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Conduction Mechanism Of Zno Nanoparticle Doped Polypyrrole Films

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ZnO nanoparticles were synthesized by Sol gel method which are doped at different concentrations in polyprrole and formed films. The films are thermally and electrically polarized for each 1 hr. The electrical properties for both pure and doped films are measured at different temperature and applied electric field. From the slope of ln J versus $E^{1/2}$ plot the conduction mechanism are calculated for pure and ZnO nanoparticles doped polypyrrole films. The result shows the Poole- Frenkel mechanism of conduction are operative for all sample,

Keywords: ZnO, Polypyrrole, Nanoparticles, transition temperature, polarization, Poole-Frenkel.

Introduction:

More than four decades now, several workers have shown that certain class of polymer which are conjugated, exhibit semiconducting nature. Due to the presence of an extended π-conjugation in polymers, confers the required mobility to charge that created on the polymer backbone and make electrically conducting. The main application of conducting polymers are in the light weight rechargeable batteries, photo-detectors, surface acoustic wave devices, UV-nano laser, varistors, solar cells, nanogenerator, etc. They have also been exploited as electronic component in electronic devices such as light-emitting diodes, rectifying devices, lithium batteries, super-capacitors, electromagnetic wave shielding, sensors and electro-chromic displays (Moghaddam et. al. 2009, Vishnuvardhan et. al. 2006). As pollypyrrole exhibits good environmental stability, facile synthesis and significant electrical conducting characteristics, it has drawn considerable attention among the conducting polymers (Ramakrishnan 1997). Polypyrrole has a large variety of charge transport properties and its electrical conductivity that can be increased by doping with some other material (Kanwal et. al. 2011).

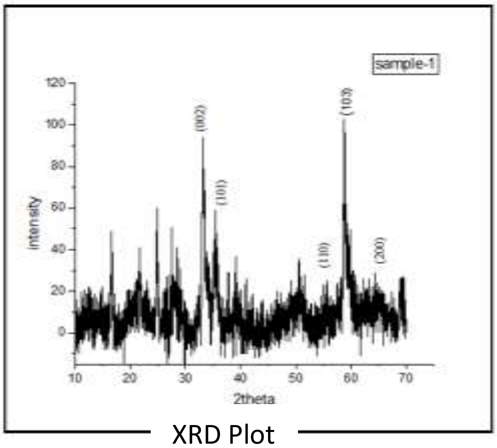
On other hand, zinc oxide (ZnO) is an important member of II-VI, is one of the attractive semiconductors due to some of its unique characteristics. It is a well-known n-type semiconductor and has got a wide band gap of 3.3 eV at 300 K with a hexagonal wurtzite type crystal exhibiting anisotropy. The properties of ZnO are affected by the degree of doping, such as electrical conductivity that range from metallic to insulating levels (Saleh R, 2012). Nanostructured ZnO exhibit novel electrical, mechanical, chemical and optical properties which are believed to be due to the surface confinement effects or nanostructures in one dimension. These one-dimensional objects are of great importance in understanding some basic physics related phenomena in the low dimension system to form the basis of next generation higher performance nanodevices (Bahadur H et. al. 2007). As ZnO has high electron mobility and wide band gap so, ZnO nanoparticle is doped in polypyrrole film, electrical property of the nanocomposite film might be changed from the pure polypyrrole film.

The present study, an attempt is made to investigate the effect of varying concentrations of zinc oxide nanoparticle doped polypyrrole film on conduction mechanism for different applied voltage and temperature.

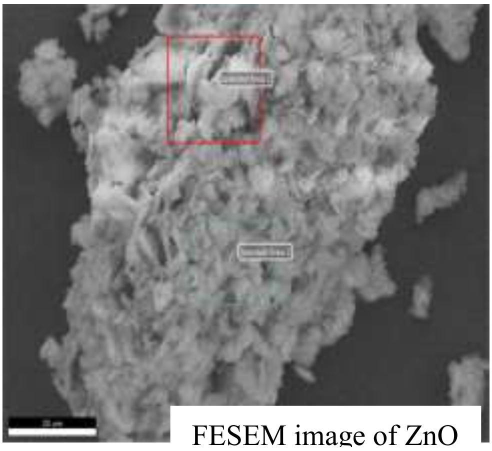
Experimental:

2.1 Synthesis of Zinc Oxide (ZnO) nanoparticle

In 40 ml of distilled water 2.0 g of Sodium hydroxide (NaOH) was dissolved and similarly in 120 ml of distilled water 10g of Zinc Sulphate (ZnSo4) was dissolved. The above two Solution are mixed and stirred for 1 hr. with a magnetic stirred. The value of the pH solution was measured to be around 7.5. The gel was further kept for 2 days (48 hr). After 48 hr filtered with water to remove sulphate concentration and washing the residue is spread on the Petri disc. Finally, it was annealed at 1500C for 1 hr. and after cooling the residue for 30 minute and the process is repeated 5 times and finally the ZnO is obtained in Powder form.



XRD Plot



FESEM image of ZnO

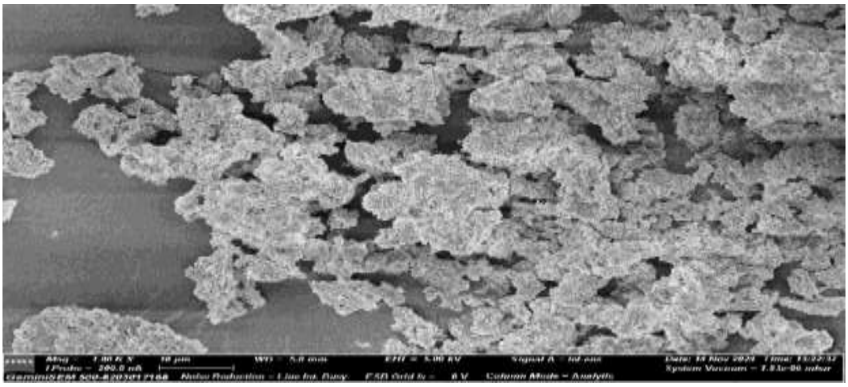
The size of the particle is calculated by finding the FWHM from XRD plot using Deby-Scherrer formula

$$D = \frac{K\lambda}{\beta\cos\theta}$$

Where K is particle shape factor and λ is the wavelength of CuK_α radiation and β is full width at half maximum (FWHM) of the selected diffraction peak. The value of the particle found as 11.20 nm.

2.2 Synthesis of Polypyrrole (PPy)

The chemical oxidative polymerization technique was employed for the synthesis of PPy, in which $(NH_4)_2S_2O_8$ (Ammonium Persulphate APS) was employed as an oxidant. 1.0 mL of pyrrole monomer was dissolved in 70 mL of 1.5 M HCl solution. Separately, 2.04 g of $(NH_4)_2S_2O_8$ has been dissolved in 20 mL of de-ionized water in a beaker and then dropwise added to the previously prepared solution. Then it was stirred continuously with a constant speed for 5 h at ambient temperature. The precipitate was washed with ethanol as well as de-ionized water repeatedly and dried in a hot air oven at 60^0C for 12 h.



FESEM image of pollypyrrole

2.3 Synthesis of ZnO/Ppy nanocomposite

To obtain a casting of ZnO/Polypyrrole nanocomposites, the mixture of ZnO and Polypyrrole is dissolved in PVA Solution. Then the solution is stirred with 250 rpm for uniformed distribution at 50 for 5h. Finally, the product was poured into a mold of the desired shape. The solvent is then allowed to evaporate slowly at room temperature or under mild heating to form a solid film or bulk casting. The drying process needs to be controlled to minimize cracking or deformation of the casting.

2.4 Measurement of current

The sample is cut circularly slightly greater than the surface area of the electrode having area 3.7994 x 10^{-4} sq. m to avoid edge effect. The sample is placed between the two electrodes under light constant pressure in the sample holder. The sample holder is placed inside the Temperature-controlled bath, (i-therm).

The different potential is applied across the sample by the High voltage power supply (EHT-11). The value of potential across the pure sample is varied from 0 to 1400 volt by an interval of 100 volt at constant temperature. The potential drop across 2 MΩ resistor is recorded by digital multimeter. Another similar film was electrically and thermally polarized at 100 volt and 60^0C for 1hr, then the two electrodes were short circuited for 1hr, so as to remove of stray of charges. The potential drop across 2 MΩ resistor is recorded as above. The same operation is repeated for different values of temperature from room temperature 303 K to 373 K by an interval of 10 K. Similarly, for the ZnO/Ppy nanocomposite film, the above operation was repeated for polarized and unpolarized sample. In order to make uniform heating the sample is kept at constant temperature for 30 minutes for each consecutive reading. The potential drop measurement is same as that reported earlier (Joy & Nabadwip 2022).

