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Mn doped Polyaniline for Supercapacitor Application

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Abstract: - Polyaniline, polypyrrole, polythiophene and their derivatives are attractive electrode materials for supercapacitors because of their easy synthetic methods and cost effectiveness. Polyaniline (PANI) in doped state is a significant conducting polymer owing to its high conductivity. 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 PANI was doped by manganese (Mn) with a varied weight percentage using chemical oxidation method. Specific capacitance of Mn doped PANI was measured by cyclic voltammetry and found to be varied due to variable doping weight percentage. Maximum specific capacitance was found 360.11 Farad/g at scan rate 1.5 mV/s in 6 M KOH electrolyte.

Keywords: ***Polyaniline, Chemical oxidation, Specific capacitance***

I. INTRODUCTION

Supercapacitors are classified in two categories on the basis of charge storage mechanism, *viz.* electrical double layer capacitor (EDLC) and Pseudocapacitor. EDLC functions to stores the charge electrostatically by the use of reversible adsorption of the ions of an electrolyte on the active material that are electrochemically stable and have high specific surface area [1, 2]. Pseudocapacitor provides capacitance from faradaic redox reactions occurring within the active materials of electrode [3, 4]. Supercapacitors can store and release energy based on single process or both processes, depending on the nature of electrode active materials [5]. Therefore, electrode active materials play an important role in the performance of supercapacitors.

Polyaniline (PANI) is among the best promising materials from the family of conducting polymers. It can be synthesized by chemical or electrochemically oxidative polymerization methods. It is the promising electrode material for pseudo-capacitor purpose because of its high conductivity (in order of 10^3-10^4 Scm^{-1}) and also four oxidation states (Emeraldine salt, Emeraldine base, Leucoemeraldine, and Pernigraniline) which are supposed to enhance its high specific capacitance. One of the challenging issues in development of high performance supercapacitor is to improve its electronic conductivity of the PANI electrode because it is less than metal oxide. Hence an extensive research has been carried out for enhancement of the electronic conduction of electrodes by the use of metal doping and eventually specific capacitance [6-11].

II. EXPERIMENTAL

Materials and Methods

The chemicals required for synthesis *viz.*, aniline, ammonium per sulphate, MnCl2.4H2O of analytical grade (AR) were purchased from commercial sources (S. D. Fine or SRL). For cyclic voltammetry study to obtain the specific capacitance Gramry Ref. 3000 potentiostate was used. XRD and EDAX were used to confirm Mn doping. SEM is used to study surface morphology.

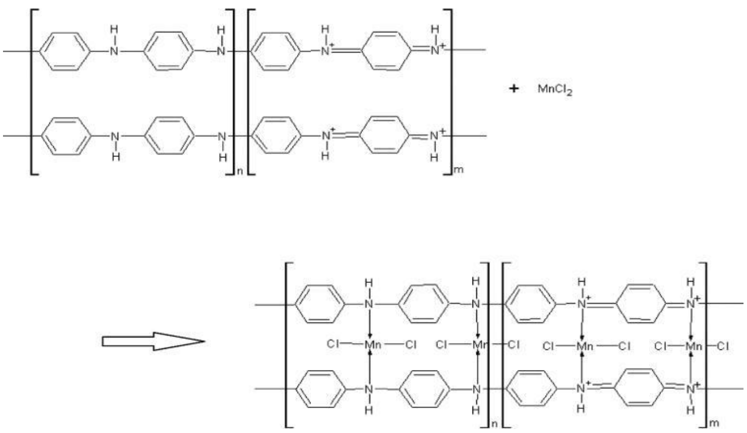
Synthesis of materials

Synthesis of polyaniline (PANI)

The material PANI was prepared at low temperature (~ 5 °C). In a beaker aniline (5.0 ml, 5.1 g, 0.055 mol) was dissolved in HCl (75 ml, 1 M). The solution was cooled in ice bath at the temperature about 0-5 ºC. To this pre cooled (0-5 ºC) solution, ammonium persulfate [(NH4)2S2O8] (12.49 g, 0.055 mol) dissolved in (70 ml HCl of 1 M solution) was added slowly with stirring. Within 2-3 minutes the deep blue-green colored suspension appeared. The reaction mixture was stirred at room temperature for 2 hours. After 2 hours the precipitate was filtered out using Buchner funnel. The precipitate was washed by deionized water till appearance of the colorless filtrate. The water suction was applied to Buckner funnel in order to dry the precipitate. Eventually after the substantial removal of water the cracked cake of PANI was obtained. It was further dried *in vacuo* at 70 °C for 1 hour to get a black free flowing powder of PANI.

