

Synthesis and Characterization of Lithium Perchlorate Doped PANI thin films

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ABSTRACT

PANI (Polyaniline) is synthesized via chemical route based on chemical oxidative polymerization and thereafter in-situ doped with hydrochloric acid and different weight percentage of Lithium perchlorate. Thin films of Polyaniline and its different doped variant are deposited on plain soda glass and ITO conducting glass with chemical bath deposition technique. The obtained sample configurations are characterized by XRD for structural consistency, FTIR for chemical identification, DSC for thermal stability and electric measurements for capacitance and conductance are carried out with LCR and Four Probe arrangements respectively. XRD analysis reveals largely the polycrystalline nature of Polyaniline and its doped variant. FT-IR study of Polyaniline is found to be in good agreement with standard pronounced peaks in the region of 2000-3500 cm^{-1} , a slight shifting in the doped Polyaniline is due to displaced hydrogen bonds. DSC reveals significant thermal stability of doped and undoped Polyaniline below 200 $^{\circ}\text{C}$. Dielectric measurements in the frequency range 50 Hz - 2 MHz with variable temperature yields the variation of capacitance, that confirms the interfacial polarization in the PANI matrix. Lithium perchlorate doped PANI exhibits conductivity of 6.19 Sm^{-1} confirming the existence of bipolaron at higher level of oxidation.

Keywords: Polyaniline, Lithium perchlorate, FT-IR, Dielectric constant, Conductivity

I. INTRODUCTION

Conducting Polymers, in preceding four decades, have caught the fancy of researchers and scientists alike. Its to their novel properties suitable for diverse applications and relative ease of synthesis. Amongst the known conducting polymers, the Polyaniline (PANI) have gained significant attention [1] due to the fact that, unlike inorganic metals and semiconductors, both the synthesis and chemical modification of PANI offer unlimited possibilities [2]. There are numerous factors that affect the conductivity of PANI, such as the degree of oxidation of the polymer, the

protonation of acid and its percentage, the degree of crystallization and the polymer chain length and the morphology of the polymer, etc. PANI can be synthesized by a number of ways and chemically oxidized to fully exploit its potential use. PANI have several intrinsic properties such as the: ease of preparation, light weight, low cost, better electronic and optical properties, highly stable, when exposed to atmosphere and solubility in common solvents thus making it and its salts highly suitable for technological application. PANI is the polymerised form of Aniline monomer beside this it can exists in three idealized oxidation states [3] Leuco-Emeraldine Base (LEB) a

fully reduced form, Emeraldine Base (EB) a partially oxidized form and (Per)nigraniline Base (PNB) a fully oxidized form, beside these the different oxidation states of PANI, the emeraldine salt (ES) is the only one that possesses electrical conductivity. The electrical conductivity of PANI salt is primarily affected by the nature of the doping [4]. A different variety of acids can be used to protonate PANI and enhances its conductivity [5,6]. In the doping process, polarons and bipolarons are generated [7], contributing to the conduction. The electrical conductivity is also influenced by several factors, such as the structure, the number charge carriers, their transport along and between the polymer chains and across the morphological barriers [8]. On treating PANI-EB with a protonic acid, such as HCl, protons are added to the unprotonated nitrogen sites (imine site) [9,10] and such systems been studied extensively. Its been long established that PANI configurations are suitable electrode material for Lithium (Li)-ion rechargeable cells [11] beside other applications e.g. anti-corrosive coating, electro-magnetic shielding etc. With progress in chemical synthesis, immergence of new dopants and solvents for soluble PANI system has made it a suitable electrode material owing to its environmental stability, higher conductivity and polymer electrolytes compatibility [12].

In presented work PANI is synthesized via chemic route, doped with Lithium perchlorate and its thin film configurations are physically characterized beside electrical measurements for dc conductivity and dielectric constant are carried out.

