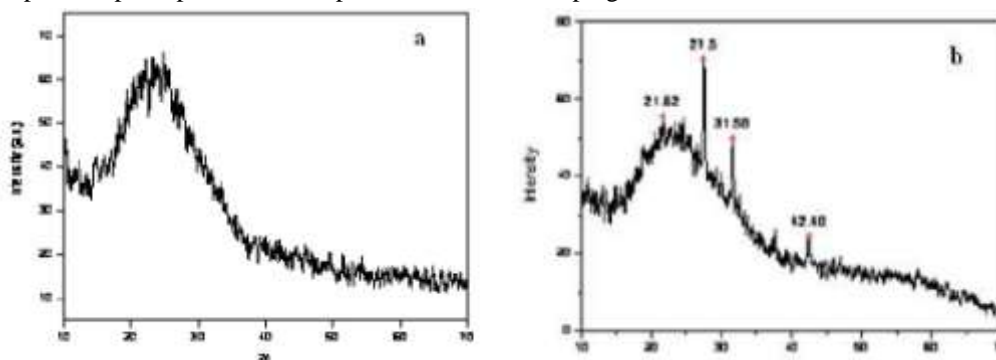


Fig. 1 XRD of (a) PANI and (b) PANI-doped with Cd

3.2. Investigation of photo physical properties by UV absorption spectroscopy

UV-Vis spectra of PANI and PANI-doped Cd materials dissolved in dichloromethane (CH₂Cl₂) are shown in Fig. 2. In case of PANI absorption peaks are exhibited at ~564, 316 and 271 nm (Fig. 2). It is in agreement of the report that PANI showed two strong absorptions at 320-340 and 600-660 nm. The PANI-doped Cd materials exhibited strong absorption bands at ~ 269 and ~ 380 nm. The region of ~320 nm showed the π-π* transition.

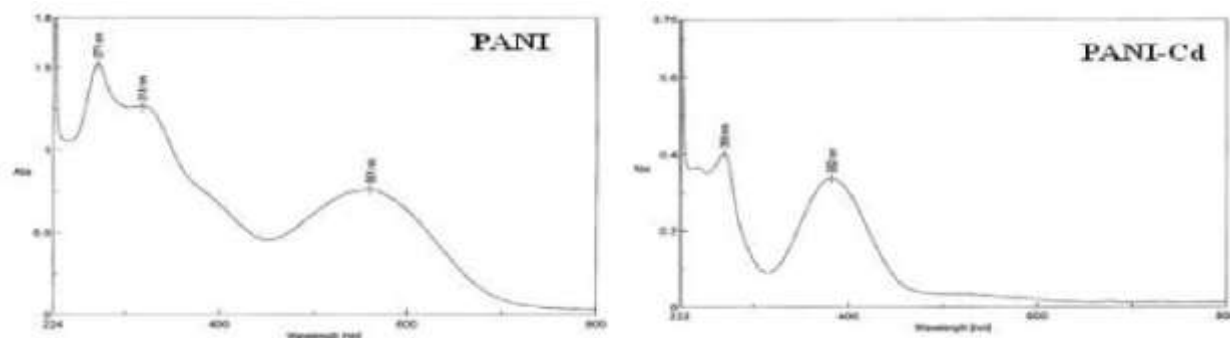


Fig. 2 UV-Visible spectra of PANI and PANI-doped with Cd

3.3. FT-IR analysis

The synthesized PANI based materials have poor solubility in water as well as organic solvents like chloroform, ethanol and even in dimethylsulfoxide. Also they were amorphous as observed from powder XRD patterns. Hence mainly FTIR is helpful for characterization of materials.

The formation of polymers, the functional group on the polymer backbone or change in the protonation-deprotonation equilibrium of emeraldine base form of polyaniline was deduced conveniently from the presence of corresponding bands in the FTIR spectrum. Also the presence of the imine and amine bands is an indication of the polyaniline in emeraldine state (EB). The vibration frequencies (v) precise for polyaniline PANI emeraldine base as well as the PANI based materials synthesized by addition of dopants were analyzed. The bands at ~ 3275 and 3050 cm^{-1} are attributable to hydrogen bonded N-H stretching and aromatic C-H stretching.

The bands around 1590 and 1510 cm^{-1} correspond to quinoid and benzenoid ring stretching vibrations respectively. The absorption band at 1310 cm^{-1} in the spectrum corresponds to the C-N stretching vibration of a secondary aromatic amine. The band at 1167 cm^{-1} is attributable to C-H bending vibrations and band at 832 cm^{-1} for C-H out-of-plane bending vibration in the 1,4-disubstituted ring. These absorption frequencies for the materials synthesized are in good agreements with the reported frequencies. The FTIR spectra are given below in Fig. 3. Similar bands were observed for Cd doped PANI with slight decrease in intensity, shifting and broadening of bands indicates the presence of Cd in PANI.

