Preparation and Electroanalytical Characterization of Polyaniline:Polyacrylonitrile Composite Films

Atika Khatoon, Mohd Khalid, Faiz Mohammad

Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002, India

ABSTRACT: Electrically conducting composite films of polyaniline:polyacyrlonitrile (PANI:PAN) prepared with varying composition ratios of aniline mixed with a fixed amount PAN. The films of optimum thicknesses (0.10 mm) were obtained using an electrically operated automatic pressure machine. The films polymerized by oxidative polymerization using $0.1M$ potassium persulphate ($K_2S_2O_8$), undoped in $1M$ aqueous ammonia (NH_4OH) and doped in $1M$ hydrochloric acid (HCl). The conductivity of composite films was studied by keeping it in $1M$ HCl for different time period using 4-in-line probe DC electrical conductivity measuring instrument and the temperature dependence of DC electrical conductivity was studied using isothermal technique. The PANI:PAN composite film is used as a working electrode in an electrochemical cell. Chemically doped composite film is used as cathode (working electrode), aluminum metal foil as anode (counter electrode) and platinum foil as reference electrode. The electrolyte is of $0.05M$ aluminum chloride ($AlCl_3$) in dimethyl sulfoxide (DMSO). The voltage of the working electrode is stabilized with respect to the reference electrode and current applied between the working and counter electrode through a 9-V battery. The change in voltage versus time is plotted as the discharge curve and reversing the cell processes results in the doping of the composite films. The diffusion coefficient of the dopant ion (Cl^-) present in the fully doped films were estimated by the galvanostatic pulse technique and found to be different in different samples in the range of 10^{-16} to 10^{-12} cm^2 s^{-1}. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3769–3780, 2008

Key words: composites; diffusion in conducting composites; polyaniline; charging-discharging

INTRODUCTION

The electrically conductive polymers have been the focus of numerous studies because of their unique chemical and electronic properties unlike we were used to polymers—i.e., plastics—being somehow the opposite of metals. But, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa have changed this view with their discovery that a polymer, polyacetylene, can be made conductive almost like a metal.[1] The ability to dope these polymers over the wide range of electrical conductivity from insulator, through semiconductor, to metal, opened a new field of research and perspective.[2] The higher conductivities are related to an oxidation state of the organic material.[3] Further conducting material of improved performance having chemical and environmental stability and desirable mechanical strength composites of a bulk material (usually nonconducting polymer) was employed as a matrix to the electrically conductive polymers. The resulting composite can also be used in applications where metals have typically been the materials of choice. These materials offer a unique combination of properties such as processibility and tailorable electrical conductivity that make them very attractive materials in the electronic area.[4] The advantages of using these materials include their lightweight, resistance to corrosion and their ability to be readily adapted to the needs of a specific application. These composites possess outstanding electrochemical, chemical, and mechanical properties. As the electroanalytical characterization of such materials is a prequalification to select them for a particular application, this article presents the preparation and electroanalytical characterization of electrically conducting composites based on polyaniline and polyacrylonitrile.

One of the most promising applications of conducting polymers, that was the focus of attention worldwide, was that of lightweight batteries. While a number of the conjugated polymers were tried, most of them failed to exhibit the desired properties, specifically with respect to stability. However, batteries made using either polypyrrole or polyaniline as the positive electrode (cathode) and lithium-aluminum alloy as the negative electrode (anode) exhibited much more respectable properties. The electrolytes in these cases were either LiClO$_4$ or LiBF$_4$ in propylene carbonate (a highly aprotic solvent, which

Correspondence to: F. Mohammad (faizmohammad54@rediffmail.com).

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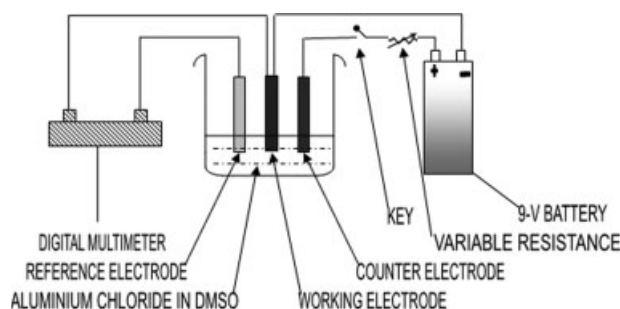InterScience®
DISCOVER SOMETHING GREAT

Figure 1 Set up of electrochemical cell for charging-discharging and diffusion study.

is also fairly resistant to oxidation). Research activities on polyaniline composites involve experimental electrochemical studies, which are explored to gain understanding of fundamentals related to several areas of applications, such as batteries, conducting polymers, electrochemical capacitors, sensors, electrocatalysis of oxidation of small organic molecules, fuel cells, electrochemical reduction of carbon dioxide, etc. In the area of batteries, various studies related to rechargeable lithium and magnesium batteries have been conducted in recent years. Preparation of positive electrode active materials and their electrochemical evaluation for battery application have been studied. The basic concept is to relate the chemical and electrochemical doping of an organic polymer to their applications as electroactive materials in rechargeable batteries. One major drawback of this battery was that the energy density or energy storage capacity was low and its recyclability (charging-discharging cycles) was relatively poor. Thus, the prospects of polymeric battery are still alive and are awaiting further technological refinement (Munichandraiah, N. Indian Institute of Science, muni@ipc.iisc.ernet.in; personal communication).

In this article, we have reported a simple chemical route to fabricate electrically conductive films, using polyacrylonitrile as supportive matrix and polyaniline (emeraldine base) as the electronically conductive polymeric filler. The resulting materials are environmentally stable and mechanically strong freestanding films.

EXPERIMENTAL

Preparation of PANI:PAN composite films

Polyacrylonitrile was quantitatively weighed and dissolved in tetrahydrofuran and kept at room temperature for 24 h. Aniline in quantitative ratio is poured dropwise in the PAN solution and stirred for homogeneous mixing of aniline. The mixture is then slowly poured in glass circle and left undisturbed to be dried completely for 2–3 days. After the film is completely dried, it is slowly removed from the glass circle and stored in airtight polybags until further processing.

A small portion is cut from the film thus prepared and pressed in electrically operated automatic Pressure (Model-PF-A15, Techno Search Instruments) in 0.1 mm die at pressure of 6 ton is applied at 120°C. The film thus obtained is of thickness of ranging between 0.1 mm. From each film a rectangular portion of cross section area (2.5×1) cm^2 is cut, weighed, and then polymerization in aniline-soaked PAN films is effected in 0.1M potassium persulphate solution (in 1M HCl) for 48 h. Composite film thus synthesized is washed in distilled water and dried in dry box for 4–5 h. Each film is then carefully weighed in an electronic balance, their density calculated from the weight and volume data and dc electrical conductivity measured by the four probe technique. The conductivity of each film is further enhanced to the range of metals by doping in 1M HCl for a maximum period.

