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Structural and Electrical Properties of LiClO_4 Doped PANi Composite Films

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Abstract: Conductive Polyaniline PANi was synthesized chemical oxidative polymerization the chemical route. PANi thus synthesized was in-situ doped with HCl acid and Lithium perchlorate in different weight percentage. PANi and its different doped variant thin films were deposited on plain soda glass and conducting ITO glass using CBD technique. Samples of different configurations are characterized for structural consistency with X-ray, for chemical identification with FTIR, for thermal integration with DSC. Electric measurements such as capacitance and conductance were carried out using LCR bridge and Four Probe arrangements respectively. X-ray analysis divulges largely the polycrystalline nature of PANi and LiClO_4 doped variant. IR study in Fourier transformed mode reveals PANi and its doped variants maintains their structural integrity in good agreement with standard pronounced peaks in the region of $2000\text{-}3500\text{ cm}^{-1}$, though displaced hydrogen bonds in doped PANi leads to a slight shifting. Significant thermal stability for doped and undoped Polyaniline nearly up to $200\text{ }^\circ\text{C}$ is noted with DSC. Dielectric measurements with variable temperature in the frequency range $50\text{ Hz} - 2\text{ MHz}$ yields the capacitance variation, confirming the interfacial polarization within the PANi matrix. Lithium Conductivity of 6.19 Sm^{-1} for lithium perchlorate doped PANi again affirms exitance of bipolarons at greater level of oxidation.

Keywords: Polyaniline, Fourier transform infra red (FTIR), Chemical bath deposition (CBD), X-ray diffraction (XRD), Lithium perchlorate

I. INTRODUCTION

On set of 21st century, have seen conducting polymers being the fancy of researchers and scientists due to their novel properties suitable for diverse applications and relative ease of synthesis. The Polyaniline (PANi) amongst them have gained significant attention [1] owing to the fact that, the synthesis and chemical modification of PANI offer unlimited possibilities unlike inorganic metals and semiconductors [2]. There are several factors that affects the conductivity of PANI; such as the degree of oxidation, the protonation of acid and its percentage in synthesized polymer and also the degree of crystallization, chain length and the morphology of the polymer, etc.

There are numerous ways to synthesize PANi and its chemically oxidized forms for varied potential use. PANi have several intrinsic properties, such as better electronic properties, optical properties, light weight beside ease of preparation, solubility in common solvents, cost effective synthesis and fairly stable when exposed to atmosphere. These properties make PANi, its salts and doped variants exceedingly suitable for varied technological applications. Aniline monomer is polymerised to PANi which is found to coexists in idealized three oxidation states [3] a fully reduced form Leuco-Emeraldine Base (LEB), a partially oxidized form Emeraldine Base (EB) and a fully oxidized form(Per)nigraniline Base (PNB). Along these the different oxidation states PANi also exist as the emeraldine salt (ES) and its the only state that is electrical conductivity. Its the nature of the doping which effects the electrical conductivity of PANi salt [4].

A variety of different acids are used to protonate PANi and augment its conductivity [5,6]. Polarons and bipolarons are generated during the doping process [7], which are responsible for the conduction in PANi. There are several factors that influence the electrical conductivity of PANi, such as the structure, the number charge carriers, transportation of charges along and within the polymer chains and also across the morphological barriers [8]. When PANi-EB is treated with a protonic acid such as HCl. The protons are added to the unprotonated nitrogen sites (imine site) [9,10]. Such systems have been studied extensively. It's well established that PANi in different configurations is a suitable electrode material for Lithium (Li)-ion cells both non-rechargeable and rechargeable [11].

There are other established applications of protonated PANi such as anti-corrosive coating, electro-magnetic shielding etc. The soluble PANi systems are a highly suitable material for electrodes due to its reasonable environmental stability, higher conductivity

and polymer electrolytes compatibility which itself has been possible with increasingly evolved chemical synthesis techniques developed [12]. The work reported in this paper involves PANi being synthesized via chemic route, thereafter being doped with Lithium perchlorate and then tacking its thin film configurations for different physically characterisation beside electrical measurements for dc conductivity and dielectric constant.

