## **CONTENTS**

а	. Abstract		I
b	. Motivatio	Motivation of the work.	
C.	. Certificate	Certificate of Supervisor	
d	. Contents		IV-VII
e	List of Tal	bles	VIII
f.	List of Fig	jures	IX-XI
g	. Acknowle	edgement	XII-XIII
СНА	PTER I : IN	TRODUCTION	
1.1	Conductir	Conducting polymers	
	1.1.1 Pol	yaniline	5
	1.1.2 Pol	ypyrrole	6
1.2	Character	istics of conducting polymers	7
	1.2.1 Str	uctural distortion in conducting polymers.	8
	1.2.1.1	Solitons	9
	1.2.1.2	Polarons	11
	1.2.1.3	Bipolarons	12
	1.2.2 Con	mparison between conventional and polymer film	
	elec	ctrodes.	13
1.3	Doping of	f conducting polymers	14
	1.3.1 Rec	lox doping	16
	1.3.1.1	Redox p-doping	16
	1.3.1.2 Redox n-doping		17
	1.3.1.3	Redox doping involving no dopant ions.	19
	1.3.	.1.3.1 Photo doping	19
	1.3.	.1.3.2 Charge injection doping.	20
	1.3.2 No	n redox doping	20
	1.3.3 Doj	ping by ion implantation	20
	1.3.4 Do	ping by heat treatment.	20
1.4	Polyanilin	ne nanofibers.	21
			IV

1 5		
1.5	Electrochemical Supercapacitor	21
	1.5.1 Electric double-layer capacitor	23
	1.5.2 Redox or ad-species pseudo capacitor.	24
	1.5.2.1 All polymer based Redox supercapacitor.	24
CHA	PTER II: THEORETICAL ASPECTS:	
2.1	Models of charge transport in electronically conducting	
	polymers.	26
2.2	Theories of electron transfer in polymer film electrodes	28
2.3	Polymerization mechanism	
	2.3.1 Electrochemical polymerization mechanism.	30
2.4	Formation mechanism of Polyaniline nanofibers.	31
2.5	Supercapacitor.	31
	2.5.1 Basic scientific principles.	31
CHA	PTER III: MATERIALS AND METHODS	
3.1	Materials	35
	3.1.1 Monomers.	36
	3.1.2 Solvents.	36
	3.1.3 Dopants	37
	3.1.4 Electrodes	38
3.2	Synthesis of conducting polymer films by electrochemical	
	polymerization	39
3.3	Synthesis of polyaniline nanofibers by interfacial	
	polymerization.	40
3.4	Fabrication of all polymer redox supercapacitor.	40
3.5	Characterizations of conducting polymer films and	
	nanofibers.	42
	3.5.1 Fourier Transform Infrared Spectroscopy	42
	3.5.2 Cyclic Voltammetry	43
	3.5.3 Conductivity measurements by using Four probe	45
	3.5.4 UV-Visible absorption spectroscopy.	46
		V

	3.5.5 Atomic Force Microscopy (AFM)		47
	3.5.6 X-ray Diffraction (XRD)		49
	3.5.6.1 Degree of crystallinity.		49
	3.5.7 Photoluminescence spectroscopy		51
	3.5.7.1 Forms of photoluminescence	2	52
3.6	Characterization of the supercapacitor		53
	3.6.1 Charge-discharge characteristics		53
CHA	APTER IV: POLYANILINE AND POLYPYRR	OLE: SYNTHESIS	
	AND CHARACTERIZATION		
4.1	Synthesis of polyaniline electrodes		58
4.2	Characterization of polyaniline conducting	g polymer films.	59
	4.2.1 Cyclic Voltammetry		59
	4.2.2 FTIR Spectroscopy.		60
	4.2.3 Conductivity studies.		61
	4.2.4 X-Ray Diffractogram studies		62
	4.2.5 AFM studies.		63
4.3	Synthesis of polypyrrole electrodes.		65
4.4	Characterization of polypyrrole conducting polymer films.		66
	4.4.1 X-Ray Diffractogram study.		66
	4.4.2 Conductivity study		67
	4.4.3 AFM study.		67
4.5	Summary.		67
CHA	APTER V: POLYANILINE NANOFIBERS: SY	NTHESIS AND	
	CHARACTERIZATION		
5.1	Synthesis of polyaniline nanofiber	s by interfacial	
	polymerization.		69
5.2	Characterization of polyaniline nanofibers		70
	5.2.1 XRD studies		70
	5.2.2 Conductivity studies		71
	5.2.3 UV-Visible Spectroscopy		72
			VI