Preparation of cathode active materials

The preparation of PANI:PAN composite films (as a cathodic material) was done by immersing aniline (doubly distilled) in PAN solution. The PANI:PAN film is pressed in electrically operated automatic press to obtained film thickness ranging between 0.10 and 0.15 mm. Aniline is polymerized within the PAN matrix with 0.1M potassium persulphate in 1M HCl for 24 h. The films were taken out and washed with doubly distilled water, undoped by treatment with excess of aqueous ammonia (2.5%) and repeat-

TABLE I
Preparation of Polyaniline:Polyacrylonitrile (PANI:PAN) Composite Films

| Sample | Quantity of PAN (g) | Quantity of aniline | | Quantity of THF (mL) | Quantity of 0.1M K$_2$S$_2$O$_8$ (mL)[a] |
		(g)	(mL)		
PANI:PAN-1	1.0	0.5	0.49	30	100
PANI:PAN-2	1.0	0.75	0.735	30	100
PANI:PAN-3	1.0	1.0	0.98	30	100

[a] Solution of K$_2$S$_2$O$_8$ prepared in HCl (1M).

TABLE II
Electrical Conductivity of Polyaniline:Polyacrylonitrile (PANI:PAN) Composites Films

Sample		Quantity of $0.1M$ $K_2S_2O_8$ (mL)	Thickness of composite film (mm)	Weight of polymerized film (g)		DC electrical conductivity of PANI:PAN composite film (S cm^{-1})	
				Before doping	After doping	Undoped	Doped
PANI:PAN-1	a[a]	30	0.14	0.0325	0.0342	2.9×10^{-2}	3.0×10^{0}
	b	30	0.15	0.0396	0.0436	2.4×10^{-3}	8.0×10^{-3}
	c	30	0.14	0.0363	0.0400	4.7×10^{-2}	1.58×10^{-3}
	d	30	0.15	0.0355	0.0380	3.7×10^{-3}	6.2×10^{-4}
	e	30	0.16	0.0362	0.0380	6.9×10^{-3}	1.7×10^{-4}
	f	30	0.17	0.0343	0.0363	1.6×10^{-3}	5.0×10^{-4}
	g	30	0.13	0.0336	0.0360	1.2×10^{-3}	2.0×10^{-3}
PANI:PAN-2	a	30	0.15	0.0271	0.0300	1.5×10^{-4}	3.6×10^{-2}
	b	30	0.15	0.0320	0.0326	3.2×10^{-4}	1.3×10^{-3}
	c	30	0.16	0.0380	0.0385	4.16×10^{-2}	6.1×10^{-1}
	d	30	0.14	0.0325	0.0340	2.7×10^{-2}	2.6×10^{-1}
	e	30	0.20	0.0350	0.0345	1.53×10^{0}	5.5×10^{-1}
	f[a]	30	0.13	0.0355	0.0388	1.13×10^{0}	1.7×10^{0}
	g	30	0.17	0.0335	0.0300	7.4×10^{-2}	6.5×10^{-1}
PANI:PAN-3	a	30	0.14	0.0331	0.0360	1.4×10^{-1}	2.2×10^{-1}
	b[a]	30	0.16	0.0361	0.0378	2.5×10^{-1}	1.2×10^{0}

[a] Selected for different measurements.

edly washed with distilled water until the filtrate became neutral. The composite films were redoped with $1M$ HCl for 48 h and then dried for 24 h at 45°C in a dry box and then stored in desiccator for experiments.

TABLE III
FTIR Peak Positions (cm^{-1}) of Polyaniline (PANI), Polyacrylonitrile (PAN), and Polyaniline:Polyacrylonitrile (PANI:PAN) Composites

PANI	PAN	PANI: PAN1-1a	PANI: PAN1-2f	PANI: PAN-3b
3259	3969	3617	3439	3469
3035	3652	3551	3239	3234
2846	3555	3440	3004	3007
2358	3442	2950	2049	2048
1587	2950	2844	1965	1959
1497	2844	2592	1736	1724
1377	2653	2.49	1580	1580
1302	2598	1965	1427	1427
1241	2414	1726	1384	1387
1143	2051	1603	1267	1266
1008	1962	1457	1104	1102
954	1726	1387	1064	1064
824	1637	1145	985	983
728	1451	1034	911	913
505	1387	988	841	841
	1069	912	826	825
	983	841	810	803
	954	827	750	751
	912	810	693	696
	842	750	583	588
	827	694	510	510
	810	618		
	750	554		
	655	509		
	524			

Set up of electrochemical cell

PANI:PAN composite films are used as working electrode in the electrochemical cell. Fully doped (chemically) composite film is considered to be
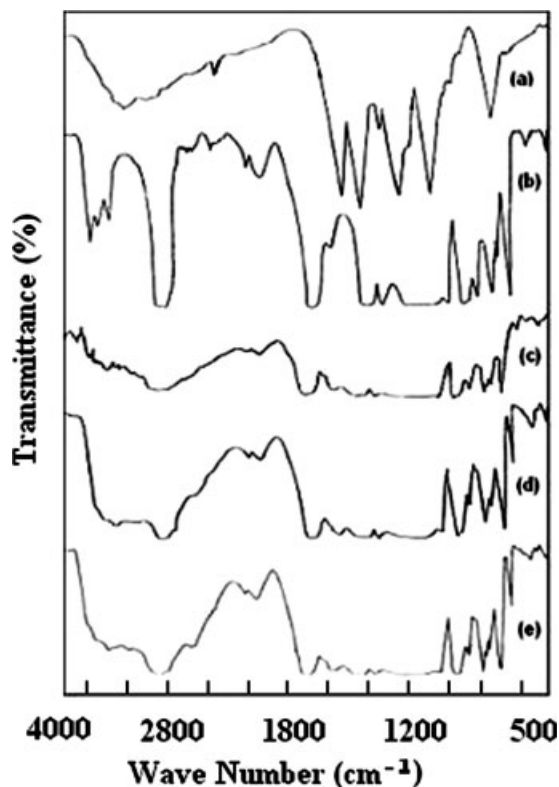

Figure 2 FTIR spectra of polyaniline, polyacrylonitrile and polyaniline:polyacrylonitrile (PANI:PAN) composite films (a) PANI, (b) PAN, (c) PANI:PAN-1a, (d) PANI:PAN-2f, (e) PANI:PAN-3b.

