


2. THEORIES

2.1 Conduction Mechanisms in Polythiophene

Polythiophene (PTh) has been extensively studied by many researchers. It is a conjugated polymer like polyacetylene (PA), poly (p-phenylene) (PPP) and polyaniliane (PANi). PTh has a heterocyclic structure similar to polypyrrole (PPY). PTh is obtained from the polymerization of thiophene a sulphur heterocycle that can be made into conducting by adding or removing an electron from the orbitals via doping process [1, 2]. PTh and its derivatives are attractive more due to their high electrical conductivity, environment and thermal stability. Conducting polymers are used in combination of other polymers or inorganic materials as composites or blends [2, 3]. PTh consist of alternating double and single-bonds in which each first and fourth carbon atom connected by sulphur atom forming a thionyl ring. Therefore, bond existing between the second and third carbon atoms get more single bond character than the other C-C bonds and consequently the bonds connecting the thionyl rings are more of single bond character [4].

Fig3. Structure of Polythiophene.
When the conductivity is below $10^{-10} \ \Omega^{-1}m^{-1}$ the materials are considered to be insulators and if conductivity was between $10^{-9}$ and $10^{-2} \ \Omega^{-1}m^{-1}$ then the materials are said to be semiconductor. If conductivity is higher than $1 \ \Omega^{-1}m^{-1}$ the material is considered as conductor. In their neutral states most of the conducting polymers are insulators or weak semiconductors. The conductivity of these polymers can be increased by the process of doping. The doping can be carried out chemically by either exposing of the polymer to the dopant or by electrochemical oxidation or reduction methods. These dopants works as charge transfer agents in the polymerization process. They occupy interstitial sites between the polymer chains and during this reaction they donate charges to or accept charges from the polymer backbone. Generally, soliton or polaron and bipolaron structures are formed due to the redox reaction. These entities are responsible for the intramolecular conductivity.

Upon doping Polythiophene, polarons and bipolarons are formed. In polymer backbone when a $\pi$ electron is removed, it becomes a radical cation that is polaron which itself get stabilised by polarising over several monomeric units. From the polymer when a second electron is removed, two polarons or one bipolaron are formed. A bipolaron usually stretches from 1 to 6 carbon atoms and has a structural deformation associated with it. Therefore bipolarons are energetically more favourable than the separate polaronic states. Polaron and bipolarons become mobile in external electric field and act like charge carriers and hence become responsible for electrical conduction in the polymer chains [5, 6]. Figure 3, shows the formation of polaron and bipolaron in Polythiophene. The first configuration depicts the neutral polymer. Initial oxidation results in polaron formation yielding a quinoidal structure.
with charge delocalized over four rings. Further oxidation results in the formation of a bipolaron. In a conjugated polymer backbone the movement of the polaron and bipolaron via rearrangement of the double and single bonds leads to conduction process at the intra-molecular level.

Fig 4. (a) The doping mechanism in polythiophene. (b) Binding energy [6].
Quantum-chemical calculations revealed that the removal of an electron out of a polyarylene system such as Polythiophene leads to the formation of polaron and associated quinoid-like structure which spreads over four to five rings. The quinoid structure has lower ionisation potential and larger electron affinity compared to the benzenoid structure. Because of lowering of ionisation energy more than increase in total electronic energy due to lattice formation, it results in the formation of polaron. The difference in energy corresponds to the polaron binding energy which is about 0.03 eV for poly (phenylene), 0.12 eV for polypyrrole and 0.2 eV for Polythiophene. Further oxidation leads to the formation of bipolaron.

**2.2 Polaron Hopping Theories**

The conducting polymers are of great interest in view of their applications in electronic and optoelectronic engineering fields. They are not only of low cost, lightweight, having flexible structure, easy to prepare, but they provide an opportunity for deeper understanding quantum transport processes which are of fundamental academic interest. In these materials, disorder related effects are reduced which makes them suitable for studying their intrinsic excitations and charge-carrier transport mechanisms [7-8].