3. Result and discussion:

The plot of LnJ versus $E^{1/2}$ (figure 1-6) show that mechanism of conduction for different applied field and temperature. For different rate of ZnO nanoparticle doping the transition field are different also due to the doping on pure pollypyrrole film the transition field are shifted from the pure polypyrrole film. The samples are under the action of applied `filed are just to that in vacuum diode-space charge limited current (Mott & Gurney 1964). Generally, in polymers the Ln J versus $E^{½}$ plot for different temperature, show straight line in high electric field region, in which $J \alpha E^{½}$, the case of hot electrode i.e. energy required by the field is greater than the thermal energy. The Schottky and Poole-Frenkel mechanism of conduction are dominant process of conduction in insulator or semiconductor at high field (Aldert 1957, Lamb 1967).

It was found experimentally that, emission current increases with increasing field strength at the cathode, which is contradictory to that independence of current in thermionic emission. Schottky showed that a lowering of the work function due to an increase in the applied field was responsible for such a behaviour. Hence due to high field Schottky emission of electron may occur from the metal contact at the negative potential into the conduction band of the insulator. This mechanism corresponds to thermal activation of electron over the metal insulator interface barrier with added effect that the applied field reduce the higher of the barrier. Considering the origin of the surface barrier, Schottky argued that, there are two regions (1) polarization field and (2) an image field. The Schottky effect is associated with the barrier of the surface of the metal and insulating material, whereas the Poole- Frenkel emission associated with the barrier in the bulk of the material. In both effect the restoring force is due to coulomb interaction between the escaping electron and a positive charge, they differ in that, the positive image charge is mobile with Schottky emission and fixed for Poole- Frenkel barrier. Hence lowering of barrier is greater for Poole- Frenkel than that for Schottky effect.

The current density for Schottky(S) and Poole- Frenkel (PF) process follows the relation Lamb D R (1967).

$$J = J_O \exp\left(\frac{\beta E^{\frac{1}{2}}}{kT}\right) \qquad \dots\dots\dots\dots (1)$$

Where $J_O = AT^2 \exp\left(-\frac{\varphi}{kT}\right)$ (Schottky mechanism)

$J_0 = \frac{\sigma_0 V}{d}$ (Poole- Frenkel mechanism)

T= absolute temperature
k = 1.36x 10^{-23} J/K Boltzmann constant

σ_0 = low field conductivity
V= applied field
d = thickness of the sample

$$\beta(s) = \sqrt{(\frac{e^2}{4\pi\varepsilon_0\varepsilon})} \quad \text{(Schottky constant)} \qquad \ldots\ldots\ldots\ldots (2)$$

$$\beta(pf) = \sqrt{(\frac{e^2}{\pi\varepsilon_0\varepsilon})} \quad \text{(Poole- Frenkel constant)} \qquad \ldots\ldots\ldots\ldots (3)$$

ε_0 = permittivity of free space

ε = permittivity of the material.

From equation (1) it is suggested that the plot of Ln J versus $E^{½}$ should be linear having slope β/kT. The value of β was calculated from such plot (putting $k = 1.36x\ 10^{-23}$ J/K**)** for all temperature.

If ZnO nanoparticle is doped to pure polypyrrole film the value of LnJ is increase with $E^{½}$. The dopant ZnO present in sufficient quantity and remarkably affect the position of Fermi level. The molecules of dopants enter either in the amorphous regions of the polymer or at the disordered regions chain folds. If they are present in low concentration they will give rise to additional molecular sites for trapping of charges. Such localized site formed by dopant molecules can be defined in molecular terms using the difference in ionization potential as an indication of trap depth. It the dopant concentration is increased, the dopant molecules starts bridging in separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between the two localized states (Balan & Widdowson 1972), the dopant ZnO has high mobility also n-type semiconductor so if it is doped to pure PVC the energy level lies just below the conduction band, i.e. the width of the band gap is decreased, which result electrons move into the conduction band with increased of applied field.

