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THE EFFECT OF DOPANT, TEMPERATURE AND BAND GAP ON CONDUCTIVITY OF CONDUCTING POLYMERS

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Abstract: Polymers by virtue of light weight and greater easy of fabrication, have replaced and are continuing to replace metals in several areas of applications. Polymers with conjugated π electron backbones displays unusual electronic properties such as low energy optical transitions, low ionization potentials and high electron affinities. They have been considered as good electrical insulators and a variety of their applications have been based upon the insulating property. Polymers which are conjugated exhibit semiconducting behaviour and can be doped to give materials with high conductivity. Conducting polymers represent an important research area with diverse scientific problems of fundamental significance and the potential for commercial applications. The effect of dopant on conductivity, mechanism of conduction, the effect of band gap and temperature has been studied. Conducting polymers like poly pyrrole, poly aniline and poly thiophene etc. have been synthesized and their conductivities have been determined. Some polar organic materials such as poly (ethylene oxide) will complex alkali salts and manifest rapid alkali-ion conductivity. Although the absolute conductivities of such polymer based materials are not as high as those of crystalline solid electrolytes in general, these may be made into thin pin hole-free plastic sheets with sufficient conductance for use in cells and batteries.

Keywords: Effect of temperature on conductivity, Conducting polymers, Band gap, Effect of dopant on conductivity

I. INTRODUCTION

High polymeric system obtained in a semiconducting or conducting form would combine the interesting electrical property of molecular crystals of condensed poly nuclear aromatic compounds with useful range of mechanical properties and thermal properties and good corrosion resistance. Organic semi conductors originated from the transfer of π electrons from molecule to molecule play an important role in fundamental physical processes of living organisms. In general polymers have very poor electrical conductivity. A number of polymers are electrically conductive or can made to be conductive by doping with an electron donor or acceptor.

Conducting polymers can be oxidized more easily and more reversibly than conventional polymers. The charge transfer agents (dopants) effect this oxidation or reduction and in doing so convert an insulating polymer to a conducting polymer with near metallic conductivity in metallic cases. Conducting polymers represent an important research area with diverse scientific problems of fundamental significance and the potential for commercial applications.

In the present investigation, the effect of dopant on conductivity, mechanism of conduction, the effect of band gap and temperature on conducting polymers has been studied and conducting polymers like poly pyrrole, poly aniline and poly thiophene have been synthesized and their conductivities have been determined.

II. EXPERIMENTAL PROCEDURES

Specific_gravity and conductivities of some metals and polymers have been determined. The resistances of metals and polymers have been calculated by Ohm-meter by

$$E=CR \qquad \text{……. (1)}$$

Where 'R' is the resistance; 'E' is the applied voltage and 'C' is the current passed Conductivity has been calculated by

$$S=1/R \qquad \text{…… (2)}$$

Conducting polymers like poly pyrrole, poly aniline and poly thiophene have been synthesized and their conductivities have been determined and the effect of dopant on some conducting polymers has been studied.

Synthesis Of Poly Pyrrole, Poly Aniline and Poly Thiophene:

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Poly pyrrole has been prepared by the electro polymersation of pyrrole, a highly coloured, dense conducting film.

Poly aniline has been obtained by the oxidation of aniline in aqueous acidic media using common oxidants such ammonium peroxy disulphide. Poly thiophene has been synthesized in the doped form and polymerized by the anodic oxidation of thiophene which is very stable in air.

III. RESULTS AND DISCUSSION

It has been observed that the electrical resistance of metals is caused by the scattering of conducting electrons when they collide with ion cores during flow under a potential gradient, thus contributing to a heating effect. The displacement of the cores from their positions arises from their thermal motion. The thermal motion of the ion cores decreases with lowering of temperature with consequent lowering in the resistance character or increase in the conductivity level.

A. Effect of Dopant:

It has been observed that conductivity is increases by doping. Addition of As increases conductivity to 400 S $cm^{-1.}$ The conductivity of natural rubber normally an excellent insulator could be significantly increased by adding carbon black which has natural conductivity. The conductivity can be increased by doping with an electron acceptor such as bromine (~ 10^{45} Scm^{-1}) {1}. The electrical conductivity of an organic polymer-poly acetylene could be increased by a factor of 10^{12} Scm^{-1} when it was doped with an electron donor such as alkali-metal ion or an acceptor such as AsF_5 or Iodine {2}. The conductivity of doped poly acetylene is comparable to that of copper on an equal weight basis. A comparison of electrical conductivities and specific gravities of some polymers and common metals and carbon is tabulated (Table 1). Addition of electron donors or acceptors causes doping that result in dramatic electronic and magnetic changes in the inherently conducting polymers along with increasing conductivity or approaching the metallic range.