	5.2.4 Photoluminescence spectroscopy.	74
5.3	Summary.	75
CHA	APTER VI: FABRICATION AND CHARACTERIZATION OF AL	
	POLYMER BASED REDOX SUPERCAPACITOR.	
6.1	Fabrication of all polymer based redox supercapacitor.	77
6.2	Supercapacitor with polyaniline electrodes	78
6.3	Charge-discharge characteristics of type I supercapacitor.	79
6.4	Supercapacitor with polyaniline and polypyrrole electrodes	80
6.5	Charge-discharge characteristics of type II supercapacitor.	81
6.6	Synthesis of polyaniline nanofiber supercapacitor.	82
6.7	Charge-discharge plot of nanofiber supercapacitor.	82
6.8	Comparision of type I, type II and polyaniline nanofiber	
	supercapacitor.	83
6.9	Summary.	84
CHA	APTER VII: CONCLUSION AND FUTURE SCOPE	
Con	clusion	
Future scope		85
References		
		89

## LIST OF TABLES

**Table 1.1:** Common dopants and their degree of doping used for doping conducting polymers

Table 3.1: Some physical properties of monomers used in the present work.

Table 3.2 Some physical properties of the solvents used

Table 3.3 Some physical properties of the dopants used.

**Table 5.1:** The dc conductivity values of polyaniline nanofibres films measured by four probe technique

**Table 5.2** The dc conductivity values of polyaniline nanofibres doped with different concentrations of HCl

Table 6.1 Characteristic parameters of the type I supercapacitor.

Table 6.2 Characteristic parameters of the type II supercapacitor.

Table 6.3 Characteristic parameters of the PNF supercapacitor.

## LIST OF FIGURES

Fig 1.1 : Molecular structures of some conjugated polymers.

**Fig 1.2**: Parent forms of Polyaniline (a) leucomeraldine (b) emeraldine (c) protonated emeraldine in the bipolaron model

Fig 1.3: Molecular structure of pyrrole and polypyrrole

**Fig 1.4:** Structural diagrams for polyacetylene: (a) *trans*-(CH)<sub>x</sub>, (b) *cis*-(CH)<sub>x</sub> and (c) the two degenerate ground states of *trans*-(CH)<sub>x</sub>.

Fig 1.5: Electronic structure leading to various charge and spin states in solitons. Another feature of the soliton terminology is the natural definition of an "antisoliton" (AS) as a reverse boundary from B phase back to A phase in Fig. 1.4(c).

Fig 1.6: Formation of a polaron.

Fig 1.7: Formation of a bipolaron

Fig 1.8: Electronic band model of a conducting polymer.

Fig 1.9 : The positive and negative solitons in polyacetylene.

Fig 1.10: An Electric double layer capacitor

Fig 1.11: Position of Electric double laver capacitors in comparision to batteries and aluminium condenser

Fig 2.1: The charge storage mechanism in EDLC.

Fig 3.1: Single-compartment three electrode electrochemical cell

Fig 3.2: Block diagram of electropolymerization of conducting polymer film.