The solid oxides in which electrical conduction take place by the motion of charge carriers in a band or by the process of a diffusion is known as hopping mechanism [9]. The conduction process in polyacetylene the polarons play an important role [10]. The concept of a polaron was set forth by Landau in 1933. Physical properties of the
polaron are quite different from those of the band-electrons. There are other interactions from which number of polaron-type quasiparticles are produced such as spin polaron. In this process, the electron interacts with atomic magnetic moments [11, 12].

In a disordered material the charge carriers move by direct tunnelling between localized states instead of occupying extended states as in the case of crystalline materials. This charge transport process is hopping type. Polaron interaction may be of two types such as long-range polaron and short-range polaron. If there are many localized sites in the interaction and that gives larger delocalization path for the movement of the charge carriers then such interaction is said to be large-range polaron interaction. If the interaction shrinks to a single localized site then it is said to be small-range polaron interaction [7, 13].

**Small Polaron Hopping**

Small polaron theories as developed by Yamashita and Kurosawa in the year 1958, Holstein in 1959 and others are based on analytical approximations as a starting point [12, 14]. As a function of temperature and electric field, changes takes place qualitatively based on the polarizability of the host lattice, the phonon spectrum and electronic bandwidth of the valence for hole transport and conduction band in the case of electron transport. Many refinements of basic ideas of Holstein have been developed, which deals with both non-adiabatic and adiabatic transport. Non-adiabatic transport which involve hopping conduction with activated like temperature
dependence where as in adiabatic transport such as tunnelling-dominated or band like [15].

Mott and Davis in 1979, the concept of small polarons was invoked to interpret the conductivity in many oxides, especially transition metal oxides. The transport of small polarons is generally via thermally activated hopping. In particular, under certain approximations, the mobility, \( \mu \), has an Arrhenius-like dependence as mentioned below [11-12]

\[
\mu_{\text{drift}} \propto T^{-1} \exp \left( -\frac{W_H}{K_B T} \right)
\]  

(2.1)

Where \( W_H \) is half the polaron binding energy. As indicated by the two different expressions the drift mobility, \( \mu_{\text{drift}} \) and Hall mobility, \( \mu_{\text{Hall}} \) differ from each other. In the theory of small polaron transport, a distinction is made between adiabatic and anti-adiabatic hopping. In adiabatic hopping the electrons are relaxed in the potential well of its lattice distortion where as in non-adiabatic hopping, the electrons jumps out of the potential well, and then the lattice attains to equilibrium with the electrons in new position.

In the adiabatic approximation of polaron theory, Emin and Holstein suggest that the activation energy is much less. Mott derived a relation for conductivity, in the non-adiabatic region for non crystalline materials and is given by

\[
\sigma = \frac{\sigma_0}{T} \exp \left\{ -\frac{E_s}{K_B T} \right\}
\]

(2.2)
Where, $\sigma_0$ is the pre exponential factor and $E_a$ the activation energy. For the present polymer samples and composites the Eq. (2.3) has been used to determine activation energy [16].

In a variety of materials such as most transition-metal oxides, amorphous materials, polymers including DNA. These are identified and characterized in a number of physical processes, including electrical transport, thermopower, photoemission and infrared absorption [11, 12, 17, 18-19].

**Variable Polaron Hopping**

The Mott’s variable range hopping model was devised for amorphous semiconductors and this model considered the movement of charge carriers between localized states which have energies comparable to the Fermi energy. The conduction process is thermally assisted. The charge carriers hop along a path such that the activation energy required to reach the next site is a minimum [20].

Mott realized that most likely hops would be between localized sites or nearest neighbours. As the range of hop increases the greater would be the probability of the electron finding a site with a small energy barrier and that such long range hops depend on the tails of the electron wave function. These leads to characteristic temperature dependence for variable range hoping which differs from the Arrhenius law normally anticipated for a thermally activated process. For hopping over a range, $R_h$ the number of available sites per unit energy is just the density of states per unit
energy at Fermi level $N(E_F)$ multiplied by the volume of the sphere $R_h$ [21, 22]. The average separation of the energy of the available site is therefore,

$$\Delta E = \left[ \frac{1}{\frac{4}{3} \pi R_h^3 N(E_F)} \right]$$

(2.3)

This is approximately the minimum energy barrier that the electron encounters for a range $R_h$. The optimum hopping distance is given by the maximum of the probability function

$$\varphi = A \exp \left( -2\alpha R_h - \Delta E / KT \right)$$

(2.4)

