

SYNTHESIS OF CERIUM DOPED POLYANILINE AND STUDY OF ITS SUPERCAPACITOR APPLICATIONS

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ABSTRACT

Polyaniline (PANI) and Cerium (Ce) doped polyaniline have been successfully synthesized using chemical oxidation method and characterized by FTIR and powder XRD analysis. Specific capacitance was measured by cyclic voltammetry and found to be increasing due to doping. Maximum specific Capacitance was found 359 F/g at scan rate 1.5 mV/s in 6 M KOH as an electrolyte.

Key words: Polyaniline, SuperCapacitor, Specific Capacitance Etc.

1. Introduction

Supercapacitors are the major source for large amount of energy in a very short period of time. Supercapacitors are considered as alternative energy source for electronic applications due to its rapid charging-discharging rates, high power density and long life. The supercapacitors are also known as ultracapacitor or electric double layer capacitor (EDLC) which differs from regular capacitor. It has very high capacitance value. EDLC stores charge electrostatically using reversible adsorption of ions of the electrolyte on to active material that are electrochemically stable and have high specific area [1, 2].

The electrode active material plays an important role in the performance of supercapacitors. Carbon materials, such as carbon nanotubes, active carbon and graphite with high surface area have been widely investigated as electrical double layer capacitor [3]. Doped polymers which have good electrical conductivity are attractive materials due to their electrochemical reversibility, fast switching properties, low toxicities and low costs [4]. Polyaniline is attractive material for supercapacitor because of their easy and less cost effective synthesis methods. Doped Polyaniline (PANI) can be synthesized by chemically and electrochemically oxidative polymerization [5, 6].

2. Experimental

2.1. Materials and Methods

The chemicals required for synthesis are aniline, ammonium per sulphate, $CeCl_3$ of analytical grade (AR) were purchased from commercial sources (S.D. Fine). For cyclic voltammetry study to obtain the specific capacitance Grammy Ref. 3000 Potentiostat was used. Powder XRD, FTIR and EDS were used to confirm Ce doping in polyaniline. SEM was used to study surface morphology.

2.2. Synthesis of Materials: Synthesis of PANI doped with $CeCl_3$

Synthesis of Sample S-1 (Base)

In a beaker CeCl_3 (5.5 g) was dissolved in an aqueous solution of HCl (1 M, 286 ml). It was treated as solution 1. In another beaker aniline (10 g) was dissolved in solution 1 (150 ml) and cooled at 0°C . It was treated as solution 2. Ammonium peroxydisulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ (24.6 g) was dissolved in remaining 136 ml of solution 1 and cooled at 0°C using ice bath label it as solution-3. After 10 min solution 3 added drop by drop to solution 2 with stirring and kept for 24 h at 0°C using ice bath. The dark blue colored precipitate appeared. It was filtered using Bunker funnel and washed with deionized water. The precipitate was added to NH_4OH (1 M) and the mixture was stirred well. Then the precipitate was filtered out using Bunker funnel and the precipitate was dried at 80°C for 5 h [6].

2.3. Synthesis of Sample S-2 (Emeraldine Salt) (without Treatment of NH_4OH)

In a beaker CeCl_3 (2.784 g) was dissolved in an aqueous solution of HCl (1M, 150 ml). It was treated as solution 1. In another beaker aniline (10 g) was dissolved in 75 ml of solution 1 and cooled at 0°C . It was treated as solution 2. Ammonium peroxydisulfate, $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ (24.6 g) was dissolved in remaining 75 ml of solution 1 and cooled at 0°C using ice bath. It was treated as solution 3. After 10 min solution 3 added drop by drop to solution 2 with stirring and kept for 24 h at 0°C using ice bath. The dark blue colored precipitate appeared. It was filtered using Bunker funnel and washed with deionized water. The dark blue precipitate resulted. It was filtered out using Buckner funnel. The precipitate was washed with de ionized water and it was dried at 80°C for 5 h.

2.4. Activation of Sample

The CeCl_3 doped dry powder of PANI was added to an aqueous solution of ZnCl_2 (6 g of ZnCl_2 (in 100 ml distilled water). The resulting mixture was stirred and ultrasonicated for 20 min. Then the precipitate was filtered off and washed with distilled water followed by drying at 80°C for 6 h.