II. METHODS AND MATERIAL

The PANI base is synthesised via chemic route [13] filtered and dried. PANI thus obtained was dissolved in N-methyl pyrrolidinone (NMP) solvent at 3% wt. ratio with respect to the solvent. The soda glass and ITO glass slide are immersed in the solution (CBD arrangement) for 72 hours and PANI free-standing coating thus obtained are washed, cleaned and dried.

Doping solution of LiClO_4 was made by dissolving it in DMC (dimethyl carbonate, $(\text{CH}_3\text{O})_2\text{CO}$, $M_w = 90.08$, density = 1.07 g cm^{-3}) by weight percentage ratio 1%, 2% and 5% respectively. PANI base free-standing films was immersed in the respective solution of Li salt for 48 hours. The doped films were dried in vacuum oven for 6 hours.

Films, thus fabricated were characterised by FT-IR, Bruker Alpha II for molecular analysis in the range of $400 - 4000 \text{ cm}^{-1}$. For structural analysis, XRD was performed using Cu $K\alpha$ source and Ni filter on Bruker D8 Advance. Thermal stability was established with DSC on LINESIS L-6. Capacitance of the doped films of PANI was measured with LCR Aplab 4000E and a four-probe method was used to measure the dc conductivity [14].

III. RESULTS AND DISCUSSION

A. FT-IR Spectroscopy

IR spectroscopy can distinguish different states of PANI in the region of 1300 to 1600 cm^{-1} wavelength. The prominent peaks signifying the PANI structure pre and post doping with LiClO_4 are obtained as in Fig. 1.

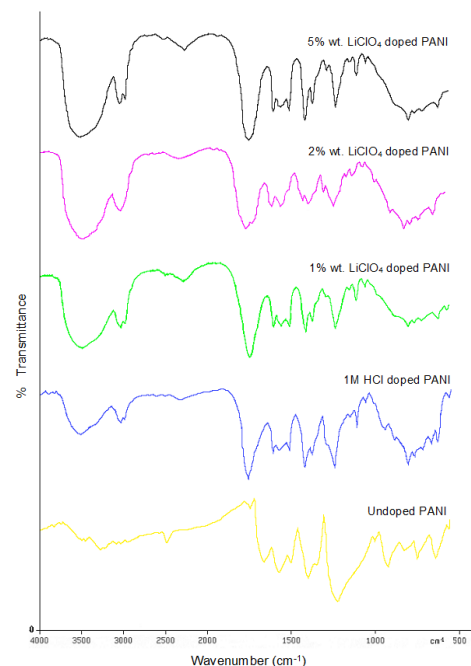


Figure 1: FT-IR spectrum of PANI Base and doped PANI with different wt. % of LiClO_4 .

The obtained FT-IR spectrum is found to be in good agreement with standard data available for PANI [15,16]. The characteristic absorption peaks are tabulated with respect to their attributes in PANI structure in Table 1.

Out of plane bending vibration of C-H bond of p-substituted benzene ring appears at 697 and 563 cm⁻¹. The stretching vibrations of N-B-N and N=Q=N structures appear at 1480 and 1404 cm⁻¹ respectively, (where -B- and =Q= stand for Benzenoid and Quinoid moieties in the polyaniline backbone). The peak appeared at 1115 cm⁻¹ corresponds to -N=Q-N⁺-B- (or NH⁺-PANI) which is characteristic of the protonated state. The absorption band at 1296 cm⁻¹ is associated with polaronic structure of PANI. Bands at 878 and 799 cm⁻¹ correspond to PANI in the para-substituted aromatic ring formation [17,18].