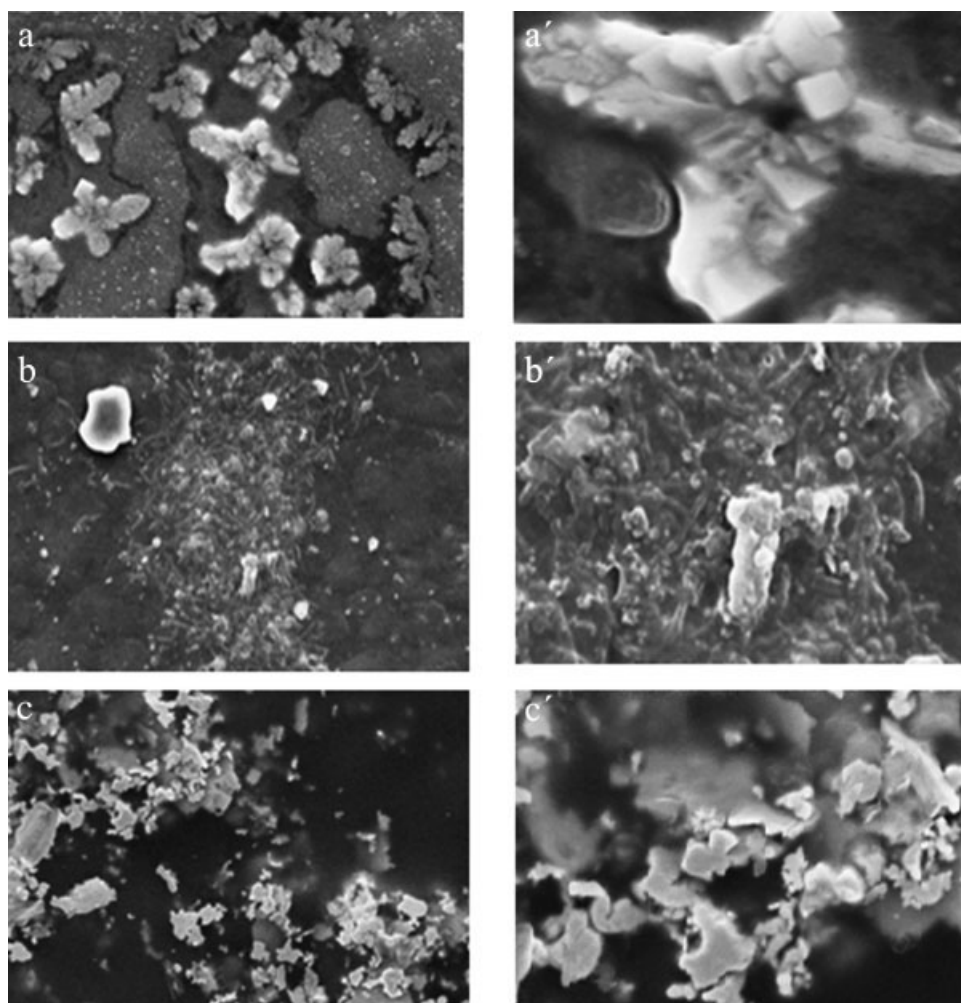**Figure 3** SEM photographs of PANI:PAN composites taken at two different magnifications. (a) PANI:PAN-1a at low magnification (a′) PANI:PAN-1a at high magnification. (b) PANI:PAN-2f at low magnification (b′) PANI:PAN-2f at high magnification. (c) PANI:PAN-3b at low magnification (c′) PANI:PAN-3b at high magnification.

charged. Thereby a fully charged composite film is used as cathode (working electrode), aluminum metal foil is used as anode (counter electrode) and platinum foil as reference electrode. The electrolyte is of aluminum chloride in DMSO and had a constant pH of around 4–5. 1 cm^2 area of these electrodes was dipped in 20 mL electrolyte solution in a glass beaker. The positive pole of a 9-V battery was connected to the counter electrode (aluminum foil) with Teflon-coated platinum wire and the negative pole to the positive electrode (PANI:PAN composite film). On the other hand, the reference electrode (platinum foil) and as well the working electrode were connected to the digital multimeter (Fig. 1).

Current is then applied between the working and counter electrode through a 9-V battery and voltage of the working electrode stabilized with respect to the reference electrode. The change in voltage versus time is recorded and the discharge curve obtained.

Estimation of diffusion coefficient into and out of composite films

The various techniques available for ionic diffusion measurement have been discussed briefly with the merits and demerits of their use for different types of materials by Foot.[5] The galvanostatic pulse technique has been used very successfully to estimate Li$^+$ ion diffusion in TiS$_2$ by Winn et al.[5] and in NiPS$_3$, FePS$_3$, and FePSe$_3$ single crystals by Foot.[6]

In this method a constant current pulse is passed through the equilibrated electrode material. This causes a change in the electrode potential against a standard electrode due to deposition of a quantity of ions equivalent to IP/F on the electrode surface. An amount of 10^{-10} to 10^{-8} mol of dopant (depending upon strength of pulse) was deposited on the polymer electrode as the diffusion equation would be valid only for small changes in electrode potential i.e., small change in y value. Clean Al or Pt foil was used as standard electrode. Potential of this

TABLE IV
Discharging of Polyaniline:Polyacrylonitrile (PANI:PAN) Composite Films

(a) PAN:PAN-1a		(b) PANI:PAN-2f		(c) PANI:PAN-3b	
Time (min)	Voltage (V)	Time (min)	Voltage (V)	Time (min)	Voltage (V)
0	−15	0	−15.7	0	−9.97
0.5	−15.25	1	−15.82	5	−10.32
1	−15.4	2	−15.9	10	−10.48
1.5	−15.52	3	−15.98	15	−10.6
2	−15.63	4	−16.1	20	−10.66
2.5	−15.72	5	−16.18	25	−10.74
3	−15.78	6	−16.22	30	−10.86
3.5	−15.8	7	−16.24	35	−10.94
4	−15.84	8	−16.25	40	−11.00
5	−15.87	10	−16.26	45	−11.04
6	−15.93	12	−16.27	50	−11.08
7	−15.97	15	−16.28	55	−11.11
8	−16.02	17	−16.3	60	−11.12
9	−16.05	20	−16.31	65	−11.12
10	−16.06	22	−16.32	–	–
11	−16.07	25	−16.318	–	–
12	−16.08	28	−16.32	–	–
13	−16.09	30	−16.33	–	–
14	−16.08	–	–	–	–
15	−16.07	–	–	–	–
16	−16.08	–	–	–	–

"quasistandard" electrode may be assumed to be constant during the experiment, as equilibration does not take too long. As the deposited ions diffuse into the electrode material, the surface concentration changes and the electrode potential recovers. A plot of recovery voltage (E_t) against $t^{-1/2}$ should follow a straight line, if the diffusion behavior is governed by Fick's law. The following expression was used for the estimation of the diffusion coefficient for the ions into and out of the electrode material.

$$\exp\left(\frac{(E_t-E_0)F}{RT}1\right) = \frac{IP}{(1-y)FAC_o\sqrt{\pi Dt}} \quad (1)$$

Plot of $(E_t - E_o)$ versus $t^{-1/2}$ follows a straight line of slope,

$$S = \frac{IPRT}{(1-y)^2F^2AC_o\sqrt{\pi D}} \quad (2)$$

$$D\pi = \left(\frac{IPRT}{(1-y)^2F^2AC_oS}\right)^2 \quad (3)$$

$$D = \frac{I^2P^2R^2T^2}{(1-y)^4F^4A^2C_o^2S^2\pi} \text{ cm}^2 \text{ s}^{-1} \quad (4)$$

where I is the current strength of impulse (A), P is the duration of the impulse (s), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the experimental temperature (K), F is Faraday's constant (96,487 mol^{-1}), A is the area of working electrode (cm^2), C_o is the

dopant concentration in the composite film (mol cm^{-3}), $(1-y)$ is the concentration correction factor and E_o is the original equilibrium potential of the electrode. This method is preferred because during data acquisition, the current does not pass through the electrode material. So no correction has to be made for electron transfer kinetics or variable Ohmic (IR) potential difference.