Synthesis of polyaniline (PANI) doped with Mn (A)

Sample-A (Mn wt. % 1): MnCl2 (7.22, 0.0365 mol,1%) was dissolved in 200 ml of HCl (1 M) and cooled at 0 ºC which is treated as solution S1.100ml of solution S1 was mixed with pre cooled solution (at 0 ºC) of aniline (10 ml,. 10.2 g, 0.109 mol). This solution is treated as solution S2. Ammonium peroxydisulfate [(NH4)2S2O8] (24.62 g, 0.108 mol) was added slowly with stirring to remaining solution S1 (100ml). This solution is treated as solution S3. The solution S3 is added drop by drop 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 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 ºC for 5 hours to give dark green compound.



Scheme 1: The desired framework of PANI doped with $MnCl_2$

By following the same procedure the variously doped PANI compounds were prepared *viz.*, 0.5, 0.8, 1.5, 2, 3 weight percentage of Mn by addition of 3.61 (**B**), 5.78 (**C**), 10.83 (**D**), 14.44 (**E**) and 21.66 (**F**) g of MnCl2.4H2O respectively, during synthesis.

Activation of PANI and PANI doped with Mn

The obtained material were finely powdered and then soaked in activating agent, 60% MnCl2.4H2O for 24 hours. The material was filter out and washed with deionized water to remove excess activating agent until the pH of water obtained near to 7. The material was dried at 40 °C for 48 hours.

III. RESULTS AND DISCUSSIONS

A cell was fabricated to evaluate the specific capacitance (F). The test 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. The assembly was kept together by the use of Perspex plates which were screwed to have a system with two electrodes as shown in Fig. 1. Then the cell was immersed in electrolyte KOH with concentration 6 M. The specific capacitance was tested for PANI (samples **P-W**, Table 1) and PANI doped with Mn (samples **A-F**, Table 2) using cyclic voltammetry at different scan rates of 1.5, 2.5, 5, 10, 50, and 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 fashion of the specific capacitance (F) can be related to the parts of the surface of the electrode material which are hard to find at higher scan rates. Therefore the specific capacitance (F) resulted at slower scan rates is considered to be the closest to that of complete use of electrode material.

The Specific Capacitance (Farad/g) was calculated by following formula:

Capacitance (F) = Current (mA) / Scan Rate (mV) = X Farad

Specific Capacitance (F / g) = X Farads / Total mass of sample (g) = Y Farad/g.

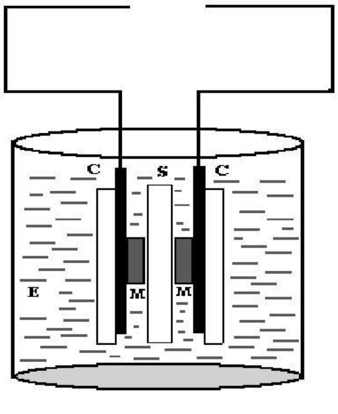


Fig.1: Schematic diagram cell

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.

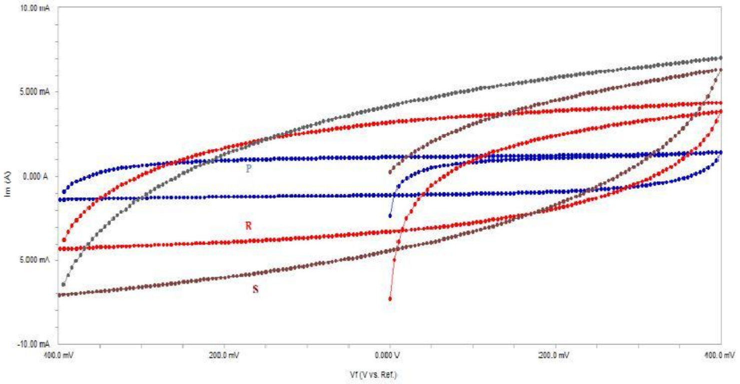


Fig. 2: Cyclic voltammograms PANI

Table 1: Specific capacitance of PANI

PANI	Scan Rate mV/s	Specific capacitance Farad/g
P	1.5	224.00
Q	2.5	207.10
R	5	165.30
S	10	108.74
T	25	62.45
U	50	42.54
V	75	32.23
W	100	28.55