Where $\alpha$ is the decay length of the wave function. This will occur when sum of the exponents has a minimum value or when

$$2\alpha = \left[ \frac{1}{4\pi R_h^3 N(E_F)KT} \right]$$

or

$$R_h = \left[ \frac{1}{8\pi N(E_F)\alpha kT} \right]^{1/4}$$

(2.5)

Thus the hopping probability and hence the conductivity has the form

$$\phi = A \exp \left( -\frac{B}{T} \right)^{1/4}$$

(2.6)

Several of the experimental and theoretical studies revealed that the low-temperature conductivity in disordered semiconductors deviates from an Arrhenius behaviour and obeys a temperature dependence of the form

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\[ \sigma = \sigma_0 \exp \left( -\frac{T_o}{T} \right)^\gamma \]  

(2.7)

With \( \gamma < 1 \) and \( \sigma_0 \) a prefactor that depends weakly on temperature.

Mott showed that the value of \( \gamma \) in Eqn.(2.8) is given by the relation \( \gamma = 1 / (1+d) \), where \( d \) is the dimensionality of the system [23-27].

Where, \( \sigma_o = e^2 v_o R^2 N(E_F) \) and \( T_o = \left[ \frac{18.1\alpha^3}{k_B N(E_F)} \right] \)

Where \( v_o \) is phonon frequency, it can be evaluated using Debye temperature, and \( k_B \) the Boltzmann constant. \( N(E_F) \) the density of states at Fermi level and \( R \) is the hopping distance between two sites. Quantity \( \alpha \) is coefficient of exponential decay of the wave function of the localized states [28-30].

Eqn. (2.7) is rewritten as,

\[ \sigma = A \exp \left\{ -BT^{\frac{1}{4}} \right\} \]  

(2.8)

Where, 
\[ A = 4 \left[ \frac{2\alpha^3}{9\pi k_B} N(E_F) \right]^{\frac{1}{4}} \]  
\[ B = \left[ \frac{e^2}{2(8\pi)^{\frac{1}{2}}} v_o \left[ \frac{N(E_F)}{\alpha k_B T} \right] \right]^{\frac{1}{2}} \]

The Eqn. (2.8) has been used for determining density of states at Fermi level for the present polymer and its composites by considering the coefficient of exponential
decay $\alpha$ of the wave function of the localized states in hopping process is equal to the size of the monomer unit.

2. 3 Dielectric properties

The functional dependence of complex dielectric function, $\varepsilon^*(\omega)$ on frequency and temperature originates from the following different processes such as 1) Microscopic fluctuation of molecular dipoles (rotational diffusion), 2) The propagation of mobile charge carriers (translational diffusion of electrons, holes or ions) and 3) The separation of charges at interfaces that give rise to an additional polarization [31]. The later can take place at inner dielectric boundary layers (Maxwell/Wagner/Sillers polarization) on a microscopic scale or at the external electrodes contacting the sample (electrode polarization) on a macroscopic scale [32, 33]. Its contribution to the dielectric loss is of few orders of magnitude higher than the dielectric response due to molecular fluctuations.

It has specific features in the temperature and frequency dependence of the real and imaginary parts of $\varepsilon^*$ for each of the above mentioned processes. The relaxation processes are characterized by peaks in the imaginary part, $\varepsilon''$ and step like decrease in the real part, $\varepsilon'$ of the complex dielectric function $\varepsilon^*(\omega)$ with increasing frequency. In contrast, the conduction phenomenon shows an increase in the imaginary part of $\varepsilon$ with decreasing frequency. In pure ohmic conduction, the real part of $\varepsilon^*$ is independent of frequency where as in non-ohmic conduction its real part increases
with decrease in frequency [34]. Alternate representation of the dielectric properties of the materials are the complex conductivity, $\sigma'(\omega)$ or complex modulus, $M^*(\omega)$.