The theoretical values of β(s) and β(ps) were calculated from equation (2) and (3) using $e=1.6$ x 10^{-19}C, $\varepsilon=3.0$ and $\varepsilon_0=8.85x\ 10^{-12}$ F/m. It is clear from the table below that the Poole- Frenkel mechanism of conduction is operative. it is doped to pure PVC the energy level lies just below the conduction band, i.e. the width of the band gap is decreased, which result electrons move into the conduction band with increased of applied field.

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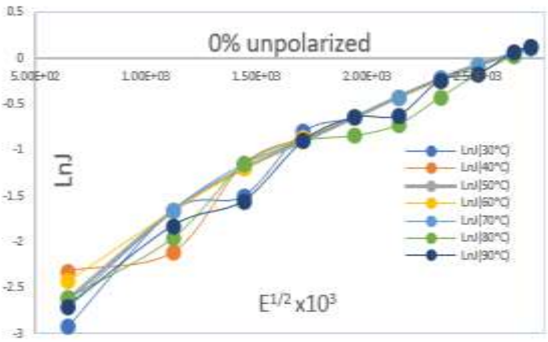

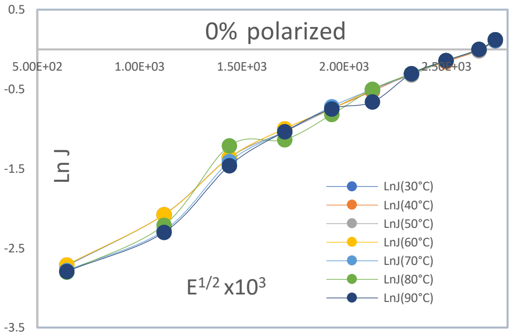

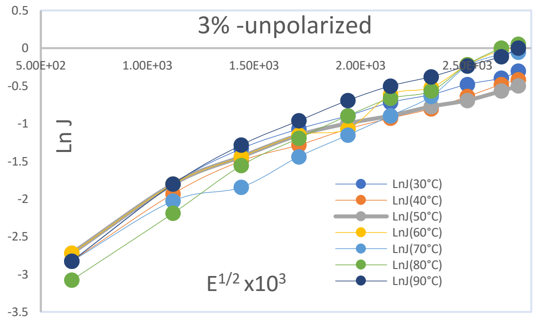

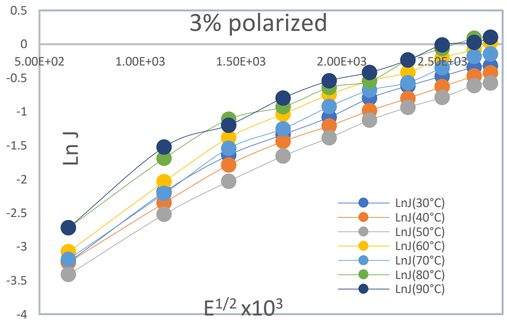

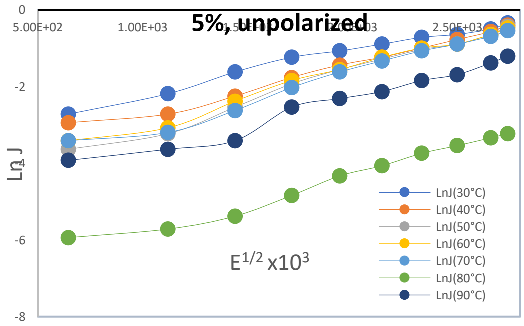

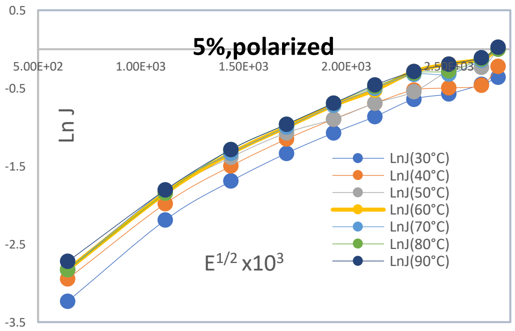

Tem	Experimental value of β_{PF} (of the order of 10^{-23})	Theoretica

p (in K)	0%		3%		5%		l value β_{PF} (of the order of 10^{-23})
	Unpolarized	Polarized	Unpolarized	Polarized	Unpolarized	Polarized	
303	0.5180	0.5402	0.6773	0.7693	0.3643	1.3221	0.7019
313	0.5299	0.5563	0.6565	0.7605	0.4421	1.3657	0.7019
323	0.5513	0.5754	0.7622	0.7978	0.5602	1.4094	0.7019
333	0.5679	0.5941	0.7904	0.8823	0.5343	1.4530	0.7019
343	0.5845	0.6143	0.5301	0.9088	0.5619	1.4967	0.7019
353	0.6016	0.6323	0.9304	0.8037	0.5587	1.5403	0.7019
363	0.6151	0.6472	0.8916	0.8265	0.5466	1.5839	0.7019

The pure polypyrrole (0% doped) film shows a stable, low, and gradually increasing Poole-Frenkel coefficient across the temperature range of 30°C to 90°C. it suggests that the conduction mechanism dominated by shallow intrinsic traps, moderate field assistance, and a thermally responsive yet stable electronic structure. The absence of sudden changes in β shows that the film's microstructure remains consistent across the measured temperatures (Choudhury & Singh 2009). When the sample is electrically and thermally polarized, the values Poole-Frenkel coefficient indicates a consistent and linear increase with temperature from 30°C to 90°C. This nature refers a stable charge transport environment, influenced moderately by thermal energy and electric field, without introducing excessive disorder or nonlinearity. The enhanced PF coefficients compared to unpolarized films point to the subtle ordering effects introduced by polarization, making this approach a potentially useful strategy for tuning the electronic properties of polymer-based materials (Patra et al 2020)

For the unpolarized 3% ZnO-doped polypyrrole films in the given range of temperature shows a dynamic and non-linear evolution of the conduction process. The values suggest shifting dominance among various trap levels, structural rearrangements within the polymer matrix, and changing dielectric properties of the composite (Sengupta & Ram 2013). The results give valuable insight into the nature of conducting polymer nanocomposites. If the same sample is polarized as above the thermally activated and field-sensitive conduction process, is characterized by a sharp transition around the polarization temperature and non-linear variations at higher temperatures (Roy & Sharma 2010). These results suggest the importance of structural stability in determining the charge transport mechanisms in conducting polymer nanocomposites.

