INTRODUCTION

1.0 Background

The study of polymers has become important due to the need to make and understand new kinds of plastics, rubbers and fibers. Chemically, polymers are long chain molecules of very high molecular weight, often measured in hundreds of thousands. Each polymer contains a number of monomers or repeating units and they are frequently called macromolecules. [1]

Traditionally, polymers are poor conductors of electricity because of covalent bonds, which put them together. Most of these polymers are conventionally regarded as insulators, not able to conduct electricity because the electrons in their covalent bonds are tightly bound and not free to move. However, recent advances have made it possible to produce polymers which are able to conduct electronically and ionically. This has introduced a new field in polymer chemistry, namely that of conducting polymers. [2]

Conducting polymers can be divided into two types. They are 1) Electron conducting polymers and 2) Ion conducting polymers.

(1) Electron conducting polymers

As the name suggests, *Electron conducting polymers* are polymers that conduct electrons along their backbone chain. This phenomenon can only occur in polymers with extended systems of conjugated double bonds along their backbone chain as shown in Figure1.1.For electron conducting polymers, the conductivity can be enhanced by doping the polymer with small quantities of electron accepting or electron donating species [3,4]. The ionization process in polymers such as polyacetylene, polypyrrole and polythiophene, consequent upon electron-acceptance or donation, may be described in terms of the formation of localized charges in the polymeric chain with attendant relaxations in the lattice structure (Fig 1.1). These localized charges, termed polarons, bipolarons or in the case of polyacetylene, solitons, are identified as electronic states situated between the valence and conduction bands, that is, within the band gap. As the redox processes proceed in extent, the states overlap with the formation of inter-gap bipolaronic or solitonic bands which allow the charge transport. Consequently the counterions X^- (or M^+), must diffuse along the polymeric chain to compensate the movement of the positive (or negative) charges [3,4].

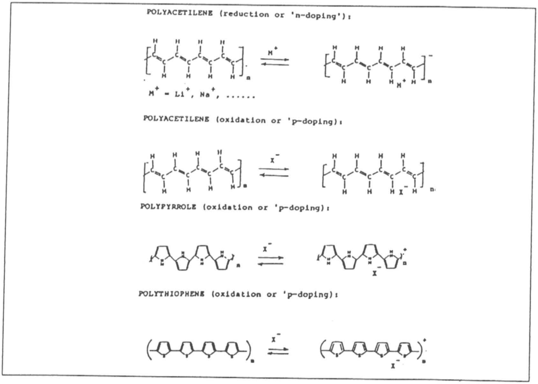

Figure 1.1: Schemes of electrochemical doping process of polyacetylene, polythiophene and polypyrrole [3].

(2) Ion Conducting Polymers

Ion conducting polymers are solid polymers containing mobile anions or cations which act as the conducting species in the medium. The ionic conductivity, σ, is proportional to the product of ion concentration and mobility. Ionic conductivities can be achieved in polymer systems by incorporating additives in the form of inorganic salts with or without solvents into the polymer matrix. [5]. Table 1 shows some of the different ways in which ions can be incorporated into polymers.

Table1.1: Different methods of ion incorporation into polymers.

Type	Composition	Mobile species	Examples
Gel polymer electrolyte	Polymer, salt and solvent	Cations , anions and solvent	PVF_2 , $PC+LiClO_4$
Ionomer or polyelectrolyte	Polymeric Salt	None , unless wet	Nafion
Solvating polymer	Polymeric solvent / salt	Cations and anions	$PEO + LiClO_4$

Abbreviations: PVF_2 = Polyvinylidine difluoride ; PC = Propylene carbonate; Nafion = $(C_2F_4)_x - (C_2F_3)_y - (O\ C_3F_6)OC_2F_4SO_3H$;
PEO =Polyethylene oxide.

The gel polymer electrolyte is simply a polymer swollen with a solution of a salt in a solvent. The salt is dissolved in the solvent, which is in solution in the polymer. In the case of the polyelectrolyte, the polymer chain contains either anions (e.g. $-CF_2SO_3$) or cations (e.g. $-R_3N^+$) which are linked to it. These anions or cations act as counter - ions to small, unbound and potentially mobile ions. However the mobility of the latter is severely restricted by strong coulombic attraction if there is no solvent present. Upon addition of the solvent, the unbound ions become mobile as in the case of ionomers (crosslinked and therefore insoluble, solvent - swollen polymers used as ion exchange resins) and polyelectrolytes (soluble polymers used as surfactants).

The most important class is the solvating polymer in which the polymer itself has the ability to dissolve certain salts and support ionic mobility. This ability is an essential pre-requisite for fast ion conduction in a dry polymer. Since the solvating polymers do not require the addition of a liquid supporting solvent, they can be called as genuine solid polymer electrolytes [6]. Some examples of these solid polymer electrolytes are polyethylene oxide (PEO), polypropylene oxide (PPO) and polyethylene adipate (PEA).