TABLE 1

ASSIGNMENT OF FT-IR PEAKS FOR UNDOPED AND DOPED PANI

IR Peak Assignment (stretching - str, bending - bnd, deformation - def, torsion - trn)	Characteristic absorption peaks (Wave number cm ⁻¹)				
	PANI - EB	1M HCl doped PANI	1% wt. LiClO ₄ Doped PANI	2% wt. LiClO ₄ doped PANI	5% wt. LiClO ₄ Doped PANI
N-H str.	3756	3424	3419	3439	3430
C-H / NH ₂ ⁺ str.	3145	2927	2933	2933	2936
C=N ⁺ str.	2365	2164	2148	2149	2140
C=C 'Q' str.	1654	1660	1657	1664	1661
N=Q=N str.	1571	1505	1507	1506	1507
N=B=N 'B' str.	1480	1471	1460	1460	1462
C-N str.	1404	1407	1408	1407	1408
C-N-C bnd.	1296	1302	1304	1303	1304

C-H bnd.	1115	1118	1115	1114	1115
C-C def.	878	986	986	986	986
C-N-C trn.	657	658	659	659	659

The bands corresponding to stretching mode of C-N bond appear at 1296 cm⁻¹ respectively. The FT-IR spectra of doped PANI shows a little deviation from the undoped PANI spectra.

B. Differential Scanning Calorimetry (DSC)

The thermal analysis based on Differential calorimetry reveals the behaviour of PANI and its doped variants upon heating and is given in Fig. 2 & 3. The thermal

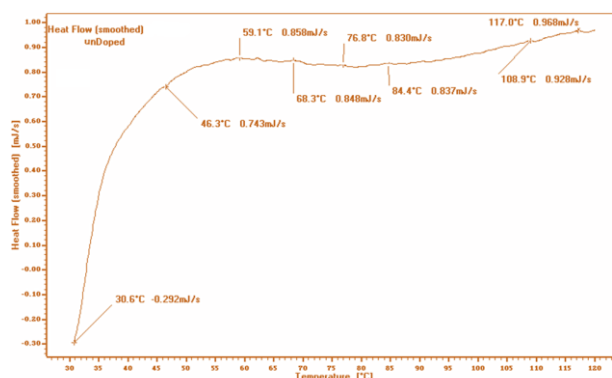


Figure 2: DSC analysis of PANI Base

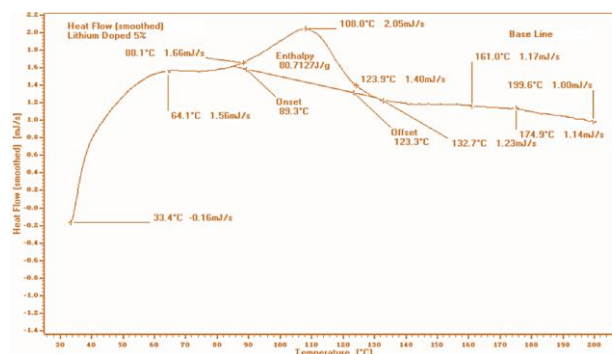


Figure 3: DSC analysis of 5% by wt. LiClO₄ doped PANI

properties were obtained for the temperature range 30 - 200 °C. The undoped PANI base exhibits high thermal stability, while the protonated PANI (doped with 1M HCl) have significantly lower thermal stability. A gradual decrease in thermal conductivity below 200 °C and rapid decrease at temperature above 200 °C is recorded for PANI. DSC of undoped PANI samples does not show any specific pronounced

thermal transitions below 200 °C, suggesting robust thermal stability with little weight loss except for expected dehydrations of samples. Very similar observations are made for HCl and LiClO₄ doped samples of PANI, thus indicating their suitability for most practical applications in batteries and other electronic devices.

C. X-Ray Diffraction (XRD)

XRD pattern of PANI base shows to an extent the amorphous nature, while XRD patterns of doped samples of PANI show slight semi-crystalline nature Fig.4. The semi-crystalline nature of polymers arises