II. METHODS AND MATERIAL

The chemicals used were obtained directly from Sigma-Aldrich and S D Fine Chemical. The Emeraldine base of PANi was synthesized via standard chemic route [13] and precipitate was filtered, dried and preserved . A solution of PANi was made dissolving it in N-methyl pyrrolidinone (NMP) solvent at 3% wt. ratio that to the solvent. Thin films were deposited on the soda glass and ITO glass slides by immersing them in the solution prepared (CBD arrangement) for about 72 hours. PANi free-standing coatings hence obtained were washed, cleaned, dried and preserved in desiccator. The doping solutions were made by dissolving LiClO₄ directly in dimethyl carbonate [(CH₃O)₂CO, Mw = 90.08, density = 1.07 g cm⁻³] (DMC) by weight percentage ratio of 1%, 2% and 5% respectively. The PANi base free-standing films were then immersed for 48 hours in these different percentage by wt. solutions of Li salt. The doped films thus obtained were dried for 6 hours in vacuum oven. Fabricated doped PANi films were characterized for molecular structure and analysis using FT-IR (Bruker - Alpha II model) in the range of 400 - 4000 cm⁻¹. The structural analysis XRD of doped PANi was carried out using Cu K_α source and Ni filter on Bruker D8 Advance XRD model. Thermal stability of films were established with DSC on LINESIS L-6. Capacitance was determined for the doped films of PANi with measurements on LCR meter Aplab 4000E and to measure the dc conductivity [14] a four-probe method was used.

III. RESULTS AND DISCUSSION

A. IR Spectroscopy

The IR spectroscopy can revel different states of PANi base in the region of 1300 -1600 cm⁻¹ wavelength. The prominent peaks obtained from FTIR spectrum signifying the PANi structure both pre and post doped with LiClO₄ are shown in Fig. 1.

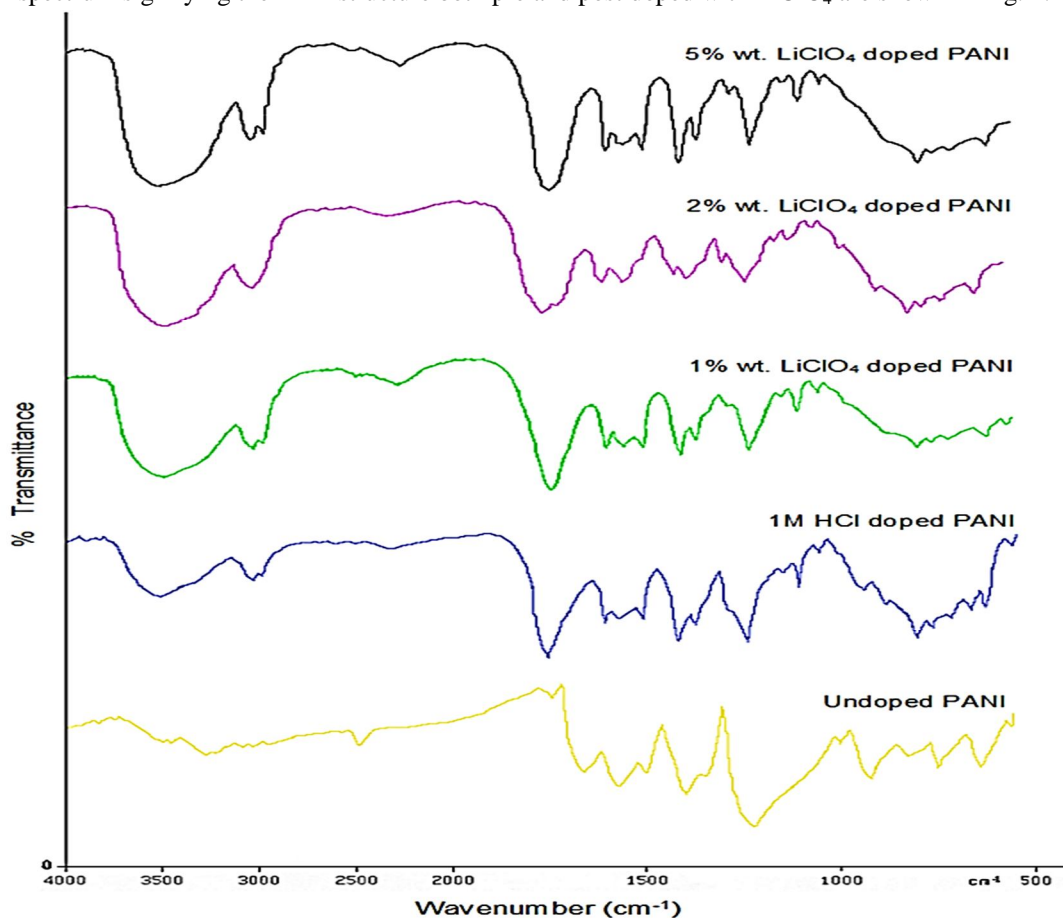


Figure 1: PANi Base and doped PANi FTIR spectrum with different wt. % of LiClO₄.

The FT-IR spectrum of PANi obtained was found to be in agreement to a large extent with different standard data available [15,16]. The peaks corresponding to characteristic absorption were tabulated with respect to their attributes in structure, Table 1. C-H bond of p-substituted benzene ring having out of plane bending vibration corresponds to peaks at 697 and 563 cm^{-1} . N-B-N and N=Q=N structures stretching vibration appear at 1480 and 1404 cm^{-1} respectively, (Where Benzenoid and Quinoid moieties in the polyaniline backbone are represented by -B- and =Q=). The peak appearing at 1115 cm^{-1} corresponds to -N=Q-N⁺-B- (or NH⁺- PANi) the characteristic of the protonated state. is associated with The polaronic structure of PANi gives the absorption peak at 1296 cm^{-1} . The bands at 878 and 799 cm^{-1} correspond to PANi in the para-disubstituted aromatic ring formation [17,18].