It is essential to know that the extent of dopant present in the polymer for the estimation of the diffusion coefficient, therefore, as-prepared PANI:PAN composite films were undoped in electrochemical cell containing appropriate electrolyte solution by applying a limiting current of few-microamperes at 40°C, some before and some after diffusion measurements, to establish that there is no loss of dopant by any other reaction such as moisture compensation during data acquisition. The voltage against an aluminum electrode was recorded at regular intervals.[7]

$$\text{Mol. Ratio } y = \frac{itM_m}{FW} \quad (5)$$

$$\text{Dopant concentration, } C = \frac{yd}{(M_m + yM_d)} \text{ mol cm}^{-3} \quad (6)$$

where C_o is the dopant concentration in polymer composite (mol cm^{-3}), y is the mol ratio (number of mol of dopant present per monomer unit), I is the strength of the current passed (A), t is the time taken in undoping (s), M_m is the formula weight of monomer residue (g), F is the Faraday's constant (96,487 C mol^{-1}), w is the weight of polymer (g), d is the density of the poly-
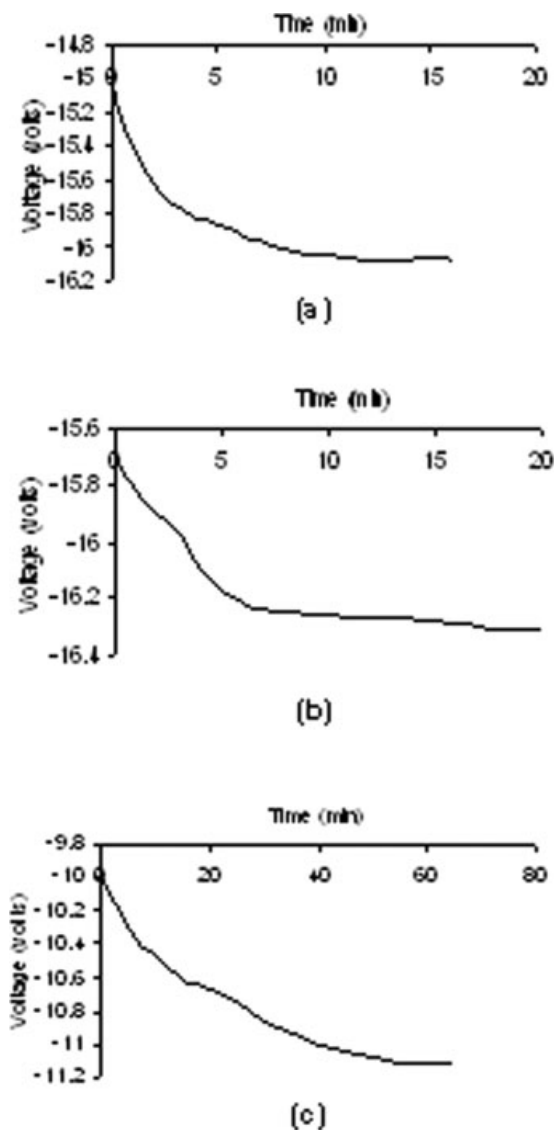
Figure 4 Electrochemical discharging of PANI:PAN composite films—(a) PANI:PAN-1a, (b) PANI:PAN-2f, and (c) PANI:PAN-3b in AlCl₃ (DMSO).

mer, and M_d is the formula weight of dopant ion (g). The highly conducting film from each sample was selected for different measurement.

RESULTS AND DISCUSSION

Preparation of conducting polymer composite materials

The different samples of PANI:PAN composite films were prepared by casting a homogeneous mixture of aniline with polyacrylonitrile dissolved in tetrahydofuran solution (Table I). The conductivity of each film is enhanced to the range of metals by doping in $1M$ HCl for a maximum period and the dc electrical conductivity of each film tabulated Table II. On the basis of high electrical conductivity the samples

PANI:PAN-2a PANI:PAN-2f PANI:PAN-3b for electrochemical and diffusion studies.

The composite films are oxidized in an aqueous acidic (HCl) medium with potassium persulphate, the protonated conducting form of polyaniline is produced as per the following equation:
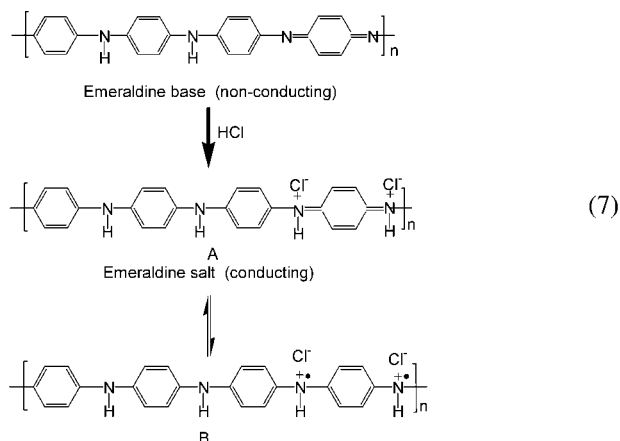

Both the conducting form of PANI, A and B, exists in equilibrium with each other. The mechanisms of the two forms are explained on the basis of proton induced spin unpairing mechanism, but with no change in the number of electrons in the polymer chain.[8]

The conducting PANI:PAN composite films so formed are undoped with either gaseous or aqueous ammonia. Schöllhörn and Zagefka[9] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides, which has been further supported by the work of Foot and Shaker.[10] The overall chemical reaction for the disproportionation of ammonia is given by the following equation:

$$8NH_3 \rightarrow 6NH_4^- + 6e^- + N_2 \qquad (8)$$
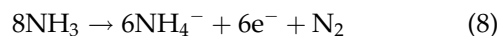
In addition, the analogous redox reaction for chemical compensation by water is suggested by Mohammad[11] as per the given equations:

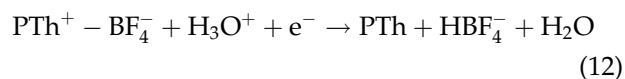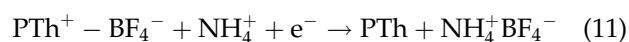$$6H_2O \rightarrow 4H_3O^+ + 4e^- + O_2 \qquad (9)$$
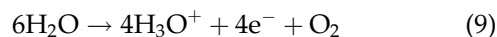
When aqueous ammonia is taken for undoping the disproportionation reaction is explained by the following equation:

$$NH_4OH \rightarrow NH_4^+ + OH^- \qquad (10)$$
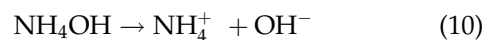
The electrochemical undoping and chemical compensation behavior of polythiophene and polypyrrole [PTh-BF₄ and PPy-BF₄] can be well explained.[8] The gaseous or aqueous ammonia compensation of PTh-BF₄ is chemically neutralized for its electronic charge as per the equations given below:

TABLE V
Diffusion Behavior of Polyaniline:Polyacrylonitrile-1 (PANI:PAN-1a) Composite Films and Estimation of Diffusion Coefficient

Film specification		t (s)	E_t	$t^{-1/2}$	$E_t - E_o$
$w = 0.0295$ g	1	3	0.15	0.577	0.08
$d = 0.05$ g mm^{-3}		5	0.12	0.447	0.05
$\sigma = 1.47$ S cm^{-1}		10	0.11	0.316	0.04
$i = 150$ mA		12	0.10	0.288	0.03
$P = 5$ s		15	0.09	0.258	0.02
$I = 1 \times 10^{-4}$ A		18	0.08	0.236	0.01
$y = 4.7115$		25	0.07	0.2	0
$C_o = 9.055 \times 10^{-4}$		$E_o = 0.07$ V	$S = 0.0755$		$D = 1.665 \times 10^{-13}$
	2	5	0.07	0.447	0.07
		8	0.06	0.354	0.06
		10	0.05	0.316	0.05
		15	0.04	0.258	0.04
		18	0.03	0.236	0.03
		30	0.02	0.183	0.02
		32	0.01	0.177	0.01
		$E_o = 0$ V		$S = 0.0787$	$D = 1.298 \times 10^{-13}$
	3	8	0.06	0.354	0.08
		10	0.05	0.316	0.07
		15	0.04	0.258	0.06
		18	0.03	0.236	0.05
		20	0.02	0.224	0.04
		30	0.01	0.183	0.03
		45	0	0.149	0.02
		75	−0.01	0.115	0.01
		90	−0.02	0.105	0
		$E_o = -0.02$ V	$S = 0.0873$		$D = 1.100 \times 10^{-13}$
	4	4	0.04	0.500	0.08
		10	0.02	0.316	0.06
		12	0.01	0.288	0.05
		15	0	0.258	0.04
		30	−0.01	0.183	0.03
		60	−0.02	0.129	0.02
		$E_o = -0.04$ V	$S = 0.0892$		$D = 1.55 \times 10^{-3}$

$$PTh^+ - BF_4^- + NH_4^+ + e^- \rightarrow PTh + NH_4^+ BF_4^- \quad (11)$$

$$PTh^+ - BF_4^- + H_3O^+ + e^- \rightarrow PTh + HBF_4^- + H_2O \quad (12)$$

The explanation given for the undoping of polythiophene and polypyrrole on the basis of eqs. (11) and (12) cannot satisfactorily explain the undoping phenomenon in polyaniline or its composites. Hence, the analogous reactions[12] explaining undoping with either gaseous or aqueous ammonia and doping with HCl (1M) of polyaniline component of the composite has been suggested as:


(13)
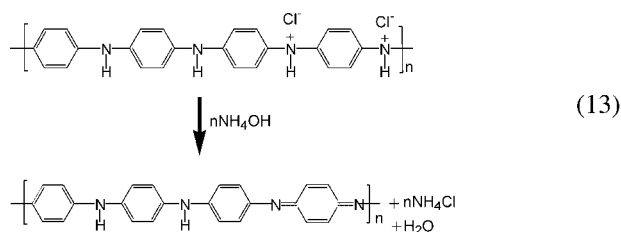
The A form of the doped polyaniline (eq. 7) undergoes undoping with aqueous ammonia and similar equation is also been suggested for the B form:


(14)
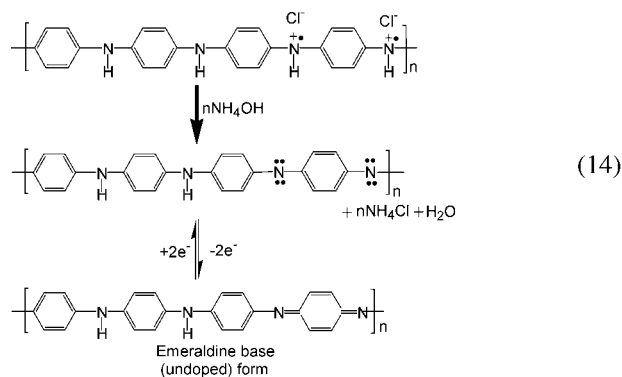
In addition, both the forms of the doped polyaniline A and B (eq. 7) have also been suggested to react with gaseous ammonia and in both the case the product is the fully reduced form of polyaniline, i.e., leucoemeraldine.

TABLE VI
Diffusion Behavior of Polyaniline:Polyacrylonitrile-2 (PANI:PAN-2f) Composite Films and Estimation of Diffusion Coefficient

Film specification		t (s)	E_t	$t^{-1/2}$	$E_t - E_o$
$w = 0.0335$g	1	4	0.71	0.500	0.09
$d = 0.1$ g mm^{-3}		8	0.68	0.354	0.06
$\sigma = 0.55$ S cm^{-1}		11	0.67	0.302	0.05
$i = 150$ mA		12	0.66	0.288	0.04
$P = 5$ s		15	0.65	0.258	0.03
$I = 1 \times 10^{-4}$ A		45	0.64	0.149	0.02
$y = 7.780$		60	0.63	0.129	0.01
		$E_o = 0.62$ V	$S = 0.958$		$D = 8.234 \times 10^{-12}$
$C_o = 2.109 \times 10^{-4}$	2	2	0.69	0.707	0.09
		3	0.67	0.577	0.07
		5	0.66	0.447	0.06
		7	0.65	0.378	0.05
		10	0.64	0.316	0.04
		12	0.63	0.288	0.03
		25	0.62	0.200	0.02
		60	0.61	0.129	0.01
		$E_o = 0.60$V	$S = 0.0825$		$D = 1.863 \times 10^{-12}$
	3	5	0.66	0.447	0.08
		6	0.63	0.354	0.05
		12	0.62	0.258	0.04
		20	0.61	0.224	0.03
		40	0.60	0.185	0.02
		85	0.59	0.108	0.01
		$E_o = 0.58$V	$S = 0.0854$		$D = 7.700 \times 10^{-13}$
	4	2	0.65	0.707	0.08
		4	0.63	0.500	0.06
		5	0.62	0.447	0.05
		7	0.61	0.378	0.04
		12	0.60	0.288	0.03
		25	0.59	0.200	0.02
		50	0.58	0.141	0.01
		$E_o = 0.57$V	$S = 0.0858$		$D = 1.852 \times 10^{-12}$