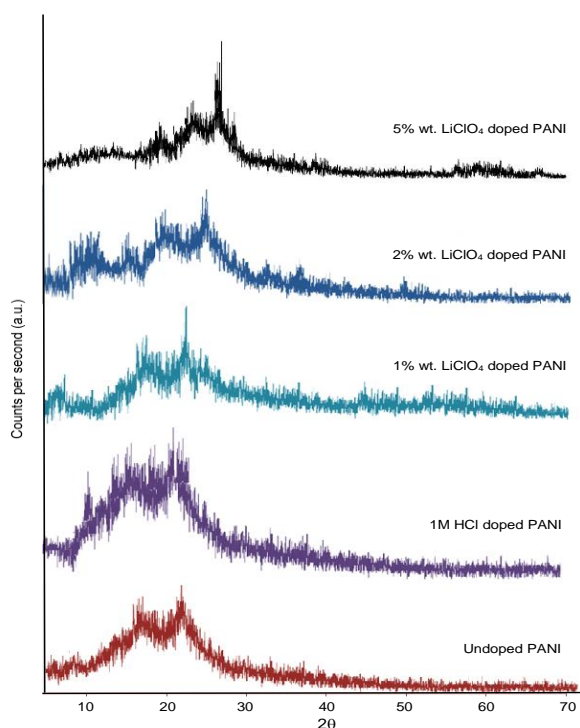


Figure 4: XRD of PANI Base and doped PANI with different wt. % of LiClO₄ salt thin films.

owing to the systematic alignment of polymer chain folding or by the formation of single or multiple helices, for part of their length [19]. XRD pattern of undoped PANI sample shows an amorphous hump or diffused peaks around 20 to 25 degrees and the doped samples have slight peaking shifted towards higher angles. There is slight variation in diffraction intensity with dopant ratio exhibiting the interaction

of dopant with PANI network and thus indicating semi-crystalline nature becoming increasingly prominent, though not sufficiently to be classified as crystalline as sharp peaks are absent throughout the XRD scan.

D. Dielectric Measurements

The dielectric constant (ϵ') determined from the measured capacitance with LCR meter PDI controlled at room temperature and plotted for the frequency range 50 Hz – 2 MHz as given in Fig. 5. Maximum value for

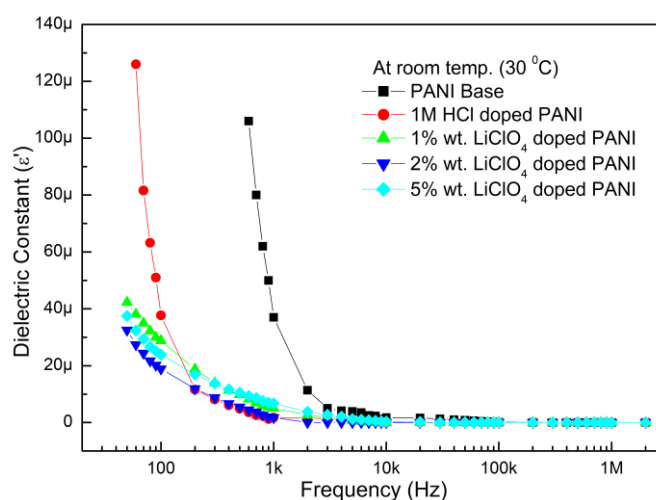


Figure 5: Dielectric Constants of PANI Base and doped PANI with different wt. % of LiClO₄ thin films at 30 °C temperature

PANI Base is 1.06 obtained at 600 Hz, while for HCl doped is 1.26 at 60 Hz and 3.2 for 1%, 2%, 5% by wt. lithium perchlorate doped PANI. With increasing LiClO₄ weight percentage there is decrease in the dielectric constant, which themselves are significantly lower than the undoped PANI. The frequency dependence of dielectric constant can be attributed to the interfacial polarization in the PANI matrix predominantly observed in the sandwiched cell arrangement. It's the Debye relaxation mechanism responsible for higher value of dielectric constant at lower frequencies [20]. A comparative value at 600 Hz frequency is given in Table 2.