The criteria for polymer - salt complexations are

a) Polymers should have low glass transition temperature,T_g .

b) The concentration of polar groups or solvating heteroatoms should be as large as possible.

c) Lattice energy of the salts should be as large as possible.

The application of solid polymer electrolytes to solid state batteries has been one of the technological justifications for the continuing investigation of new electrolyte materials. Interest in polymer batteries and other devices using polymer electrolytes has been sustained for the past 15 years. Armand *et al* [9] developed the pioneering work of Wright and co-workers [7] to produce the first polymer electrolyte [7-13]. Although unmodified polymer electrolytes exhibit relatively poor conductivities (typically 10^{-7} S/cm or below at room temperature), the ease of achieving a thin film configuration provides a conductance that is adequate for some purposes. Initial interest focused on solutions of alkali metal salts of soft anions in an immobile solvent matrix of polyethylene oxide (PEO). For technological reasons, applications rapidly focused on lithium polymer electrolytes because of advantageous energy density accruing to devices incorporating lithium anodes, and the relative ease of reversible intercalation of Li^+ in a range of candidate intercalation materials.

Lithium systems are not the only focus of present interest. Lithium polymer batteries can suffer from adverse effects at the anode/electrolyte interphase and lithium as an anode material has a propensity for migration, dendrite formation and other undesirable side effects. Therefore other candidate high energy density systems including those based on lead, magnesium, zinc, nickel and silver [14-21] have been examined from time to time, but such cell systems are beset by ion mobility problems associated with local structure complications. Conductivity enhancement of two, three and also five orders of magnitude from 10^{-8} S/cm to 10^{-3} S/cm has been observed when γ - Al_2O_3 particles were dispersed into the PEO plasticized polymer matrix [22]. Many other similar systems with a room temperature conductivity of 10^{-5} S/cm have also been developed. Many applications ranging from sensors, fuel cells, solid state batteries and electrochromic devices have been attempted from these materials.

In this introduction we will restrict our discussion to PEO and PVC - based tin polymer electrolytes with triphenyltin chloride, dioctyltin bis{p-[N-(3,4 dinitrophenyl)]aminobenzoate]}, dibutyltin bis{p-[N-(3,4 dinitro phenyl)]aminobenzoate]} as the added salts and their applications in solid state batteries. The choice of organotin compounds as the additive salts was prompted by the fact that these compounds have not previously been explored as doping materials. Another factor favouring their application in this study was their ready availability in the organotin laboratories of the Institute of Postgraduate Studies and Research (IPSR). The preparation of tin based solid electrolytes and the understanding of the phenomenon of ionic conduction in solid polymer electrolytes will be the main focus of the investigation in this thesis.

1.1 Why PEO?

PEO has attracted considerable attention because of the following characteristics:

- Good ion solvating property.
- Lone pair of electrons on the oxygen has sufficient donor power to form co-ordinate bonds with cations.
- Low barriers to bond rotation so that segmental motion of the polymer chain can take place readily.

Subsequently, several monovalent, divalent and trivalent salts have been found to dissolve in PEO leading to a variety of polymer electrolytes. Following this Wright and co-workers reported on the enhanced conductivity of PEO containing NaI, NaSCN, or KSCN [23-24]. These additives were found as crystalline complexes with a 1:4(salt/EO) stoichiometry and melting points well above that of pure PEO.

In fact, the salts easily form complexes when the common solvent used has a low electron pair donor power (e.g. acetonitrile) and does not compete with the ether oxygens. In many cases, the complex precipitates upon mixing solutions of the polymer and salt in low dielectric constant liquids (e.g. LiBr and PEO in THF). Three parameters are important for the control of salt / neutral molecule interactions.

- Donor number(DN)
- Acceptor number (AN)
- Entropy term

Donor number (DN) measures the ability of the solvent to donate electrons to solvate the cation considered as Lewis acid. On the other hand, the acceptor number quantifies the possibility for anion solvation. The entropy term depends on the optimal spatial disposition of the solvating units. The PEO helix has a much more open structure as shown in Figure1.2. The other cell parameters are reported to be a = 0.805nm and b = 1.304nm and $\beta = 125.4^0$, with the most probable space group $P_{21/a}$ - C_{2h} and molecular structure (compared with that in Figure 1.2) is equal to 7.2 helix,

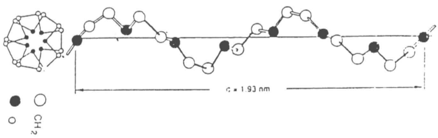

Figure 1.2 : Schematic model of poly (ethylene oxide)[25]

Ionic solids dissolve in polymers such as PEO because the lone pair of electrons on the polymer oxygens coordinate with the cations in a manner similar to crown ethers. This implies that the spacing and conformational flexibility provided by the PEO unit, - CH_2 - CH_2 - O is optimal for coordination.