TABLE I
FTIR Peak assignment for Undoped and Doped PANi

IR Peak Assignment	Characteristic absorption peaks (Wave number cm^{-1})				
	Undoped PANi	1M HCl doped PANi	1% wt. LiClO ₄ Doped PANi	2% wt. LiClO ₄ Doped PANi	5% wt. LiClO ₄ Doped PANi
N-H stretching	3756	3424	3419	3439	3430
Aromatic C-H stretching / NH ₂ ⁺	3145	2927	2933	2933	2936
C=N ⁺	2365	2164	2148	2149	2140
C=C stretching of Quinoid ring "Q"	1654	1660	1657	1664	1661
N=Q=N stretching	1571	1505	1507	1506	1507
N=B=N stretching of Benzenoid ring "B"	1480	1471	1460	1460	1462
C-N stretching	1404	1407	1408	1407	1408
Aromatic C-N-C bending	1296	1302	1304	1303	1304
C-H bending	1115	1118	1115	1114	1115
C-C ring deformation	878	986	986	986	986
C-N-C torsion	657	658	659	659	659

The stretching mode of C-N bond corresponds to the peak at 1296 cm^{-1} . The doped PANi FTIR spectra shows little deviation from that of an undoped PANi spectra.

B. Differential Scanning Calorimetry (DSC)

Differential calorimetry used for thermal analysis reveals the behaviour of PANi and its doped variants with temperature as given in Fig.2 to 6. PANi and its doped variants were characterised for their thermal properties in the temperature range 30 - 200 °C. PANi base exhibits considerable high thermal stability, where as the protonated PANi (doped with 1M HCl) exhibit significantly lower thermal stability. For undoped PANi a gradual decrease in thermal conductivity below 200 °C and rapid decrease at temperature above 200 °C is recorded. Undoped PANi samples does not show any specific pronounced thermal transitions below 200 °C in DSC, signifying thermal stability at normal temperatures. Very little weight loss is observed except for expected dehydrations of samples. Similar observations are recorded for HCl and LiClO₄ doped PANi samples, indicating their suitability in batteries and other electronic devices for most practical applications.