Table 2: Specific capacitance (Farad/g) of Mn doped PANI at different wt. %

Sample code	Scan rate mV/s	Specific capacitance (Farad/g)					
		0.5 % **B**	0.8 % **C**	1 % **A**	1.5 % **D**	2 % **E**	3 % **F**
S1	1.5	242.17	244.33	360.11	253.00	213.93	207.00
S2	2.5	184.84	195.5	335.2	207.25	205	178.6
S3	5	110.52	138.15	294.48	103.6	172.93	109.03
S4	10	56.29	83.97	225.19	72.92	147.15	49.64
S5	25	20.28	39.1	144.35	29.54	104.09	15.26
S6	50	8.13	19.55	104.78	12.28	77.09	7.03
S7	75	4.72	12.92	87.17	6.89	66.15	4.97
S8	100	3.64	8.84	75.07	5.145	57.88	2.66

The cyclic voltammograms for PANI doped with $MnCl_2.4H_2O$ are exhibited in the following figures (Fig. 3-11).

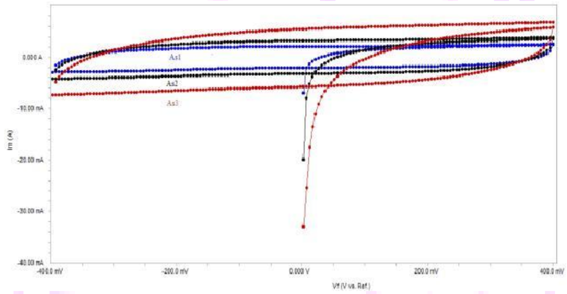


Fig. 3: 1% doped Mn in polyaniline

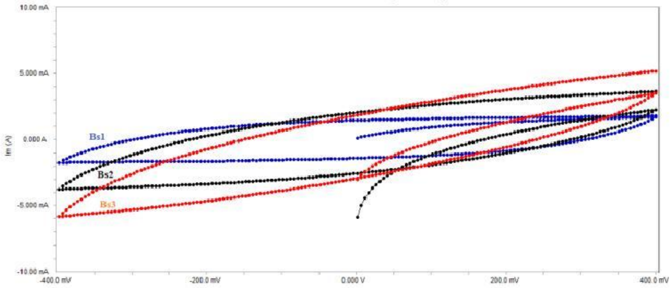


Fig. 4: 0.5% doped Mn in polyaniline

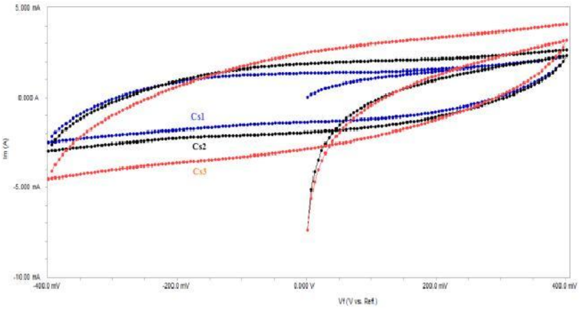


Fig. 5: 0.8% doped Mn in polyaniline

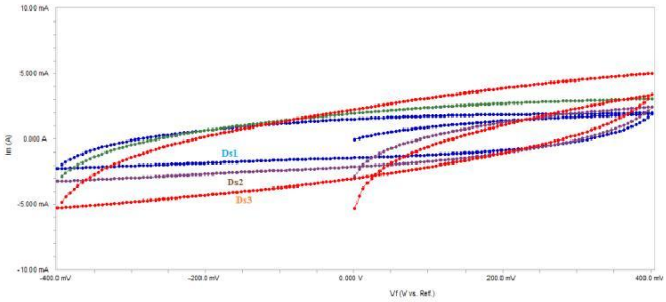


Fig. 6: 1.5% doped Mn in polyaniline

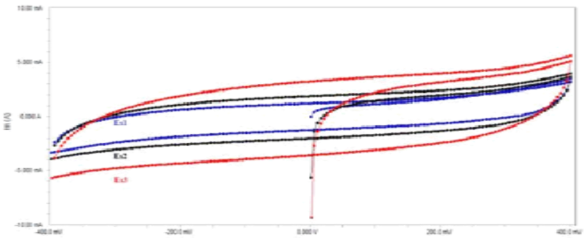


Fig. 7: 2% doped Mn in polyaniline

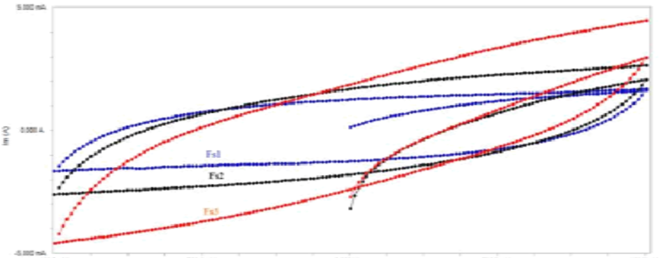


Fig. 8: 3% doped Mn in polyaniline

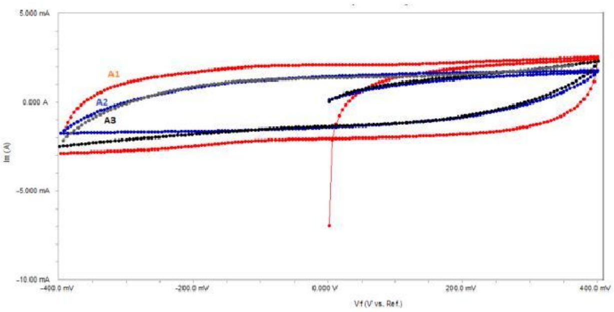


Fig. 9: 0.5%, 0.8%, 1% doped Mn in polyaniline

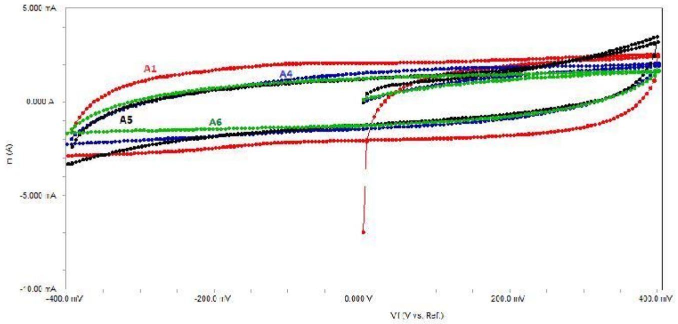