Doping is the oxidation or reduction of polymer molecules of poly cations or poly anions. Doping is reversible, removal of dopant or dedoping produces the original low conducting, semi conducting or insulating polymer usually without degradation of the polymer backbone. Doped derivatives of PA are ionic compounds and doping of PA is a redox reaction {3}, In PA, a conjugated polymer {4&5}, the spare electrons are hold by formation of alternate double bonds and single bonds in the polymer structure.

B. Effect of Temperature:

Accumulation of heat and consequent rise in temperature and thermal expansion cause the conducting filler particles in such filed polymer systems move further apart there by leading to a doping trend in conductivity with time of passage of electricity.

The resistivity of the semi conducting materials decrease with rise in temperature because of the fact that with higher thermal excitation more electrons are released from inter atomic bonds and the applied electric field enables the released electrons in higher numbers more through the mass giving rises to increased electronic conduction with rise in temperature.

C. Effect of Band Gap:

It has been observed that conductivity increases with decreasing band gap which is the amount of energy needed to promote an electron from the highest occupied energy level or valence band to the empty band (conduction band) immediately above it. Metals have zero band gaps, while insulators like many polymers have large band-gaps (1.5 to 4 eV) which impede electron flow. The lowest band gap observed for a polymer is ~1ev reported for poly iso thio naphthalene (Table 2).

IV. CONCLUSION

Polymers which are conjugated exhibit semi conducting behaviour and be doped to give materials with high conductivity as high as 10^5S/Cm. Due to the presence of this extended conjugation along with polymer back bone, the chains are rigid and possess strong interaction, interactions resulting in insoluble and infusible materials, which are difficult to process. Conjugated polymers can be made soluble without significant loss in their conductivity. Conducting polymers that are stable even in the doped form can be prepared. Although the electrical conductivities of poly pyrrole, poly aniline and poly thiophene are lower than poly aniline these polymers are more stable to effects of oxygen moisture. These polymers capable of transporting electrical charge is due to conjugated π electron consisting of alternating single and double bonds along the polymer chain backbone or ring structure. Doping results in an electron imbalance, and the extended π conjugated structure of the conductive polymer allows the new electron population to move along the backbone when an electric potential is applied.

Potential advantages of polymeric batteries include high reliability, light weight, non-leakage of electrolyte solution, ultra-thin form, flexibility and high electron density can be used as cathode material, while lithium dissolved in aluminum foil serves as the anode. Some polar organic materials such as poly (ethylene oxide) will complex alkali salts and manifest rapid alkali-ion-conductivity. Although the absolute conductivities of such polymer based materials are not as high as those of crystalline solid electrolytes these may be made into pin hole free plastic sheets with sufficient conductance for use in cells and batteries. Plasticity of the polymers over comes other major problems with solid- state battery systems, that of maintaining good contacts.

TABLE 1: COMPARISION OF ELECTRICAL CONDUCTIVITIES AND SPECIFIC GRAVITIES OF SOME POLYMERS AND MATERIALS

Materials	**Specific gravity**	**Conductivity (Scm^{-1})**
Silver	10^5	10^6
Copper	8.9	6×10^5
Aluminum	2.7	4×10^5
Poly acetylene (doped)	1	1.5×10^5
Platinum	21.4	10^5
Poly thiophene (doped)	1	10^4
Mercury	13.5	10^4
Carbon fiber	1.7-2	500
Carbon-black filled poly ethylene	1	10
H_2SO_4 electrolyte	2	10^{-1}
Polymer electrolyte	1	10^{-4}
Poly tetra fluoro ethylene (Teflon)	2.1-2.3	10^{-18}
Poly ethylene	0.9-0.97	10^{-22}

TABLE 2: CONDUCTIVITIES OF SOME ELECTRICALLY CONDUCTIVE POLYMERS

Conductive polymer	**Dopants**	**Conductivity (Scm^{-1})**	
		Undoped	**Doped**
1) Poly pyrrole (Ppy)	$FeCl_3$, $Cu(ClO_4)_2$, AsF_5	$<10^{-7}$	$10-10^3$
2) Poly aniline(PANI)	HCl, $HClO_4$, Camphor, Sulphonic acid	$<10^{-7}$	$10^{-1}-10^2$
3) Poly thiophene (PPy)	SO_3, CF_3^-, ClO_4^-, BF_3	$<10^{-7}$	$10^{-2}-10^2$
4) Poly (3-alkyl-thiophene)	BF_4^-, ClO_4^-, $FeCl_4^-$		10^3-10^4
5) Poly isothio-naphthalene	BF_4^-, ClO_4^-,		50
6) Poly acetylene (PA)	I_2, AsF_3, $AlCl_3$, $FeCl_3$, K, Li	$<10^{-7}$	$10-10^5$
7) Poly (p-phenylene) (PPP)	AsF_5, $AlCl_3$, $FeCl_3$, K, Li	$<10^{-7}$	$10^{-2}-10^2$
8) Poly (p-phenylene sulphide) (PPS)	AsF_5, FSO_3, H, SbF_5	$<10^{-7}$	$10^{-9}-10^1$

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