TABLE 2
DIELECTRIC CONSTANT OF PANI AND DOPED PANI AT
30 °C AND 600 HZ

Sandwiched thin film material	Highest Dielectric Constant at 600 Hz and 30 °C ($\times 10^{-6}$)
PANI Base	106
1M HCl doped PANI	2.24
1% wt. LiClO ₄ doped PANI	3.57
2% wt. LiClO ₄ doped PANI	2.86
5% wt. LiClO ₄ doped PANI	1.42

E. Electrical conductivity

The resistivity and conductivity of the PANI and doped PANI film was measured with a collinear Four-probe array. The volume resistivity ρ ($\Omega\text{-cm}$) is defined as the ratio of the potential gradient parallel to the current in the material to the current density. The schematic arrangement of electrical circuit for the Four probe resistivity measurement is shown in fig. 5.

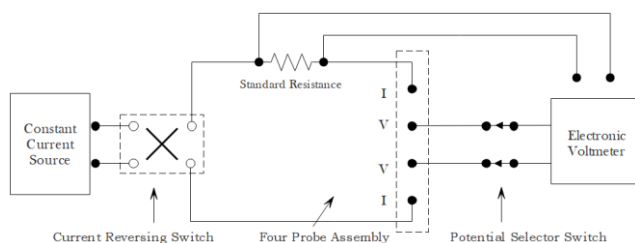


Figure 5: Schematic arrangement for the measurement of Electrical Resistivity of PANI Base and doped thin films.

The variation in conductivity of PANI and doped PANI was observed. Conductivity PANI base film sample was found to be $6.98 \times 10^{-4} \text{ Sm}^{-1}$, while for HCl doped film samples it increased to a value of 0.106 Sm^{-1} and 6.19 Sm^{-1} for 5% by weight lithium perchlorate doped samples. The resistivity and conductivity measured for PANI base and doped

PANI thin film samples at room temperature is given in the Table 3.

TABLE 3
RESISTIVITY AND CONDUCTIVITY OF PANI AND DOPED
PANI AT (~ 30 °C) ROOM TEMPERATURE

Thin film samples	Resistivity ρ (Ωm)	Conductivity σ (Sm^{-1})
PANI base	1.43E+03	6.98E-04
1M HCl doped PANI	9.45E+00	1.06E-01
1% wt. LiClO ₄ doped PANI	3.10E-01	3.27E+00
2% wt. LiClO ₄ doped PANI	2.70E-01	3.64E+00
5% wt. LiClO ₄ doped PANI	1.60E-01	6.19E+00

Electrical conductivity of doped PANI is associated with the mobile p-electrons excited from the valence band with highest occupied molecular orbital (HOMO) to the conduction band with lowest unoccupied molecular orbital (LUMO) state and also to the charge hopping among the polymer chains. In PANI, the conduction mechanism as observed in the above setup, can be explained with the formation of polaron and bipolaron in the polymer structure [21]. Polarons are associated with lower level of oxidation, while the higher level of oxidation yields bipolaron. Polarons and bipolarons are equally mobile and transverse through the polymer chain via rearrangement of double and single bonds in the conjugated system. Conduction by polarons and bipolarons was supposed to be the dominant factors which determine the mechanism of charge transport in polymer with non-degenerate ground states.

IV. CONCLUSION

Polyaniline base was successfully prepared via chemical route and thin films were deposited on soda glass and conductive glass with CBD method. In-situ oxidation of prepared thin films with hydrochloric acid and

different weight percent of Lithium perchlorate solution was carried out and films formed were subjected to various characterisations. FT-IR spectra reveals standard peaks of PANI and slight shifting of peaks in doped films towards higher wavenumber, as the quinoid stretching diminishes on doping. XRD analysis reveals semi-crystalline nature of PANI and its doped variant. Dielectric study suggest PANI can hold substantial charge and have high capacitance. DSC analysis establish significant thermal stability of PANI and its Lithium doped films at normal temperatures. Resistivity drops significantly on doping with Lithium perchlorate making it a suitable configuration for electronic devices including batteries. These results encourage to venture into device fabrication with Lithium salt doped PANI for practical applications.

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