The chemical stability of the ether functional group strengthens the superiority of PEO as a host for a SPE (solid polymer electrolyte), although the conductivities at room temperature are poor. The main rationale of investigating low molecular weight analogues of the more widely studied PEO complexes is to eliminate complications such as chain entanglements, while retaining the essential features of ion solvation by the polyether segments.

1.2 PEO Content, Electrical Conductivity and Glass Transition Temperature (T_g)

The material(s) added to PEO in the effort to maintain the high electrical conductivity at room temperature is (are) commonly called impurity(ies). The ionic mobility correlates closely with the relaxation modes of the host polymer. This is demonstrated by the observed increases in glass transition temperature(T_g) of polymeric systems as the concentration of the added salt is increased. The reduction in segmental motion is usually interpreted as being the result of the effects of an increase in intramolecular and intermolecular coordination between coordinating sites on the same or different polymer chains caused by the ions acting as transient cross links. The availability of vacant coordinating sites is greatly

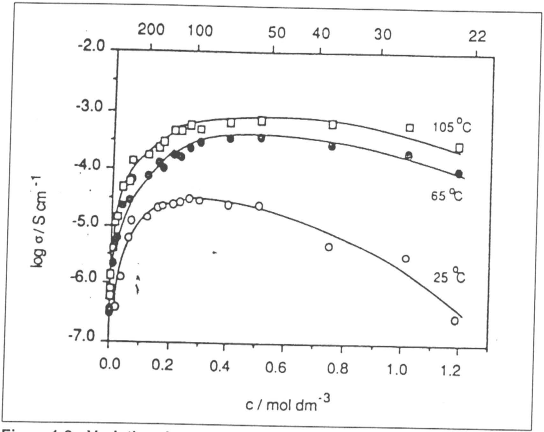

Figure1.3: Variation in conductivity with salt concentration for an amorphous poly (ethylene oxide) polymer containing $LiClO_4$ [25].

reduced at high salt concentrations by the stiffening of the matrix which reduces the conductivity. Also, as the salt concentration varies the degree of crystallinity of the polymer correspondingly varies but not proportionately. It was observed that as the crystallinity of the polymer decreases, the conductivity increases[25]. Thus it is necessary to control the degree of crystallinity. In general, if a graph is plotted with conductivity along Y - axis and concentration of the salt along X - axis, a trend as shown in Figure 1.3 is observed, whereby the electrical conductivity increases with the salt concentration, reaches a maximum at a particular salt concentration and then decrease with additional salt content.

1.3 What are Polymer Electrolytes?

Polymer electrolytes are thin solid films consisting of ionic salts 'dissolved' in an appropriate polymer. Mechanically they behave like solids but the internal structure, and consequently the conductivity behavior closely resembles that expected of the liquid state. The polymer acts as an 'immobile solvent', a term introduced by Michael Armand in 1983 [26]. The salt remains in solution only if an appropriate polymer is used. Such polymers contain heteroatoms such as O or N; the most common example is poly(ethylene oxide), PEO. Polymer electrolytes based on PEO are normally written as $PEO_n : MX_Z$ where 'n' is the oxygen - to -cation ratio, i.e. $[O] : [M^{2+}]$; M is the cationic species, usually Li, although a wide range of other monovalent [Na, K, Rb], divalent [Hg , Ca , Co, Ni, V, Cu, Zn, Cd, Hg, Pb] and even trivalent [Al , Nd] species have been studied; X is a suitable anion, usually one that can be described as 'soft' such as CF_3SO_3(triflate),ClO_4(perchlorate),CNS(thiocyanate),BF_4(tetrafluoroborate) and halides and Z is the cation valency.

The PEO repeat unit is the same unit as found in crown ethers, which are used as phase-transfer agents for promoting the solubility of ionic salts in low polarity organic solvents. In the case of crown ethers the lone pair of electrons on the oxygen atoms co-ordinate with the metal cations and the methylene groups interact with hydrocarbon or similar solvents. The crown ethers can be thought of as amphiphilic molecules, the oxygen containing regions being hydrophilic and $- CH_2 -CH_2 -$ portions being hydrophobic. The situation in polymer electrolytes based on PEO is similar to that in crown ethers i.e. the cations appear to coordinate with the lone pairs on the oxygens. For both PEO based elecrolytes and crown ethers, the anions are held loosely by the coulombic attraction in not precisely known locations in the vicinity of the cations. In most polymer electrolytes, both cations and anion conductivity is possible.