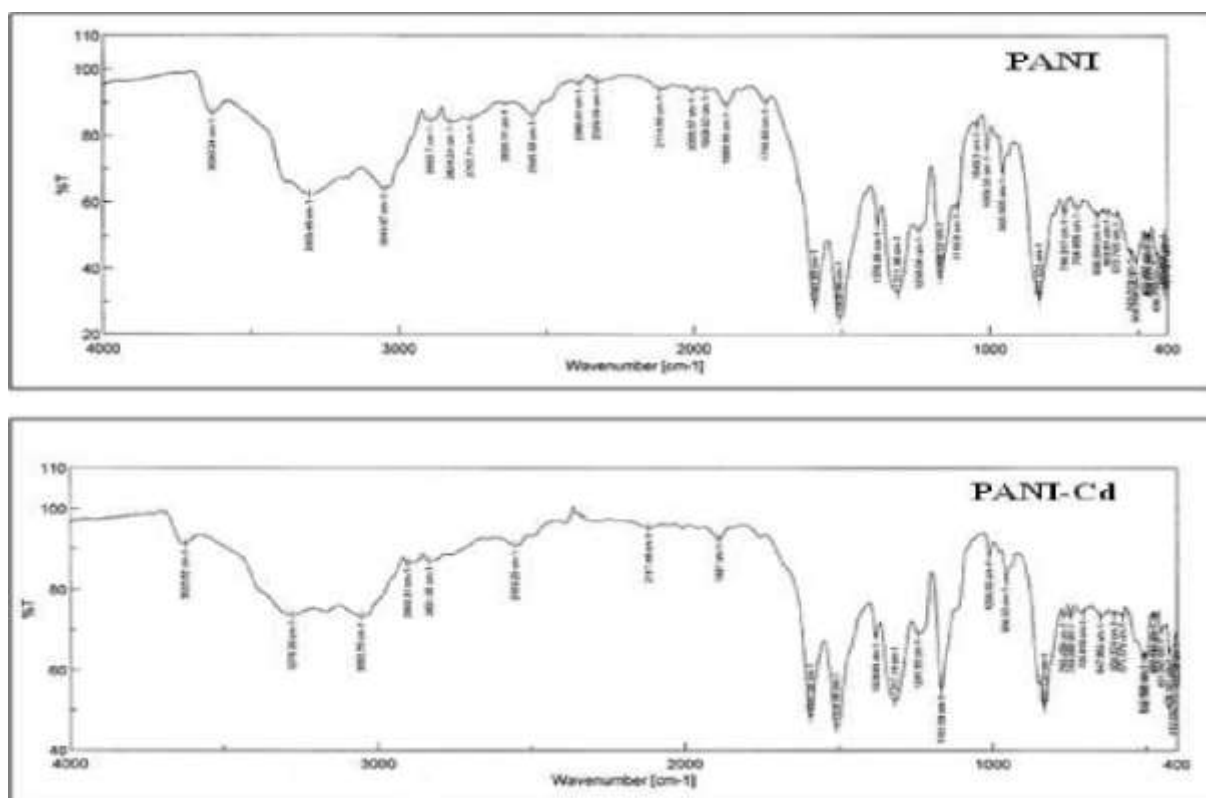


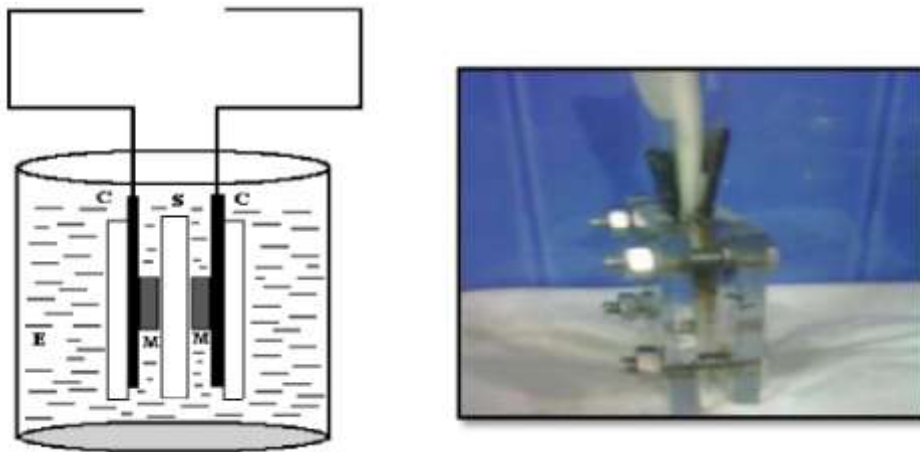
Fig. 3 FTIR spectra of PANI and PANI-doped with Cd