Fig. 10: 1%, 1.5%, 2%, 3% doped Mn in polyaniline

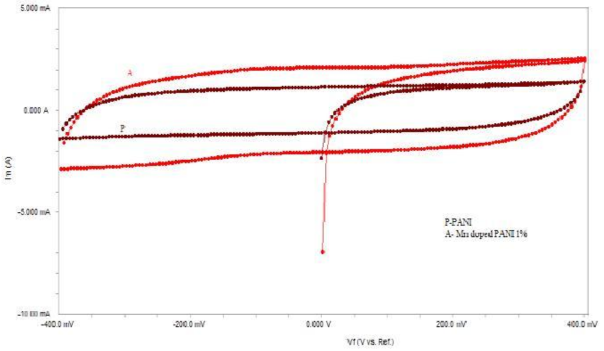


Fig. 11: PANI and 1% doped Mn in polyaniline

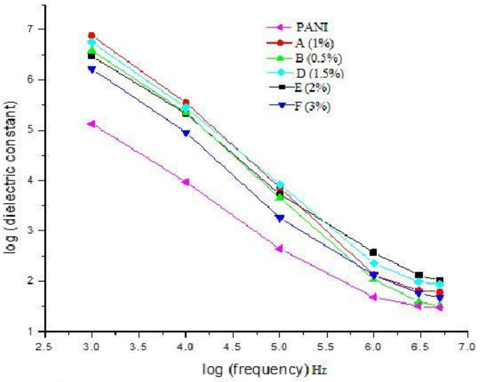


Fig. 12: log(Frequency) against log dielectric constant

Table 3: Maximum specific capacitance of PANI and PANI doped with Mn at different weight %.

% of doping	----	0.5%	0.8%	1%	1.5%	2%	3%
Sample code	**P**	**B**	**C**	**A**	**D**	**E**	**F**
Specific capacitance at scan rate 1.5 mV/s (Farad/g)	224.00	242.17	244.33	360.11	253.00	213.93	207.00

The Fig. 12 shows the variation of dielectric relative permittivity ( ) as function of frequency. It shows dielectric permittivity decreases with frequency. This may be due to orientation of dipoles in polymeric samples in the direction of the applied field. However the decreasing trend seems not sharp as compared for lower frequency region at the high frequency range 100 kHz to 5 MHz. This trend is observed for all graphs for different concentration of dopants. It could be explained by dipoles orientation, which is difficult to rotate at higher frequency .and the high value of at low frequency might be due to the electrode effect and effect of sample. The highest dielectric relative permittivity was observed for sample-A, which is Mn doped (wt. 1%) in Polyaniline.