Fig 3.3: Block diagram for the synthesis of Polyaniline nanofibers

Fig 3.4: Configurations of Type I, II, III supercapacitors

Fig 3.5: Four-Probe set up for dc Conductivity measurement

Fig 3.6: Types of electronic transitions

Fig 3.7: Block diagram of UV-Visible spectrometer

**Fig 3.8**: Cartoon showing the AFM technique. (A) General concept behind the technique. (B) Force distance curve. Parts of the curve below zero are in the attractive realm. Parts of the curve above zero are in the repulsive regime. (D) tapping mode AFM. Tip is oscillated with large peak to peak amplitude resulting in brief forays into the repulsive regime. Hence the name intermittent contact mode. Tapping mode is a Digital Instruments trademarked name. (E) Noncontact mode AFM. The tip is oscillated with snmall peak to peak amplitude. Operated exclusively in the attractive part of the potential.

**Fig 3.9:** Typical X-ray diffractogram of a polymer sample

Fig 3.10: XRD pattern with crystalline peaks and a broad amorphous hump

Fig 3.11: Experimental set up for Photoluminescence spectroscopy

Fig 3.12: Circuit diagram for charging and discharging of a capacitor

Fig 3.13: Charge-discharge cycle of an ideal capacitor

Fig 3.14: Charge discharge cycle of a real capacitor

Fig 4.1: LiClO<sub>4</sub> doped polyaniline conducting polyaniline film

**Fig 4.2:** Cyclic voltammogram of HClO<sub>4</sub> doped polyaniline at a scan rate of 10 mV/s.

**Fig 4.3**: FTIR spectra of LiClO<sub>4</sub> doped polyaniline.

**Fig 4.4**: Conductivity vs Temperature curve for (a) LiClO<sub>4</sub> doped polyaniline in acetonitrile (b) LiClO<sub>4</sub> doped polyaniline ethanol.

**Fig 4.5:** XRD patterns of LiClO<sub>4</sub> doped polyaniline in (a) acetonitrile and (b) ethanol

Fig 4.6 (a):AFM image of polyaniline doped with LiClO<sub>4</sub> in solvent acetonitrile

Fig 4.6 (b): 3D image of the sample

Fig 4.7 (a): AFM image of polyaniline in ethanol

Fig 4.7 (b): 3D AFM image of the sample.

**Fig 4.8:** Polypyrrole conducting polymer film doped with LiClO<sub>4</sub>

**Fig 4.9:** XRD pattern of polypyrrole doped with LiClO<sub>4</sub>

**Fig 4.10:** The AFM image of the polypyrrole conducting polymer film doped with LiClO<sub>4</sub>

**Fig 5.1:** Different stages of formation of polyaniline nanofibers by interfacial polymerization.

**Fig 5.2:** XRD patterns of Polyaniline nanofibers doped with hydrochloric acid of different concentrations (a) 0.5 M, (b) 1M, (c) 2M, (d) 3M.

Fig 5.3 (a): UV-Vis spectra of Polyaniline nanofibers doped with  $H_2SO_4$ 

Fig 5.3 (b): UV-Vis spectra of polyaniline nanofibers doped with HCl.

Fig 5.3 (c): UV-Vis spectra of polyaniline nanofibers doped with HClO<sub>4</sub>

Fig 5.3 (d): UV-Vis spectra of polyaniline nanofiber doped with oxalic acid.

Fig 5.4: PL spectra of polyaniline doped with HCL (a) 1M, (b) 2M, (c) 3M.

Fig 5.5: PL spectra of Polyaniline doped with (a) H<sub>2</sub>SO<sub>4</sub> and (b) HClO<sub>4</sub>.

Fig 6.1: Geometrical structure of supercapacitor fabricated

**Fig 6.2:** Type I supercapacitor fabricated with two polyaniline electrodes with PEO as electrolyte.

**Fig 6.3:** Charge–Discharge characteristics of type I supercapacitor with polyaniline electrodes and PEO as electrolyte.

**Fig 6.4:** Type II supercapacitor fabricated from one polyaniline electrode and one polypyrrole electrode with PEO as the Gel polymer electrolyte.

Fig 6.5: Charge discharge plot of a type II supercapacitor.

Fig 6.7: Charge-Discharge plot of a polyaniline nanofibers

**Fig 6.8 (a):** Comparison of the discharge resistance and coulombic efficiency of the three supercapacitors

Fig 6.8 (b): Comparison of the internal resistances of the three supercapacitors