$$nNH_3 \rightleftharpoons nNH_4^+ + ne^- \tag{15}$$

and

$$nNH_3 \rightleftharpoons nNH_4^+ + ne^- \tag{16}$$
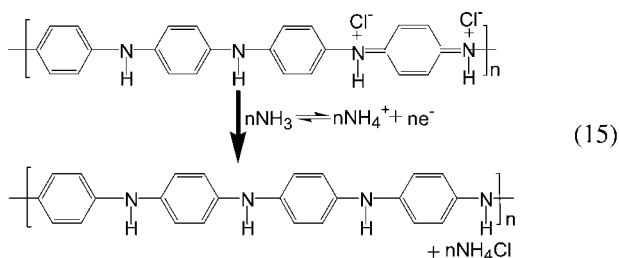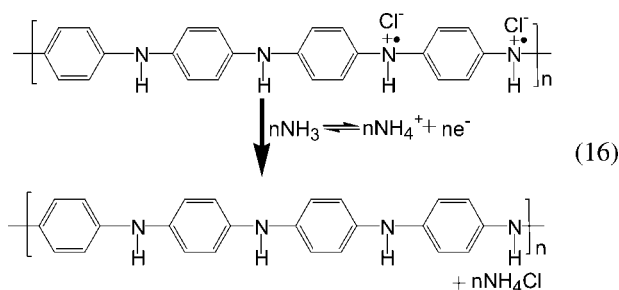
The charge neutralization reaction depends on the rate of chemical reaction between the conducting polymer and undoping agent, which in turn depends upon the reactivity of the polymer chain and basic strength of undoping agent.

On doping the PANI:PAN composite film with HCl (1M) solution results in the conversion of nonconducting emeraldine base form to the conducting emeraldine salt form of the polyaniline as per the general equation:

Emeraldine base (non-conducting)

$$\downarrow HCl \tag{17}$$

Emeraldine salt (conducting)
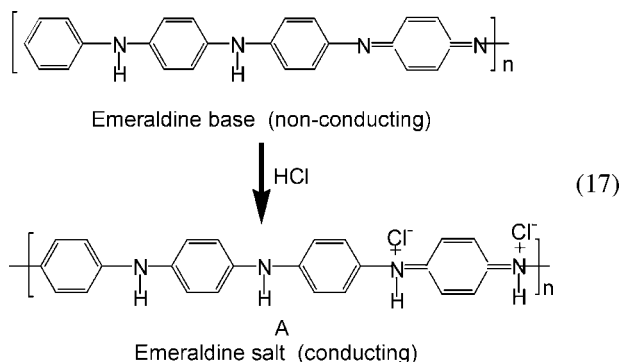
FTIR studies

The FTIR values shown in Table III and spectra of PANI:PAN composites are presented in Figure 2. The band corresponding to out of plane bending vibra-

TABLE VII
Diffusion Behavior of Polyaniline:Polyacrylonitrile-3 (PANI:PAN-3b) Composite
Films and Estimation of Diffusion Coefficient

Film specification		t (s)	E_t	$t^{-1/2}$	$E_t - E_o$
$w = 0.0403$ g	1	1	−0.04	1	0.25
$d = 0.611$ g mm^{-3}		2	−0.15	0.707	0.14
$\sigma = 1.2$ S cm^{-1}		3	−0.16	0.577	0.13
$i = 150$ mA		4	−0.17	0.500	0.12
$P = 5$ s		10	−0.22	0.316	0.07
$I = 1 \times 10^{-4}$ A		15	−0.24	0.258	0.05
$y = 6.466$		20	−0.25	0.224	0.04
$C_o = 1.226 \times 10^{-2}$		35	−0.26	0.169	0.03
		65	−0.27	0.124	0.02
		105	−0.28	0.098	0.01
		$E_o = -0.29$ V		$S = 0.0989$	$D = 2.855 \times 10^{-16}$
	2	7	−0.27	0.378	0.08
		15	−0.32	0.258	0.03
		20	−0.33	0.224	0.02
		30	−0.34	0.183	0.01
		$E_o = -0.35$ V		$S = 0.0901$	$D = 4.282 \times 10^{-16}$
	3	1	−0.20	1	0.18
		2	−0.27	0.707	0.11
		4	−0.28	0.500	0.10
		10	−0.33	0.316	0.05
		15	−0.34	0.258	0.04
		25	−0.35	0.200	0.03
		$E_o = -0.38$ V		$S = 0.1034$	$D = 3.432 \times 10^{-16}$
	4	1	−0.20	1	0.16
		2	−0.25	0.707	0.11
		4	−0.26	0.500	0.10
		7	−0.29	0.378	0.07
		10	−0.30	0.316	0.06
		12	−0.31	0.288	0.05
		15	−0.32	0.258	0.04
		20	−0.33	0.224	0.03
		40	−0.34	0.158	0.02
		$E_o = -0.36$ V		$S = 0.1039$	$D = 3.282 \times 10^{-16}$

tion of C—H bond of *p*-disubstituted benzene rings appears at 824 cm^{-1}. The bands corresponding to stretching vibration of N—B—N and N=Q=N structures appear at 1497 cm^{-1} and 1587 cm^{-1} respectively, where —B— and =Q= stand for benzenoid and quinoid moieties in the polyaniline. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C—N bond appear at 1143 cm^{-1} and 1302 cm^{-1}. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in the polyaniline. The characteristic broad band for CN groups in polyacrylonitrile appears around 1995 cm^{-1}. Two characteristic bands for CH$_2$ appear around 1451 cm^{-1} and around 750 cm^{-1} for the bending and rocking vibrations, respectively. In the composite, the gradual increase in the intensities of the bands corresponding to PANI and decrease in the band corresponds to PAN support the gradual change in the composition of the composite formulation as evident from Figure 2.

SEM Studies

Figure 3 refers to the SEM photographs of PANI: PAN composite films at two different magnifications.

Evidently, the composite of polyaniline in the polyacrylonitrile matrix is observed, and the film morphology studied.

Electrochemical Studies

The PANI:PAN film is applied in the electrochemical cell as working electrode. The Al foil as a counter electrode and Pt foil used as a reference electrode immersed in solution of AlCl$_3$ in DMSO to monitor the potential of PANI:PAN cathode. The variation of charging-discharging cycles was recorded by a digital multimeter and data tabulated (Table IV).