3. Characterization of Ce-doped Polyaniline

The characterization of the polyaniline doped with Ce compounds was done with FTIR, powder XRD, NMR spectral analyses for the Ce doped PANI materials. Prominent peaks were observed in the FTIR and confirm polymerization of the aniline monomer. Powder XRD pattern indicates the amorphous state of PANI. As the cerium was incorporated in the polymer matrix, sharpened distinct peak of XRD pattern was found at $2\theta = 29^\circ$ [7]. The FTIR spectra of the Ce doped PANI powder samples were recorded in the range $4000\text{-}400\text{ cm}^{-1}$ to confirm polymerization. The IR spectrum of the Ce doped PANI shows seven principal absorptions at 1591, 1499, 1379, 1318, 1239, 1167 and 833 cm^{-1} . The peaks at 1591 and 1499 cm^{-1} are assigned to C-C ring stretching vibrations. The peaks at $1318\text{-}1310\text{ cm}^{-1}$ correspond to N-H bending. The bands at 1166 and 833 cm^{-1} can be attributed to the in plane and out-of-plane C-H bending modes, respectively [8, 9].

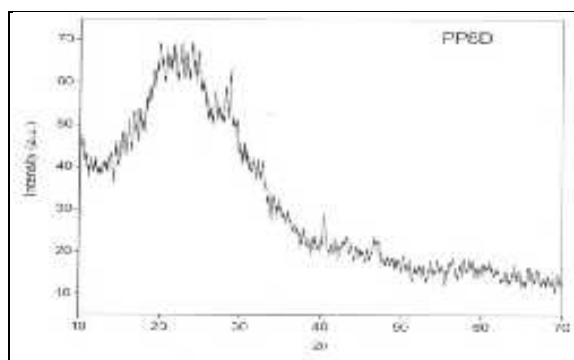


Figure 1: Powder XRD of Ce doped PANI

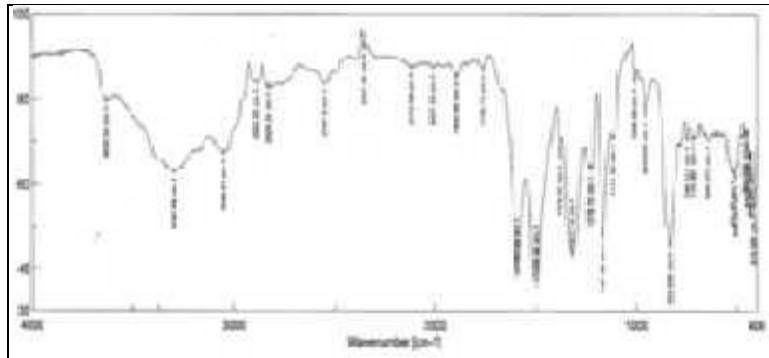


Figure 2: FTIR of PANI range 400 to 4000 cm^{-1}

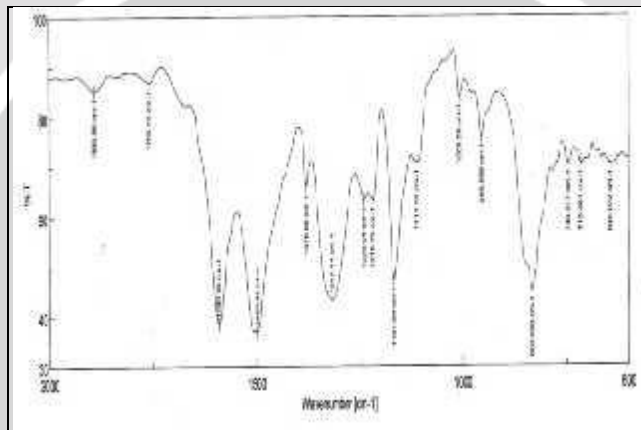


Figure 3: FTIR of Ce doped PANI in Range 600 to 2000 cm^{-1}

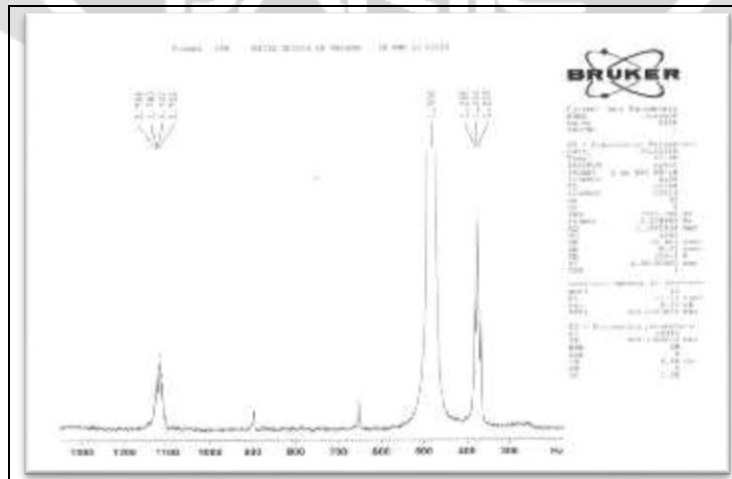


Figure 4: N.M.R of Ce doped PANI

4. Results and Discussion

A cell was fabricated to measure specific capacitance. Material was sandwiched between filter paper and flexible graphite sheet with stainless steel gauze inside (2 mm 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 acrylic plates and screwed to make a two electrode system as shown in Fig. 5. Then the cell was immersed in electrolyte KOH solution (6 M). The specific capacitance was tested using cyclic