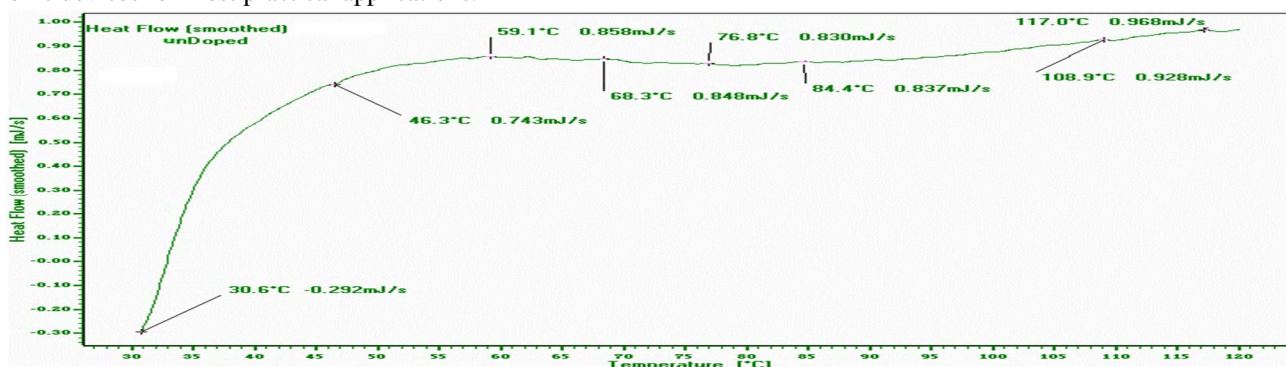


Figure 2: DSC of Undoped PANi

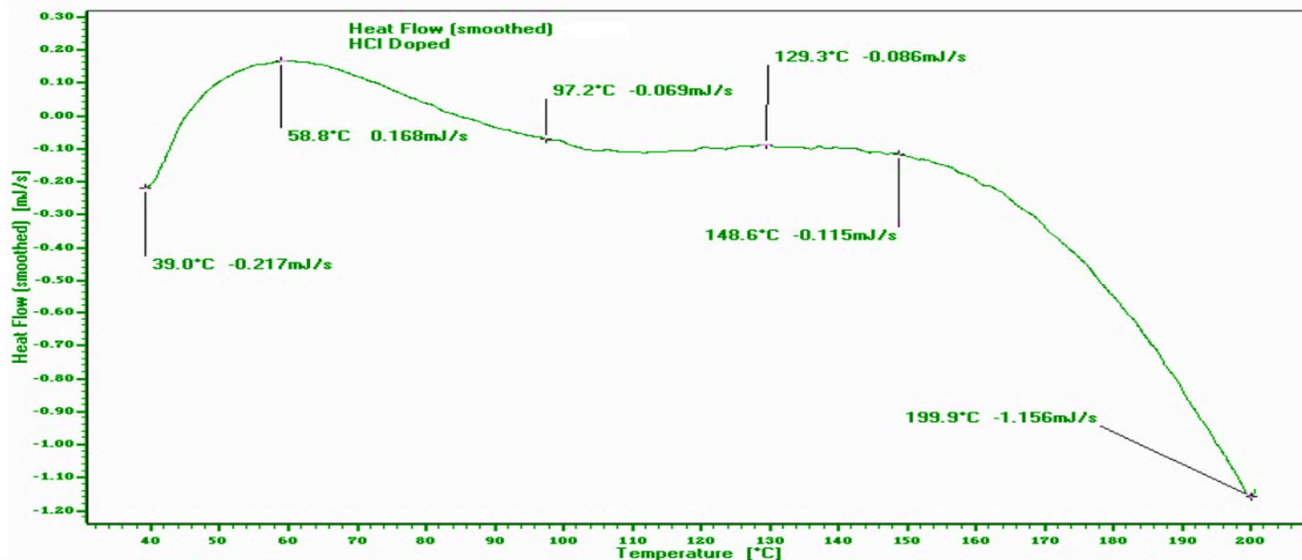


Figure 3: DSC of HCl doped PANi

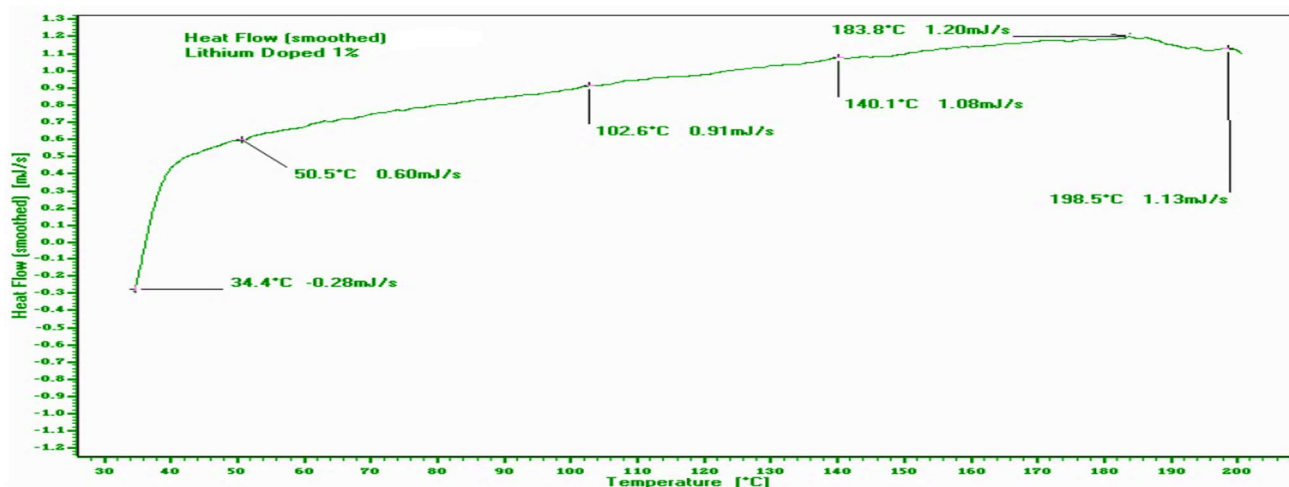


Figure 4: DSC of 1% Lithium Perchlorate doped PANi

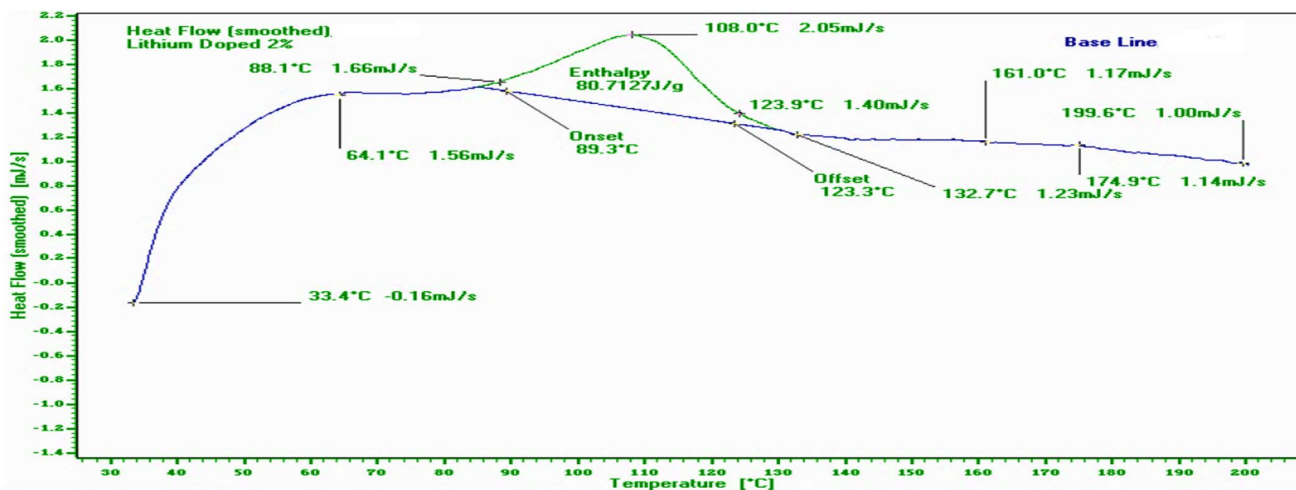


Figure 5: DSC of 2% Lithium Perchlorate doped PANi

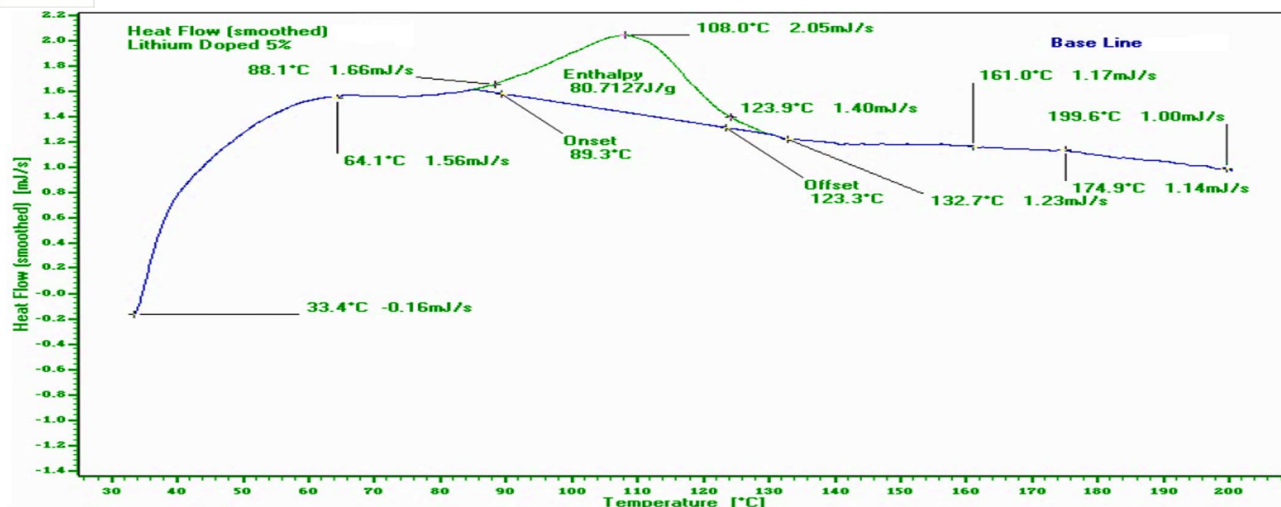


Figure 6: DSC of 5% Lithium Perchlorate doped PANi

C. X-Ray Diffraction (XRD)

To an extent the amorphous nature of PANi base is established with XRD analysis. The XRD patterns of doped PANi samples show slight semi-crystalline nature Fig.7. The systematic alignment of polymer chain folding or by the formation of single or multiple helices for part of their length is responsible for semi-crystalline nature of polymer [19]. XRD pattern shows an amorphous hump or diffused peaks around 20 to 25 degrees for PANi base while the doped samples have slight peaking shifted towards higher angles. The interaction of dopant with PANi network exhibits slight variation in diffraction intensity with dopant ratio and thus indicating semi-crystalline nature which becomes increasingly prominent; though not adequately to be classified as crystalline since there is absence of sharp peaks throughout the XRD scan.