The prime difficulty in developing polymer electrolytes is to achieve a successful balance of ion - polymer interactions. These must be strong enough to permit the ions to move. If the cation - polymer interaction is too strong , then clearly the cations will have a very low mobility. This is not the only problem that results from overtly strong cation - polymer interactions. Typically a given cation is linked at any one instant to four or more oxygens, which often are located on more than one polymer chain. Transient ionic crosslinks are thus formed which greatly restrict the local freedom of motion of polymer chains. Torrell *et al* [27] have shown that ionic motion depends on the ability of the polymer chains to flex and so the rigidity imposed by the transient cross links (induced by the cations) also impedes the mobility of the anions. In addition, many cations interact with PEO in such a way that crystalline, high melting salt polymer complexes are formed. This obviously reduces the number of ionic carriers available for conduction.

1.4 Multiphase Behavior

Polymers can hardly be regarded as single-phase solids because they are composite materials consisting of many phases. The elastomeric phase is unique to polymer. This is a high temperature state, above T_g, in which long range mobility is prohibited either by chain entanglement or crosslinking. Macroscopically, samples in this state are essentially soft, elastic solids which retain their shape without containment. However, microscopically they are mobile and contain much interstitial space.

At a relatively low temperature where organic polymers can be studied and used, ionic conduction is nearly always greater in liquid than in their solid state. Naturally if the samples contain liquid or the closely related elastomeric phases, then the phase will bypass any conduction paths through solid or glass. Samples which do not contain these phases will be relatively poor conductors and also will be mechanically brittle,showing very little advantage of plasticity. This tells us that polymers with liquid-like transport mechanism property have to be selected to study electrical behavior [28 -34].

Among the four phases investigated, it was observed that elastomeric phase is solid but behaves really, like a liquid. Based on this observation, we can argue that the host phase for conduction in a polymer electrolyte is not really a liquid but an elastomeric phase. This is a phase in which local motion is liquid-like but long range displacement is forbidden. An elastomer will fulfill the following solid like properties.

a) negligible low vapor pressure

b) well defined shape under constant stress
c) negligible long range self diffusion

This behavior gives us evidence to stress that the elastomeric phase is a state which is neither liquid nor solid. It is this approach that we are trying to understand in order to grasp the polymer electrolyte's conduction properties.

Many studies on polymer on electrolytes have been directed towards understanding the fundamental questions regarding the structure, mass and charge transport, ion polymer interaction, ion-ion interaction, solvation mechanism and ion conduction mechanism. No unified theory has emerged to explain all the properties of polymer electrolytes except for the conclusion that ionic conduction occurs principally in the amorphous phase. It is hoped that this continued work on PEO - organotin systems studied for this work will throw some light on some of the matters mentioned above.

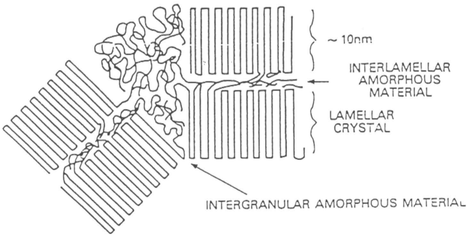

Figure 1.4: Example of a polymer microstructure, showing amorphous regions of PEO [28].

1.5 Description of Polymer Structure and Mobility

Figure 1.4 shows a two dimensional, molecular scale representation of a polymer. Relatively at low temperature,a network of coulmbic, hydrogen bond or van der Waals attraction between the monomer units ensures that it is in solid state in the conventional sense. In addition to these forces, we have the characteristic strings of directional and essentially unbreakable covalent bonds which are not closely packed. As long chain polymers are not closely packed, they can show amorphous nature in their arrangement. This brings about glass formation. A single long chain molecule can wind (refer to Figure1.4) its way through crystalline and amorphous regions. The columbic, hydrogen and van der Waals bonds are generally weak and these bonds can be disrupted by raising the temperature or adding a solvent in exactly the same way as in our assembly of small molecules. However, the covalent bonds are very strong and they are not easily broken. If these bonds do break, then the material decomposes.

1.6 Phase Changes

On heating, the amorphous region of the polymer becomes elastomeric or liquid at the glass transition temperature, Tg, and one or more melting points may be subsequently observed as the various possible ordered structures transform into elastomers or liquids. Generally at intermediate temperatures, polymers often contain crystalline regions, separated by thick elastomeric grain boundaries. If the chains are long enough to pass through the crystals, the crystals can act as cross links which mechanically stabilize the elastomer as shown in Figure 1.4. Low molecular mass liquid like components may also be present. The elastomeric phase is the main concern, in which the ion is coupled to that of the elastomeric host. The mobility of the elastomer and its guest ions will be considered with reference to free volume theory, which explains the nature of the coupling between polymer segment and ionic motion.