The unpolarized 5% ZnO nanoparticle-doped polypyrrole film shows a strong dependence on the Poole-Frenkel emission mechanism. The high and temperature-sensitive values of β show a conduction dominated by deep, disordered trap states (may cause by uncontrolled nanoparticle dispersion) and random polymer chain orientations (Mandal et al 2013). The polarized film shows a smooth, temperature-dependent increase that refers a well-organized and thermally stable charge transport mechanism dominated by field-assisted emission. The increasing trend of the value of β from 1.32×10^{-23} to 1.58×10^{-23} indicates that the material remains trap-dominated, with deeper traps becoming active at higher temperatures. The unpolarized film is in contrasts sharply with the nature of polarized films, where the conduction mechanism is more stable, trap states are more uniformly distributed, and PF coefficients are lower and more consistent (Ghosh & Pal 2000). This nature, facilitated by polarization-induced structural order, makes the film for the applications that require stable electrical characteristics across varying thermal environments, including flexible electronics, capacitive sensors, and advanced thermoelectric materials.

Conclusion:

The present experimental result shows that, both the doping concentration of ZnO and the application of polarization significantly influence the charge transport properties of ZnO-polypyrrole nanocomposite films. But the unpolarized doped samples may suffer from irregular conduction as a result of heterogeneous trap distributions and microstructural instability, the application of polarization supports structural order and improve electronic performance. This has important implications for the design of polymer-based electronic devices. Polarized, ZnO-doped polypyrrole films, particularly at optimal doping levels, emerge as promising materials for applications requiring stable electrical characteristics over a range of temperatures, such as in flexible electronics, sensors, and thermoelectric devices. The result shows the need for careful control over nanofiller dispersion and the value of post-processing treatments like polarization to achieve desirable electronic functionalities in conducting polymer nanocomposites.

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Conflicts of Interest: The authors declare no conflict of interest.

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