voltammetry at different scan rates of 1.5, 2.5, 5, 10, 50, 100 mV/s in the potential region between -0.4 V to +0.4 V. Capacitance is inversely proportional to scan rate. Lower the scan rate higher the capacitance. The decreasing trend of the specific capacitance can be related to parts of the surface of the electrode material are inaccessible at higher scan rates. Hence, the specific capacitance obtained at slow scan rates is thought to be closest to that of full utilization of the electrode material [2].

Formula used for calculating Specific Capacitance (Farad/g) is:

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

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

The Ce doping increased the specific capacitance from 224.00 F/g (obtained from PANI) [10] to 359 F/g at 1.5 mV/s.

The results obtained from cyclic voltammetry were confirmed by charge-discharge experiments.

In constant current charging and discharging, $C_{cd} = 2(i)/(s \times m)$

(i) Is the constant current applied, m is total mass of sample and s is slope of charge or discharge curve.

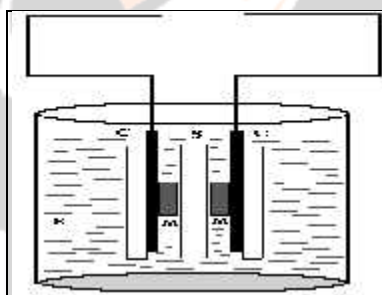


Figure 5: Schematic Diagram of Double Layer Capacitor Cell

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.

Study of Specific Capacitance for Ce doped PANI

Table 1: Specific Capacitance for Ce doped PANI

Scan Rate mV/s	Sample S-1 (Base), (capacitance per gram)	Sample S-2 without activation (capacitance per gram)	Ce-S1, Base activated (capacitance per gram)	Ce-S2, activated acidic (capacitance per gram)
1.5	150	194	238.9	359
2.5	75	187.5	213.6	343.3
5	52	160.5	165.32	278.83

10	29	112.8	125	173.88
25	10.86	58.88	63.38	72.05
50	4.74	35.5	38.46	34.39
75		24.66	27.61	25
100	2.16	19.23	21.45	15

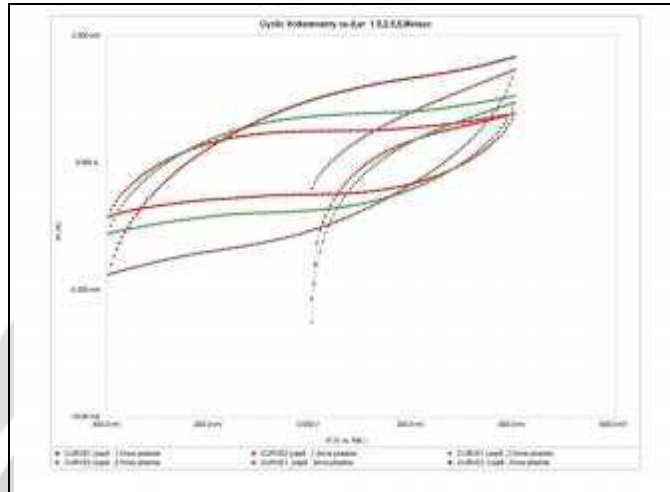


Figure 6: Cyclic Voltammogram [1] for S1 (BASE)