1.7 Mass Transport in Elastomer Phase

The covalent bond chains prevent the polymer from forming close packed structure. The resulting vacancies are randomly arranged and static below the glass transition temperature (T_g). Although the vacancies are quite abundant, forming about 2.5 percent of the total volume, they are unlikely to percolate into continuous tunnels allowing diffusion of foreign molecules [31, 35].

However, at temperatures above T_g, the labile bonds can be broken by thermal energy, so that a chain segment which is now capable of independent motion, can move into a neighboring vacancy provided it is sufficiently large. The movement represents a change in the conformation of the polymer chain, of the kind that is required for elastic deformation on the macroscopic scale. This also gives a mechanism for a continuous, random redistribution of the vacant space and allows long-range diffusion of small molecules through the structure. The same vacancy distribution is the primary route for ion transport, and therefore a major factor in determining the ion mobility. Therefore T_g marks the onset of three transport processes,

a) short range translations of chain segments
b) small molecule diffusion
c) ionic conductivity

1.8 Factors which Determine the Conductivity

1.8.1 Tortuosity Factor

Polymer solvates are similar to liquid solutions in having solubility limits. For example, regular PEO which has symmetry to form crystals, exhibits the phase behavior illustrated in Figure 1.5. It can be seen from the figure that the non-conducting crystalline fraction is a major component above the O/Li ratio of 6:1 over a wide range of temperatures. The conductivity in this range is due to a residual elastomeric phase which

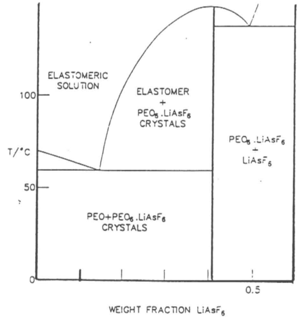

Figure1.5: Phase diagram for PEO - $LiAsF_6$ system [28]

percolates an extensive insulating crystal network [28]. The ratio between the conductivity of the conducting elastomer and the actual mixed phase is called the tortuosity factor. This appears to be the primary factor controlling the conductivity below or at about 80°C.

1.8.2 Effective Mobile Ion Concentration

Although cations and anions are well separated in very dilute solute solutions, ion association effects come into play well before the optimum concentrations for high conductivity are reached. This is the weak electrolyte model, which assumes that only a small portion of the ion concentration contributes to the conductivity while the majority of the ions are paired, neutralized and therefore immobilized. At high concentrations, an increase in mobility is often encountered, and this has been rationalised in terms of triple ion formation. Applying these results to polymer electrolytes, is however, fraught with difficulties. There are a couple of reasons for this. Firstly, the concentration range of interest is so high that even triple ion models break down in favour of the fused salt model, in which ion pairs are so close to neighboring ions that they cannot be considered as separate entities. Secondly, because of the long-range immobility of the solvent, the strong cation-solvent interaction is expected to play a greater role in an elastomer than in a liquid. Systematic analysis of the variation of conductivity with concentration is complicated due to the simultaneous increase in glass transition temperature, T_g.

1.8.3 Transport Numbers

On account of the experimental difficulties in measuring transport numbers, conductivity values are usually quoted as the sum of contributions from anions and cations. This is unfortunate because many of the expected differences in transport mechanism between the species are masked in the available data [31-36]. For most applications, the transport number is important only as a scaling factor to obtain conductivity of the electrode reversible ion from the total conductivity. For the lithium ion conductors as an example, the average transport numbers reported is about 0.4 with small anions. In this thesis, the total conductivity value will be taken as a measure of the net mobility of the ionic species.

1.9 Conduction Mechanism

Electrical conductivity is the movement of charge in response to an electric field. In solid conductors, i.e metals and semiconductors, the charge movement, or current is due to electrons or holes and is described as electronic conductivity. Also, it has been established that conductivity occurs by the migration of ions in the form of cations and anions which takes place preferentially in the amorphous phase of PEO-salt complexes. This ionic transport is co-operative with the segmental motion of the main chains, because cations in the polymeric phases are strongly solvated by the PEO segments. The segmental motion normally involves more than 10 repeat units, which is a main reason for the WLF-type large temperature dependence of ionic conductivity of the polymer electrolytes in spite of the small size of carrier ions. Many theoretical models [37] have been proposed to explain the ionic transport mechanism in polymer electrolytes and their conductivity variation as a function of temperature and composition. Of these, the mechanism commonly propounded [38] for the inorganic salt doped polymers such as PEO involves the solvating hetero atom, here oxygen, acts as a donor for the cation and the anion stabilizes the PEO-salt complex. The ionic transport in such PEO - salt complexes may be interpreted on the basis of a hopping mechanism between the polymer chains (Figure 1.2) in which the cation jumps from one oxygen atom to the other.