In disordered systems, the charge transport is possible due to hopping of carriers [35]. Moreover, in these systems is the motion of charge is accompanied by an electrical relaxation: an ionic or electronic charge are surrounded by positive or negative counter charges. A hop of a charge carrier to a new site that can only lead to a successful charge transport if the polarization cloud follows. Otherwise, the charge carrier will jump back with a high probability. This mutual movement of the charge carrier and the surrounding polarization cloud requires an electrical relaxation time, $\tau_\alpha$, if the frequency of the outer electrical field is higher than $(1/\tau_\alpha)$ its effect on the charge transport averages out. The frequencies lower than $(1/\tau_\alpha)$, the relaxation of the polarization cloud is in phase with the outer electric field. Due to this the field supports the propagation of the charges. This kind of electrical relaxation gives rise to a contribution to the complex dielectric function that increases with decreasing frequency. It is the essence of the Debye/Huckel/Falkenhagen theory [36-42]. This explains the experimental observation that for electrolytes the real part $\varepsilon'$ increases with decreasing frequency [43-45].

**Polarization processes**

Dielectric polarization occurs due to the displacement of charged particles under the influence of the electric field to which they are subjected.
The above said displacement of electric charges gives rise to the formation of electric dipole moment in atoms, ions or molecules of the material. There are three important types of polarization are as follows 1) electronic polarization 2) ionic polarization and 3) orientational polarization.

**Electronic polarization \((\alpha_e)\)**

The electronic polarization is one in which the displacement of the positive and negative charges in a dielectric material owing to the application of an external electric field. The separation created between the charges gives rise to the dipole moment. This process takes place throughout the material. Thus the material as a whole will be said to be polarized as shown in fig 5 [46].

![Diagram of electronic polarization](image)

E=0

Charge distribution in the absence of the field.

E>0

Displacement of charge due to the applied field.

Fig. 5 Electronic polarization, charge displacement due to the applied field.
**Ionic polarization ($\alpha_i$)**

Ionic polarization takes place in those dielectric materials which possess ionic bonds such as in NaCl. When ionic solids are subjected to an external electric field, the adjacent ions of opposite signs undergo displacement. The displacement causes an increase or decrease in the distance of separation between the atoms depending upon the location of the ion pairs in the lattice. This gives rise to net dipole moment due to the shifting of electron clouds relative to the nuclei as shown in fig. 6 [46].

![Ionic polarization](image)

Fig. 6 Ionic polarization, ion displacement due to the applied field.

**Orientation polarization ($\alpha_o$)**

The orientation polarization results in polar substances. The existence of a permanent moment is purely a matter of molecular geometry. In such materials the permanent molecular dipoles can rotate about their axis of symmetry to align with an applied field which exert a torque on them as shown in fig. 7. This additional polarization effect is accounted by an orientational polarizability term ($\alpha_o$).
In electronic and ionic polarization processes, the force due to external applied field is balanced by elastic binding forces, however no such forces exist in orientation polarization. In thermal equilibrium, with no external field applied, the permanent dipoles contribute nothing to net polarization since they are oriented randomly. Dipole alignment largely offset by thermal agitation as field is applied. However it is found that the orientational polarization is of the same order as the other forms of polarization. It is only necessary for one dipole in 10^{-5} to be completely aligned with the field to account for the effect. However the orientation polarizability, \( \alpha_o \), is dependence on temperature, higher the temperature higher will be the thermal agitation and lower is orientation polarizability, \( \alpha_o \). the distorting polarizability factors \( \alpha_o \) and \( \alpha_o \) are functions of molecular structure and and are independent of temperature [46].

\[
\begin{align*}
E=0 & & E>0 \\
\text{Dipole orientation in the absence of the field.} & & \text{Dipole alignment due to the applied field.}
\end{align*}
\]

Fig. 7 Orientation in the absence of the field, Dipole alignment due to the applied field.
**Electrode polarization**

Electrode polarization is an unwanted effect that results in a dielectric experiment because it can mask the dielectric response of the sample. It takes place mainly in moderately conducting samples and influences the dielectric properties at lower frequencies. Magnitude as well as frequency position of electrode polarization depends on the conductivity of the sample and can result in extremely high values of $\varepsilon'$ and $\varepsilon''$.

The origin of electrode polarization is the partial blocking of charge carriers at the sample electrode interface. This gives rise to a separation of positive and negative charges which leads to an additional polarization [47, 48].
REFERENCES