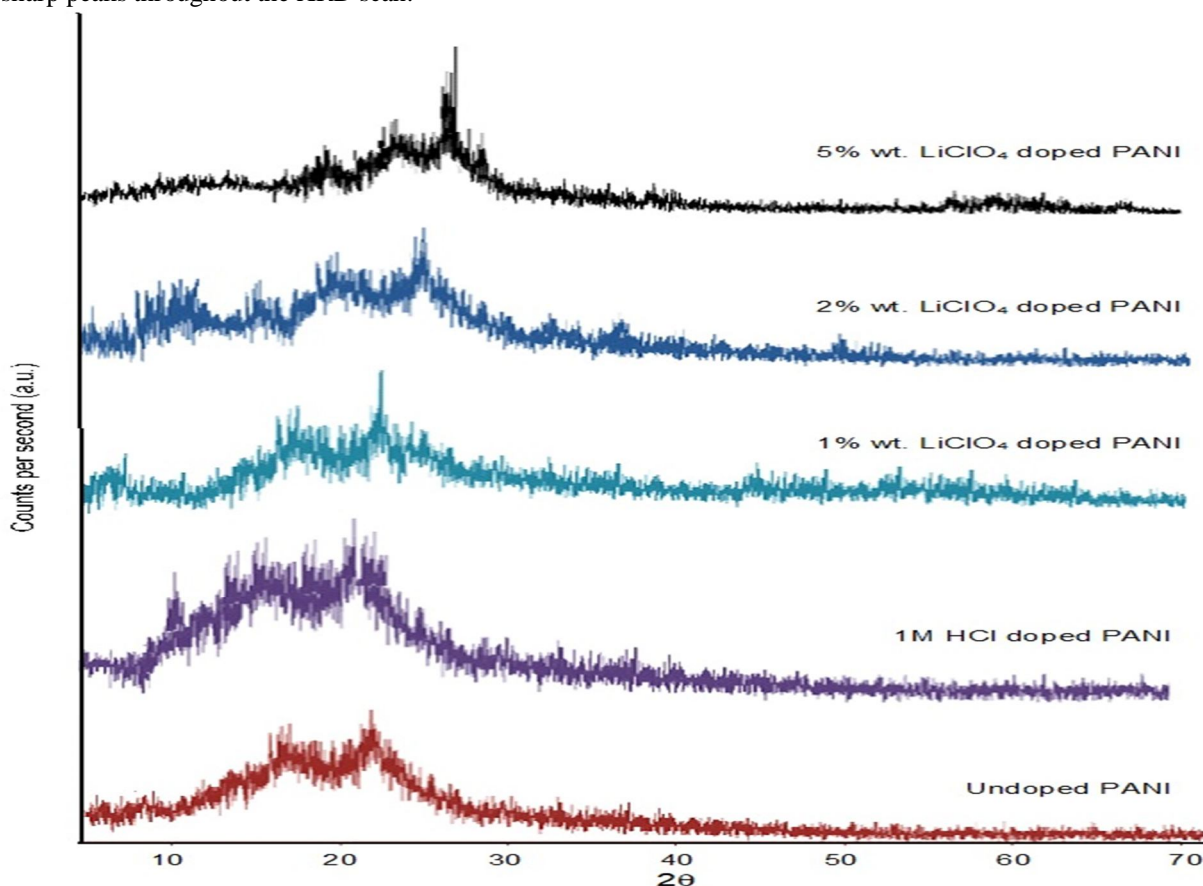


Figure 7: XRD of PANi and its different doped variants

D. Dielectric Measurements

The measurement of capacitance with LCR meter PDI controlled at room temperature was used to determine the dielectric constant (ϵ') for samples and plotted in the frequency range 50 Hz – 2 MHz as shown in Fig. 8 to 12. PANi base have a maximum value 1.06 μF obtained at 600 Hz, that of HCl doped PANi is 1.26 μF at 60 Hz and 3.2 μF for 1%, 2%, 5% by wt. lithium perchlorate doped PANi. There is a decrease in the dielectric constant with increasing LiClO_4 weight percentage and significantly lower than the undoped PANi base. The variation of dielectric constant can be attributed to the interfacial polarization in the PANi matrix predominantly observed in the sandwiched cell arrangement which is evident in its frequency dependence. Higher value of dielectric constant at lower frequencies is attributed to the Debye relaxation mechanism [20].

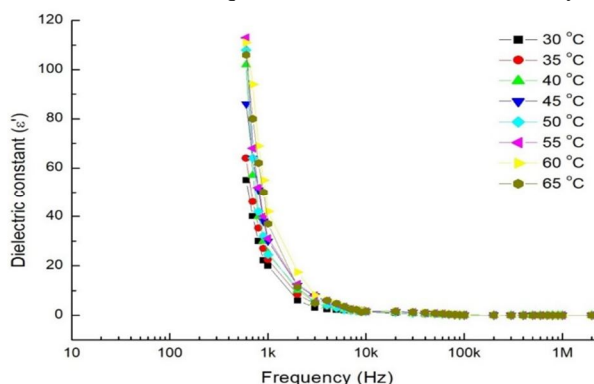


Figure 8: Dielectric constant of Undoped PANi thin film as a function of Frequency at different Temperatures