1.9.1 Some Empirical Relationships:

Ionic conductivity is electrical conductivity due to the motion of ionic charge. Ionic conductivity , like electronic conductivity, can be broken down into a product of three terms : the charge carrier (q), the concentration (number of particles per unit volume, n) and the self-diffusion coefficient D [30, 33].

$$\sigma = fnq^2 \, (D/kT)$$

f is a geometrical correction factor close to 1. According to the above expression, conductivity is proportional to n, the number of free ions. This is not so, when actually only a small proportion of the ions are sufficiently mobile to conduct.

On the macroscopic view, the concept of diffusion represents motion of particles in terms of continuous movement of matter. The diffusion coefficient can be expressed as a product of square of the average ion jump distances $< X >^2$ and frequency of jumps 'v' in a particular direction.

$$D = < X >^2 v$$

The jump distance can be taken as the distance of ether oxygens of PEO and the jump rate depends on the basic mechanism of transport. Possibilities of transport mechanism of solid like are contrastingly shown in Figure 1.6.

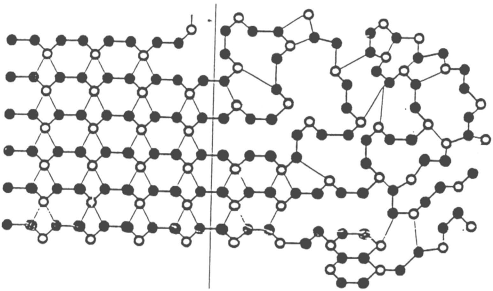

Figure1.6: Schematic representation of crystalline and amorphous regions in PEO [28]

In the solid phase, motion is thermally activated; the jump rate equals an attempt frequency, v_0 multiplied by a probability of surmounting energy barrier, E_A.

$$v = v_0 \exp [- E_A / kT]$$

In elastomer phase, an additional mode of transport becomes available using the free volume. Here the diffusing unit effectively takes a ride in the free volume as it moves around the fluid. This jump is volume activated and the jump rate is given by

$$v = v_0 \exp [-v_a / v_f]$$

where v_f is the average free volume in the vicinity of the unit and v_a is the volume of diffusing unit.

The effect of temperature on mobility in a liquid or elastomer is given by the expansion coefficient α in the expression

$$v = v_0 \exp [-v_a / \alpha(T - T_0)]$$

where 'v' is assumed to start from zero at the theoretical glass transition temperature , T_0 . With all these, we get the VTF(Vogel - Tamman - Fulcher) equation for temperature dependence of conductivity, which replaces the Arrhenius equation used for solids. The VTF equation is given below with a slightly temperature dependent coefficient A.

$$\text{VTF} : \alpha = A \exp [- B / T - T_0] \qquad (1.1)\ [28]$$

The important aspect of the equation is that it stresses the need for a low transition temperature to achieve high good conductivity value and also the requirement for a high free ion concentration.

The σ vs 1/T plots generally show a sudden conductivity jump, in most cases, approximately at the melting temperature T_m when semicrystalline to amorphous phase transition takes place. The σ vs 1/T plots are generally linear typical of Arrhenius behavior:

$$\sigma (T) = \sigma_o \exp(-E_a / kT) \qquad (1.2)$$

but for most cases, the σ Vs 1/T plot is a curve with VTF (Vogel-Tamman-

Fulcher) type behavior expressed as:

$$\sigma (T) = A\, T^{½} \exp[-E_a /k\, (T-T_o)] \qquad (1.3)\ [28]$$

where A is pre-exponential factor, E_a is psuedo activation energy, and T_o is the equilibrium glass transition temperature. The VTF behavior is more general (than exceptional) when the measurements are extended over a wide range of temperatures. In general, T_0 is 50^0 K lower than the actual glass transition temperature T_g. The above equation is the derived form of an empirical VTF equation, originally developed to explain the viscosity behavior of glassy liquids.

Another empirical relationship is based on William, Landel and Ferry (WLF) equation of viscosity, modified due to different relaxational processes in the amorphous materials. The WLF equation is:

$$\sigma (T) = \sigma_{Tr}\, \exp \boxed{\frac{C_1 (T - T_{r)}}{C_2 + (T - T_{r)}}} \qquad (1.4)\ \ [28]$$

where C_1 and C_2 are constants. The values of C_1 and C_2 depend on the choice of reference temperature, although they are commonly normalized to the reference temperature T_g [28]. C_2 relates the WLF reference temperature T_r with VTF temperature T_o as $C_2=T_r-T_o$. The reference temperature, T_r, may be chosen anywhere between T_g and T_g+150°C, according to experimental convenience. Thus a property can be specified over a wide temperature range by tuning C_1 and C_2 to give the best data fit.