During the discharging process, the decrease in voltage with current is abrupt in the beginning and then it followed a gradual drop in voltage (Fig. 4). This can be inferred that it may be due to gradual change in the oxidation states of polyaniline, i.e., from oxidized form of polyaniline (emeraldine salt) to the not fully reduced form of polyaniline (emeraldine base). Further confirmation for the discharging process is supported by the film conductivity taken before and after the process. The magnitude
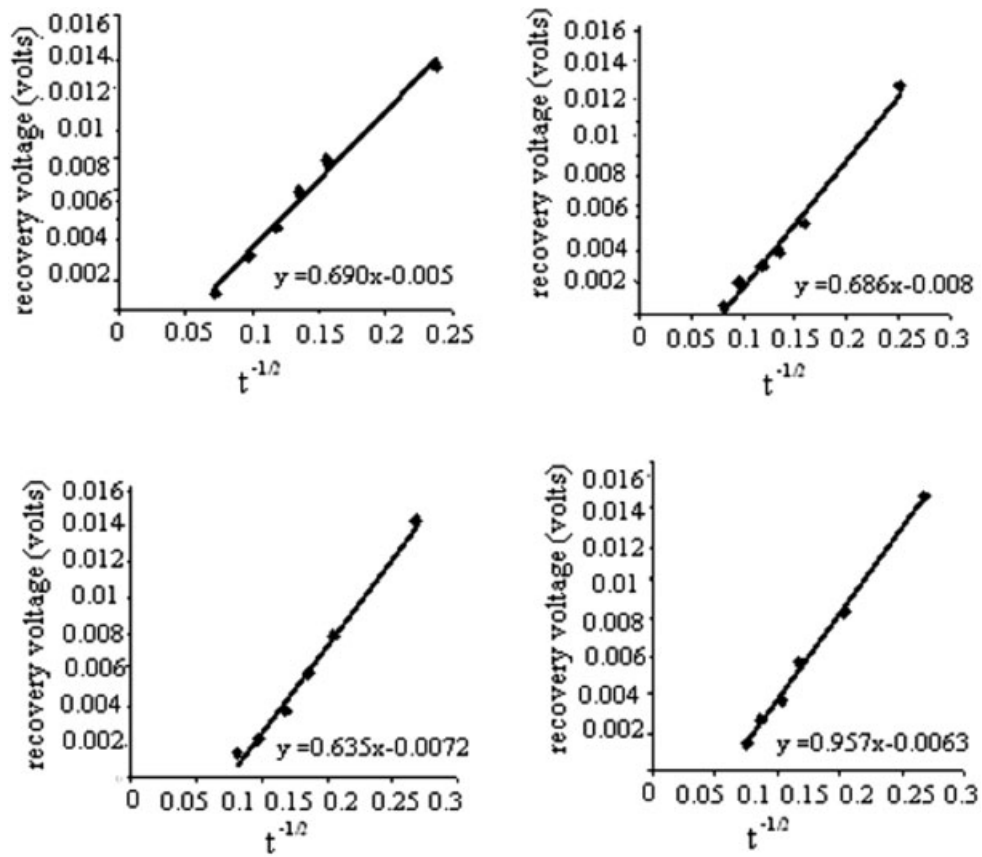
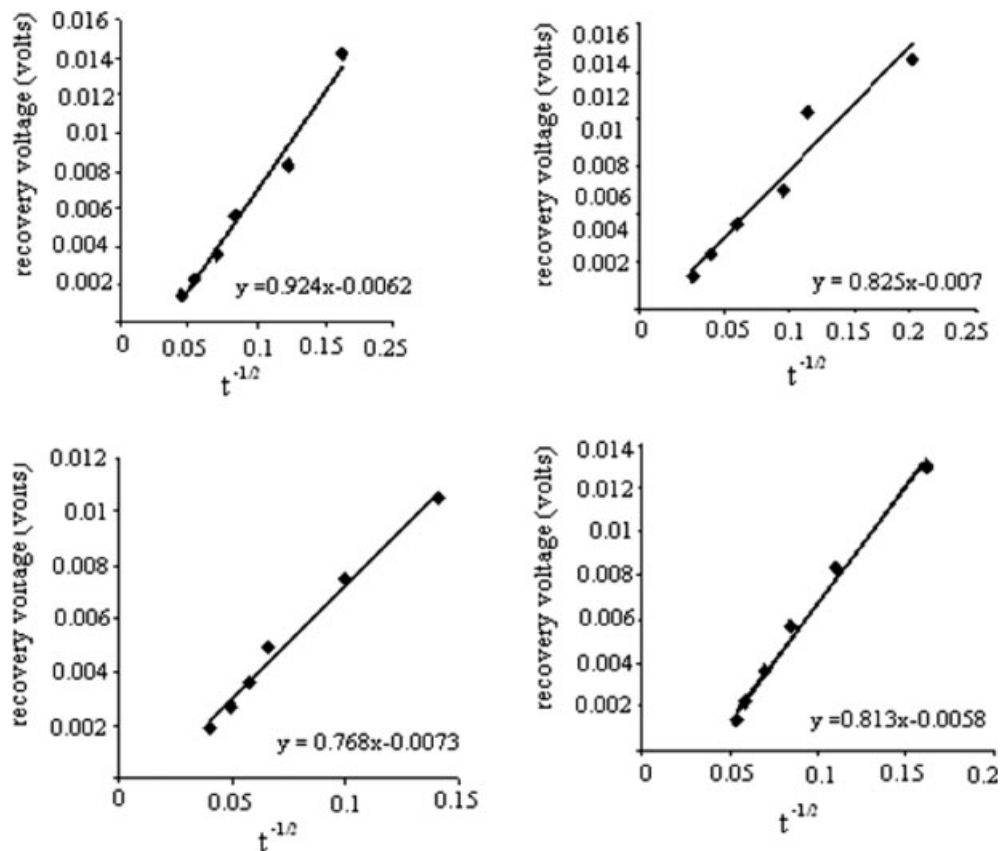**Figure 5** Diffusion behavior of polyaniline: polyacrylonitrile-1 (PANI:PAN-1a composite films).