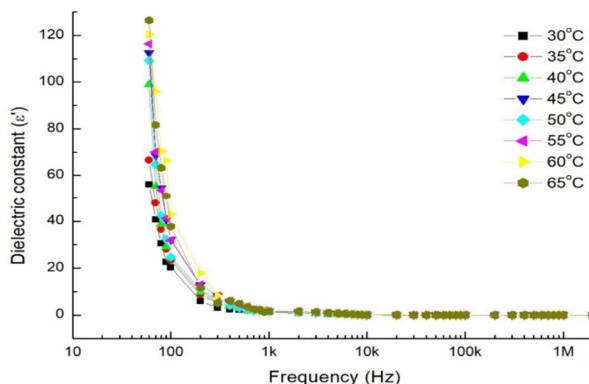


Figure 9: Dielectric constant of 1M HCl doped PANi thin film as a function of Frequency at different Temperatures

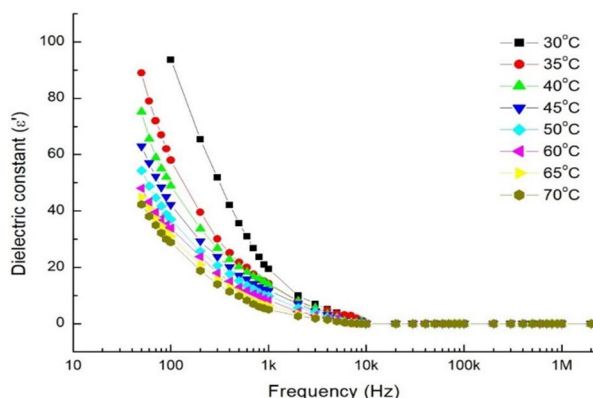


Figure 10: Dielectric constant of 1% wt. LiClO_4 doped PANi thin film as a function of Frequency at different Temperatures

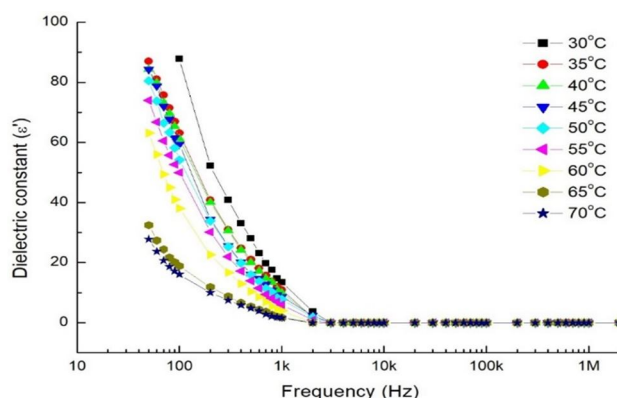


Figure 11: Dielectric constant of 2% wt. LiClO_4 doped PANi thin film as a function of Frequency at different Temperatures

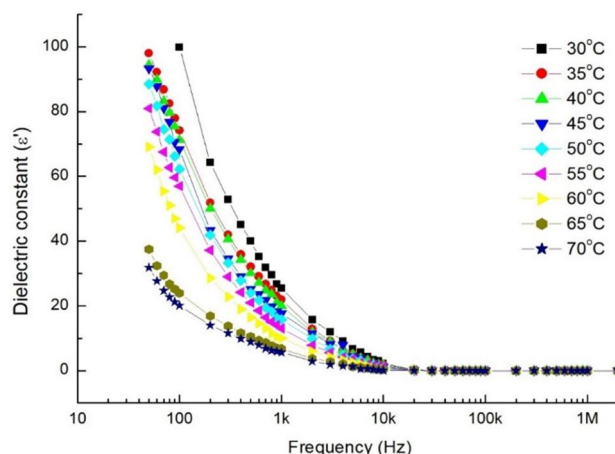


Figure 12: Dielectric constant of 5% wt. LiClO_4 doped PANi thin film as a function of Frequency at different Temperatures

E. Electrical conductivity

A collinear Four-probe array method was used to measure the resistivity and conductivity of the PANi and doped PANi film. The volume resistivity ρ (Ω -cm) is defined as the ratio of the potential gradient parallel to the current in the material to the current density. The schematic arrangement for the Four probe resistivity measurement is shown in Fig. 13.