1.9.2 Free Volume Theory and Configurational Entropy Models

The WLF and VTF fittings are empirical relations which can be explained on the basis of free volume theory. However, the free-volume picture is entirely an independent phenomenon given by Cohen and Turnbull [39]. They considered the liquids as hard spheres (ions in the case of polymer electrolytes) which are free to move in a volume fraction (voids), called free volume and derived the probability distribution of void volumes in the total volume of the system. Following the Cohen and Turnbull treatment, the free volume expression for diffusion coefficient 'D' has been derived to be:

$$D=g\ u\ a\ \exp[-\gamma\ v / \alpha\ v'_m (T - T_0)] \qquad (1.5)$$

where g is geometrical gactor, a is molecular dimension, γ is Lagrange parameter, v is critical free volume. Following the Nernst Einstein relation, the free volume theory yields the equation (1.3) which is the VTF equation that explains σ vs 1/T behavior of many polymer electrolytes.

The main attraction of the free volume theory is its simplicity. This theory, although explaining some properties of polymer electrolytes via VTF equation, only involves the consideration of motion of polymer hosts (not the ionic hopping in the polymer-salt complexes). The σ -T relationship of different polymer electrolytes does not merely follow the VTF behavior derived from free volume theory. Secondly, free volume theory is realistic only for rigid molecules. A confusion arises when the free volume model is used for the treatment of flexible molecules. When the free volume theory is corrected, it becomes similar to 'configurational entropy model' given by Gibbs and co-workers. The model was originally developed as lattice model in which the single parameter of the free volume theory has been replaced with two parameters, one counts the number of lattice points and the other the number of distorted bonds. The WLF behavior which describes the behavior of most of the polymer electrolytes has been derived using configurational entropy model by Adam and Gibbs [40].

1.9.3 Dynamic Bond Percolation Model: A Microscopic Theory

The WLF and VTF equations of the free volume theory and configurational entropy models are the quasi thermodynamic macroscopic pictures which are able to describe some broad physical properties of polymer electrolytes such as temperature dependence of conductivity, diffusivity and viscosity, etc. Secondly, these models describe only the behavior of hosts, not the ionic motion in polymer-salt complexes. Further, the free volume theory is not able to explain the microscopic behavior such as mechanistic aspects, transport properties as a function of molecular weight, dielectric relaxation, etc.

Many microscopic models based on 'percolation' have been given for ionic motion in the polymer electrolyte. The static bond percolation model deals with the ionic motion in the electrolyte of rigid framework. The well known experimentally observed property that a crystalline phase has no conductivity and an amorphous phase is responsible for ionic conduction in polymer electrolytes can be explained on the basis of static bond percolation model. But in the polymer electrolytes above the glass transition temperature ($T>T_g$) the ionic motion is due to the combination of ionic translational motion/hopping and dynamic segmental motion of the polymer hosts which assists the ionic motion.

Druger *et al* [41], have given a generalised 'dynamic bond percolation model' in which the segmental mobility has also been included along with the ionic motion. In this generalised model, the bonds which are closed or open changes with characteristic rate λ or characteristic renewal time ι_r($\lambda=1/\iota_r$). This change or renewal event is related with the segmental motion which either permits the ions to hop from one site to another site or give a pathway for ions to move, or in other words the segmental movement of the polymer facilitates the translational ionic motion. The dynamic bond percolation model is able to describe the various physical properties of polymer electrolytes such as dependence of conductivity on chain length of the polymers, molecular weight, applied pressure, effect of host polymer change, frequency dependence of conductivity, etc.

1.10 Solid State Batteries

One of the possible applications for tin-based PEO electrolytes is in solid state batteries. All batteries, including polymer batteries, involve two electrodes, an anode (negative electrode), and a cathode (positive electrode) made of an oxidising agent capable of inserting respective ions into its structure separated by an electrolyte. They produce power by a redox reaction between the anode and cathode species, oxidation taking place at the anode and reduction at the cathode. The ions involved in the cell reaction travel through the electrolyte whereas the electrons take a different pathway through an external circuit. By doing so, the electrons can do external work, providing power.

Batteries can be either primary or secondary power sources. The difference is quite simple. If the product of the cell reaction can be decomposed into the original reactants simply by applying a sufficient voltage to the battery for a long period of time, then the battery is called a secondary battery and is rechargeable. If the cell reaction is not reversible in this way, the battery is called a primary battery.

The anode should be a metal foil or sheet and the cathode a mixed conductor. If the cathode is a good ionic conductor, then the electrons can only reach the current collector and the discharge product will occur at the cathode - current collector interface. If the cathode is an electronic conductor, then the electrons can enter the cell and the discharge product will be formed at the cathode electrolyte interface. Hence for the discharge product to be formed in the bulk of the cathode, the cathode must be preferably a mixed conductor.