Figure 6 Diffusion behavior of polyaniline:polyacrylonitrile-2 (PANI:PAN-2f) composite films.
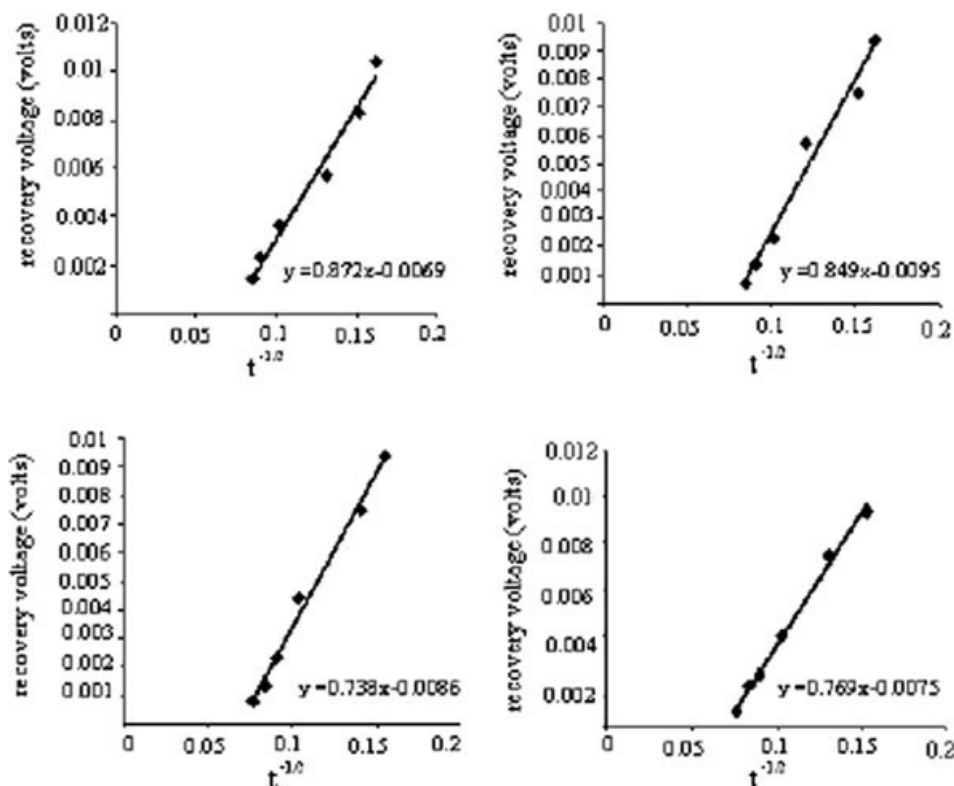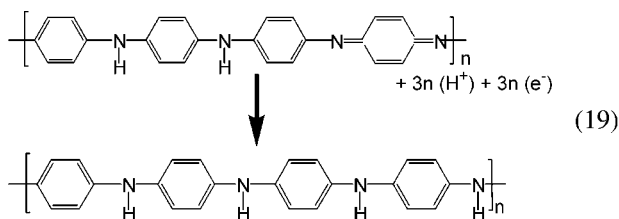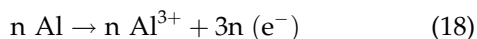
Figure 7 Diffusion behavior of polyaniline:polyacrylonitrile-3 (PANI:PAN-3b) composite films.

decrease in the electrical conductivity follows the discharging of the working electrode.

For the cell (Al/AlCl$_3$, PANI:PAN) reaction assumed for the discharging of PANI:PAN composite films is as follows:

$$n\ Al \rightarrow n\ Al^{3+} + 3n\ (e^-) \tag{18}$$

$$\tag{19}$$

at anode, and at the cathode, giving the over all discharge reaction:

$$\tag{20}$$
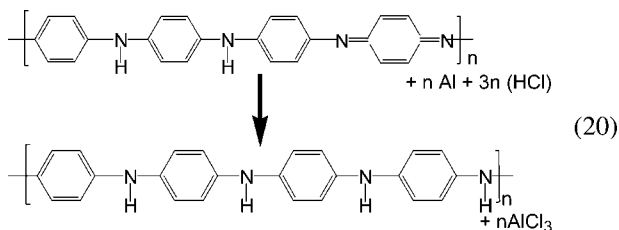
Since the reaction is reversible, the cell reaction during charging is the reverse of that during discharg-

ing. And the charging process is therefore confirmed by measuring its conductivity. The magnitude increase in the electrical conductivity follows the charging of the working electrode. Thus, the reversibility of the electrochemical cell established.

Diffusion studies on PANI:PAN composite films

The change in the electrode potential against a standard reference electrode caused due to deposition of dopant ions on the electrode surface is tabulated with respect to increasing time. The transport of ions into or out of a film can be followed by passing a short current pulse (5 s) to create an instantaneous excess, or deficit, of doping counter-ion on the surface of the film immersed in an electrolyte (AlCl$_3$ in DMSO) solution. As the deposited ions diffuse into the electrode material, the surface concentration changes and the electrode potential recovers. It is possible to determine the diffusion coefficient of dopants into PANI:PAN composite film from the plot of recovery voltage, E_t against $t^{-1/2}$. Since the diffusion behavior is governed by Fick's law the plot follow to be a straight line. The estimation of the diffusion coefficient for the ions into and out of the electrode material was estimated by the expression in equation 1.

The change in the electrode potential (E_t) against a standard reference electrode with respect to increas-

ing time is tabulated for all the three samples prepared (Tables V, VI, and VII). The different parameters for the diffusion of ions into and out of the polymer backbone are calculated as per equations 8 and 9. The discharge curve of, recovery voltage ($E_t - E_o$) against $t^{-1/2}$, is plotted (Figs. 5, 6, and 7) and the slope from the straight line deduced. The diffusion coefficient of the electrode material was estimated using equation 4.

From the estimated diffusion coefficient for the different samples of PANI:PAN composite films it is interpreted that different contents of PANI exhibit different diffusion behaviors. Although the coefficient values of PANI:PAN-1a, PANI:PAN-2f, and PANI:PAN-2b are not significantly different, yet the extent of diffusion in the composite films is of significance. The diffusion coefficient decreases with increasing dopant-ion concentration and increases with the size of dopant-ion.

CONCLUSIONS

The aim of this study was preparation of electrically conducting PANI:PAN composite films, to study the electrochemistry of the film and to estimate the diffusion coefficient of the dopant ions into the film. The PANI:PAN composite films so formed were successfully applied as an electro-active cathode material in rechargeable (secondary) batteries. Although doping chemically via acid base chemistry was more efficient yet a successful attempt was made to electrochemically undope and dope the chemically synthesized PANI composite films and successfully measure the diffusion coefficient.

The electrochemical cell model thus constructed was a wet type battery in which the electrolyte was of $AlCl_3$ in an organic solvent, i.e., diethylsulphoxide. The fact that the electrochemical processes of the secondary battery involves the interconversion of a chemical energy into electrical energy and *vice versa* led to the realization to study the doping and undoping of polymer samples. During the discharging of the cell, the anion (Cl^-) is released from the cathode and the cation (Al^{3+}) is dissolved from the anode, and *vice versa* in case of charging. Therefore, during discharging and charging, diffusion of the anions takes place into and out of the film. Diffusion of Cl^- into the PANI:PAN composite films was of Fickian type, yet the estimation study could further be improved.

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