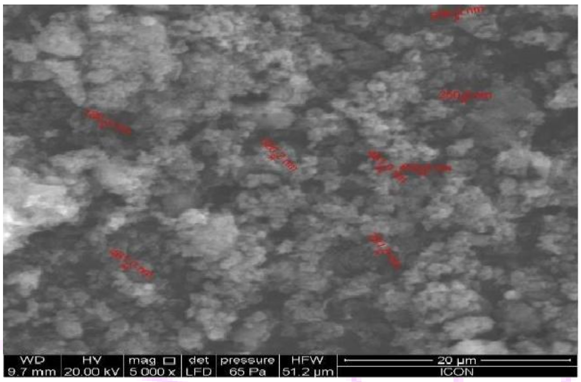


Fig. 13: SEM of 1% doped Mn in polyaniline

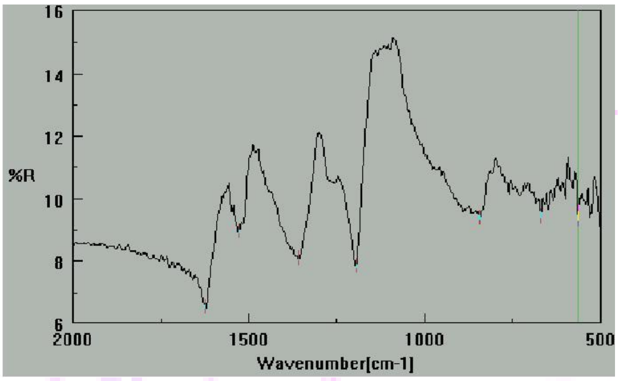


Fig. 14: FTIR of 1% doped Mn in polyaniline

The FTIR spectral analyses were performed for the samples of PANI as well as PANI doped with Mn as the KBr pallets in order to see the structural changes and insertion of Mn in PANI framework. The FTIR were recorded over a range 450-4000 cm^{-1}. The Fig. 14 exhibits the FTIR spectrum of one of such samples where 1% Mn by weight was doped in PANI. In general the FTIR spectra exhibited the bands at about 1555, 1498, 1306, 1135 attributed to the N=Q=N and N-B-N stretching (Q and B denotes the quinoid and benzenoid), N-H bending and –N= vibration. The band at 825 cm^{-1} is attributed to the CH-out of plane bending on 1,4-disubstituted benzene and both the peaks at 737 and 685 cm^{-1}are attributable to the C-H out of plane bending on 1-2 disubstituted benzene [12]. The samples doped with Mn show all these peaks like in PANI samples and also two additional peaks at 1409 and 635 cm^{-1}. The peaks corresponding to 1555, 1498 and 1306 cm^{-1} exhibited a significant shift towards the higher wavenumber indicating the doping of Mn in the PANI. From literature it is known that in the PANI skeleton there are two sites existing for proton or metal ion bonding through either protonation or complexation: amine (-NH-) and imine (-N=) nitrogen atoms. These two peaks are observed at 1306 and 1135 cm^{-1}. From FTIR analyses it is evident that the peak at 1135 cm^{-1} gets shifted to about 1105 cm^{-1} after doping PANI with Mn. This is indicative that Mn gets preferentially bonded with the imine nitrogen atoms. Hence it is evident that the characteristic absorption bands shifted according to the doping level in PANI. Also the stretch appearing at 685 cm^{-1} indicates the contact between organic framework of PANI and inorganic Mn. The intensity of this stretch at 685 cm^{-1} increases with increasing the Mn doping percentage. The presence of the same peak in doped PANI is the evidence of insertion of Mn in PANI.

IV. CONCLUSIONS

We could synthesize the PANI doped with various weight percentages of Mn using chemical oxidation method. We observed the variation of capacitance of these materials with variation of Mn percentage. Maximum specific capacitance was found 360.11 Farad/g at scan rate 1.5 mV/s in 6 M KOH electrolyte for the sample of PANI doped with 1 % of Mn.

V. REFERENCES

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