As shown in Figure 1.7 a, when the cell is connected to the external load, the cell will be discharged. Chemical reactions occur in both electrodes. At the anode (negative electrode), the discharge reaction is the oxidation of the anode material to its cation with the release of an electron

$$M \longrightarrow M^+ + e^-$$

At the cathode (positive electrode), the cathode material is reduced to its anion with the acceptance of an electron.

$$X + e^- \longrightarrow X^-$$

When these two half-cell reactions occur, the overall cell reaction is written as below;

$$M + X \rightarrow M^+ + X^-$$

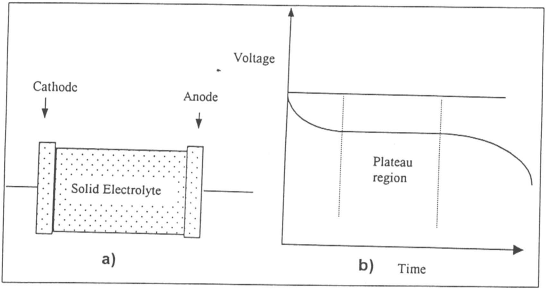

Figure 1.7 **a) Solid State Polymer battery**
b)Typical battery characteristic curve

Electrons will flow from the anode through the external load to the cathode. The electrical circuit is completed by the flow of anions and cations to the cathode and anode respectively. If the cell is secondary, it can be recharged. During charging, the current flow is reversed and oxidation takes place at the positive electrode and reduction at the negative electrode. The reaction at the negative electrode is;

$$M^+ + e^- \rightarrow M$$

At the positive electrode the corresponding reaction is

$$X^- \rightarrow X + e^-$$

And the overall reaction is as follows;

$$X^- + M^+ \rightarrow X + M$$

After charging, a secondary cell reverts to its original chemical state and is ready for further discharge.

The open circuit voltage(OCV) of the battery or cell (i.e the voltage of the cell or battery when no current is drawn from it) is governed by Gibb's free energy given by the relation ,

$$\mathbf{OCV = -\frac{\Delta G}{ZF}} \qquad (1.6)$$

where ΔG is Gibb's free energy, Z is the valency of the mobile species and F is Faraday's constant.

The development of a new generation of lithium batteries based upon the use of an amorphous tin based composite oxide as the negative electrode has met with success, and batteries for commercial use have been developed by Fuji film Cell\tech Co. This has given much impetus for the present work, aimed at exploring new tin–based polymer batteries [42].

1.11 Aims of the Present Work

Solid polymer electrolytes are at present being considered as replacements for conventional low molecular weight liquid - based systems for practical electrochemical devices such as power sources, variable transmission (smart) windows and displays. Nevertheless PEO based polymer electrolytes suffer from low conductivity at ambient *conditions and there is a tremendous research effort aimed at finding* substitutes or alternatives with improved properties, especially to achieve room temperature electrolytic conductivity together with high mechanical integrity. Poly (ethylene oxide) - based complexes are the first generation polymer electrolytes to have been reported and have received the maximum attention, especially after their usefulness was established.

The evolution of the second generation polymer ionics has seen the development of systems based on the combination of modified PEO structures (e.g. comb - shaped polyvinyl ethers containing short ethylene oxide side chains attached to a supporting inactive backbone chain) and impurity additions such as salts of monovalent, divalent and trivalent cations and / or the addition of plasticisers to the common PEO - based complexes. Unfortunately, the mechanical strength of these materials is poor and it is necessary to develop more complex structures in order to optimize both mechanical and electrical properties for practical applications. The formation of crosslinked network structures has been extensively used to produce mechanically stable materials, but some sacrifice of conductivity is inevitable unless the degree of crosslinking is limited.

Systems formed by trapping liquid solutions of lithium salts in aprotic organic solvents into a polymer matrix may be considered as the third generation polymer ionic membranes. Although such polymer electrolytes offer tremendous potential for EV and electronic applications, the inferior nature of Li anode metal / polymer electrolyte membrane interface at present seems to be an obstacle for Li battery applications due to the reaction of organic solvents trapped in the polymer matrix. In this respect, the first generation polymer electrolytes based on PEO systems seem to be a viable solution provided that the electrolytic conductivity of PEO - based polymeric ion conductors show sufficiently high ambient temperature conductivity. In this context, an attempt has been made to explore the possibility of using organotin complexes as the impurities and EC (ethylene carbonate) and PC (propylene carbonate) as plasticisers to achieve the above - mentioned task in PEO and PVC - based polymeric electrolytes for possible device applications in solid state batteries.