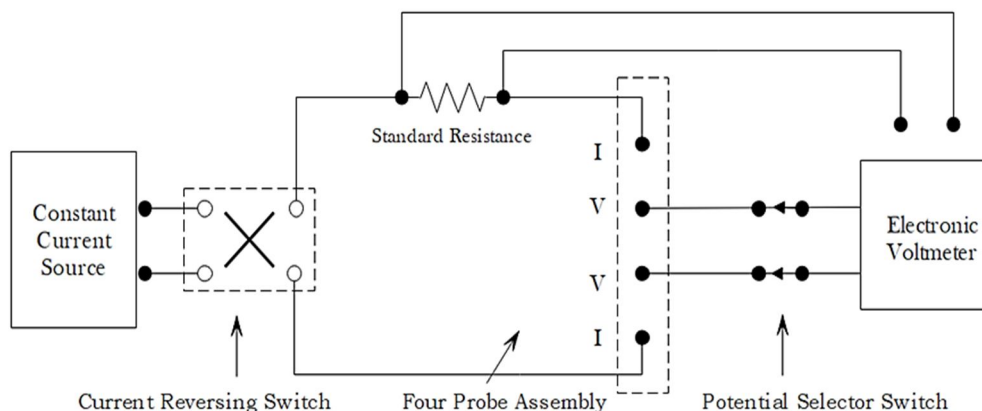


Figure 13: Schematic arrangement of setup for the measurement of Electrical Resistivity of thin films.

The clear variation in conductivity was observed for both base and doped PANi samples. Conductivity of PANi base film was found to be $6.98 \times 10^{-4} \text{ Sm}^{-1}$, that for HCl doped film samples it increased to 0.106 Sm^{-1} and is 6.19 Sm^{-1} for 5% by weight lithium perchlorate doped PANi samples. A tabulated measurement of the resistivity and conductivity for PANi base and doped PANi thin films at room temperature is given in Table II.

TABLE II
Conductivity and Resistivity of PANi samples at ($\sim 30^\circ\text{C}$) room temperature

Thin film samples	Resistivity ρ (Ω cm)	Conductivity σ (S cm^{-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

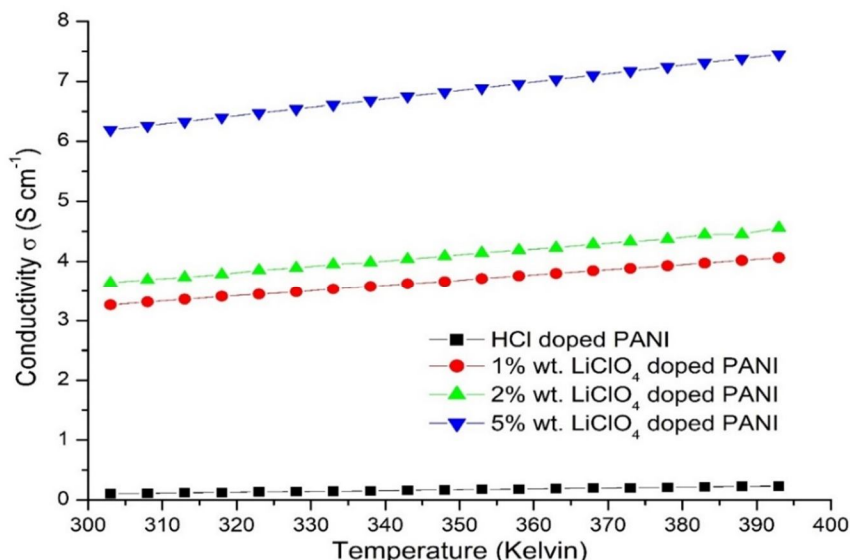


Figure 13: The Variation of conductivity of doped PANI in the temperature range 303 – 393 Kelvin

Electrical conductivity in protonated PANi with acids is associated with the excited mobile p-electrons moving from the valence band, the highest occupied molecular orbital (HOMO) to the conduction band, the lowest unoccupied molecular orbital (LUMO) state. Conductivity is also to the charge hopping within the polymer chains of aniline. In doped PANi, the conduction, as observed in the experimental setup can be explained on the basis of the formation of polaron and bipolaron within the polymer structure [21]. Polarons are associated to the lower level of oxidation, whereas the higher level of oxidation yields bipolaron. Both polarons and bipolarons are equally mobile and capable of transversing through the polymer chain with rearrangement of double and single bonds in the conjugated bond system. Conduction due to polarons and bipolarons is the prominent factors which controls the charge transport mechanism in polymers having non-degenerate ground states.

IV. CONCLUSION

Emeraldine base PANi was prepared via standard chemical route and it was deposited in thin film configuration on soda glass and conductive glass with CBD method. Prepared thin films were oxidized in-situ with hydrochloric acid and also with different weight percent of Lithium perchlorate solution. PANi films thus obtained were subjected to different characterisations. The FT-IR spectra reveals standard peaks of PANi and insignificant shifting of peaks for doped PANi films towards the higher wavenumber suggesting that the quinoid stretching weakens on doping. X-ray diffraction analysis reveals prominently the semi-crystalline nature of PANi and also for its doped variants. Upon doping the PANi can hold substantial charge and acquires high capacitance as revealed by the dielectric study. The DSC analysis found significant thermal stability for PANi and its Lithium doped variants at normal temperatures. The resistivity decreases significantly on doping with Lithium perchlorate, thus suggesting it to be a suitable configuration for various electronic devices, including batteries.

V. ACKNOWLEDGMENT

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