3.4. Cyclic Voltammograms analysis

A cell was fabricated to measure specific capacitance. Material was sandwiched between filter paper and flexible graphite sheet with stainless steel gauze inside (2mm thickness) working as one electrode. Same arrangement was made which would work as second electrode. Both the electrodes brought together and separated with thick filter paper. This assembly was held together by perspex plates and screwed to make a two electrode system as shown in Fig. 4. Then the cell was immersed in electrolyte KOH with concentration 6M. The capacitance was tested using cyclic voltammetry at different scan rates of 1.5, 2.5, 5, 10, 50, 100 mV/s. Capacitance is inversely proportional to scan rate. Lower the scan rate higher the capacitance. Formula used for calculating Specific Capacitance (Farad/g) is:

$$\text{Capacitance (F)} = \text{Current (mA)} / \text{Scan Rate (mV)} = X \text{ Farad}$$

$$\text{Specific Capacitance (F/g)} = X \text{ Farads} / \text{Total weight of sample (g)} = Y \text{ Farad/g.}$$



C: Flexible graphite sheet with stainless steel gauze inside. M: Material whose specific capacitance to be measured. S: Separator (thick filter paper soaked with electrolyte). E: Electrolyte.

Fig. 4 Schematic diagram of double layer capacitor cell and actual cell

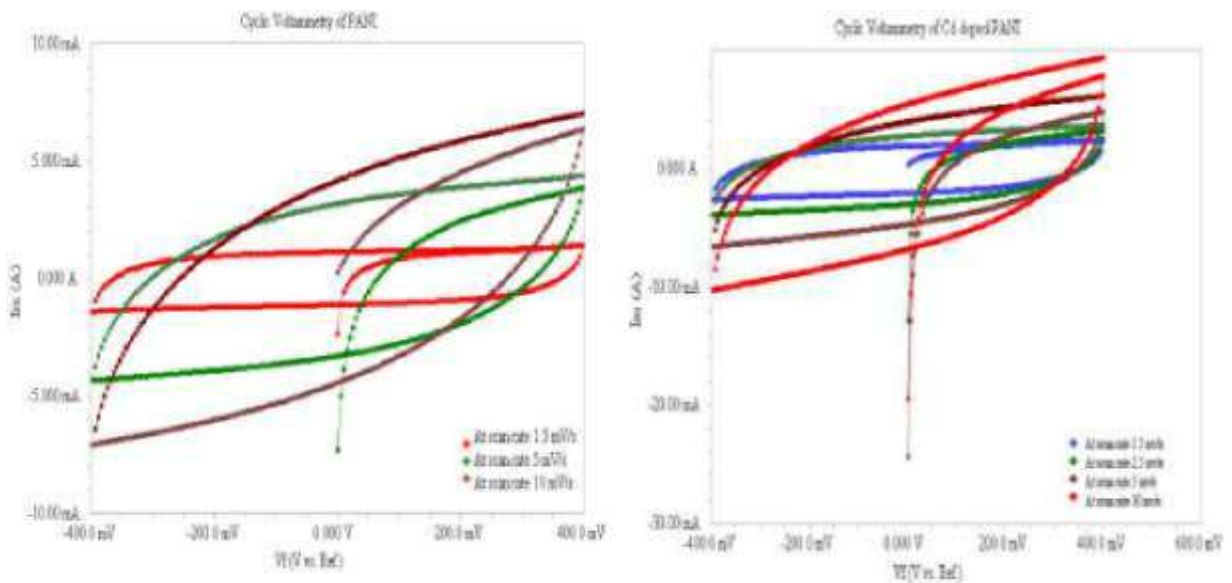


Fig. 5 Cyclic Voltammograms PANI and PANI-doped with Cd

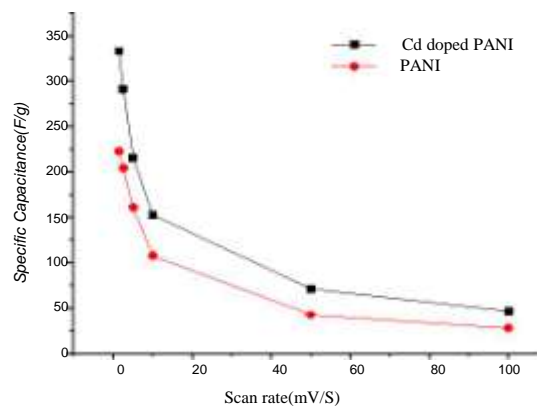


Fig. 6 Variation of specific capacitance with scan rate

The variation of specific capacitance with scan rate 1.5, 2.5, 5, 10, 50, 100 mV/s is shown Fig. 6. As scan rate increases specific capacitance decreases. The specific capacitance of Cd doped PANI is more than PANI. The specific capacitance of PANI was found to be 223.3 F/g and Cd doped PANI was found to be 333.16 F/g at scan rate 1.5 mV/s. The increase in capacitance is due to increase in its surface area and conductivity due to doped metal Cd. The surface area was measured by Single Point Dynamic N₂ BET Sorptometer and it was found for PANI 674 m²/g and Cd doped PANI 1040 m²/g.

IV. CONCLUSIONS

The specific capacitance of PANI is improved due to Cd doping. It was found to be increased from 223.3 F/g to 333.16 F/g at scan rate 1.5 mV/s.

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