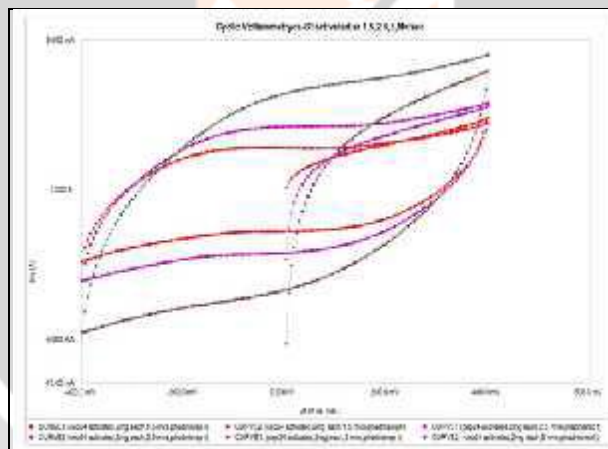


Figure 7: Cyclic Voltammogram [2] for Ce-S1

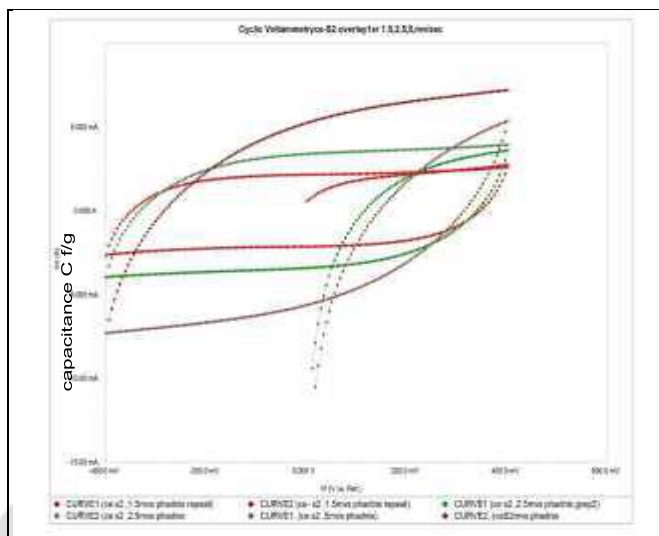


Figure 8: Cyclic Voltammogram [3] for Ce-S2

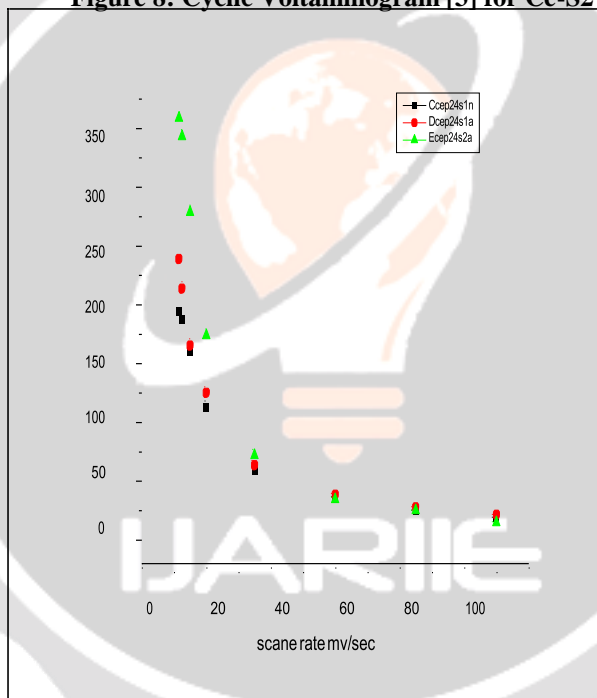


Figure 9: Specific Capacitance Variation at Different Scan Rate for Ce doped PANI

5. Conclusions

The specific capacitance for Ce doped PANI (BASE) was 150 F/g where as for PANI (SALT) it was observed as 194 F/g and it shows increase in the value to 238.9 F/g and 359 F/g after activation process at scan rate 1.5 mv/s respectively. Specific capacitance decreases with increase in scan rate.

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