CHAPTER 1
CHAPTER - 1
INTRODUCTION

1.1 Polymer electrolytes

At the turn of the last century the consciousness of the need to use energy more efficiently was realised-first by the developed countries and then this realisation spread like a wild fire all over the world. Thus, today the need for efficient production, storage and distribution of energy has become a global concern. Batteries are sources of electric power generation and are storage devices and are used in very many systems. For quite sometime, the aqueous electrolyte based batteries such as lead-acid batteries have been very dominant in the field of batteries. However, these liquid electrolytes have several inherent drawbacks such as the possibility of internal shorting, leaks, and production of combustible reactive products at the electrode/electrolyte interface. These electrolytes add weight and occupy much space and will give rise to low energy density batteries only. Further, these batteries have limited temperature range, low shelf life and cannot be discharged quickly. So search for new materials for electrolytes has been made and this search has yielded very rich dividends which have completely revolutionised the field of batteries which in turn has completely revolutionised many an industrial arena.
This search led to exploring the solid state electrolytes, otherwise called solid ionic materials, based on ceramics, glasses and inorganic crystals. The discovery of Ag$^+$ based solid electrolyte as a potential material for all solid state batteries kindled a lot of interest in solid electrolytes. Soon it was found [1] that they have only low energy density and limited potential window. The realisation that for high energy density batteries, the metallic element giving the mobile ionic species in the electrolyte should be of light weight and highly electropositive lead to intense research on lithium ion based electrolytes and this led to the development of Lithium batteries. In this regard, the invention and commercialisation of Lithium batteries after the pioneering research work of 'Sony' is worth mentioning [2].

The dimensional changes in electrodes during charging and discharging also impose a serious limitation on the selection of solid electrolytes for battery applications. For example in a typical high energy-density battery. Lithium might be used as the negative electrode. As the battery discharges, oxidation of the electrodes gradually strips Lithium metal away from the metal-electrolyte interface. Unless the interface can deform in order that lithium/electrolyte contact is maintained, the battery will cease to function. On this count also, the hard crystalline solid state electrolytes are not suitable for battery applications.
All these indicate that the solid electrolytes must be such that, in addition to having good conductivity, they are flexible and stable and deform/flow to maintain the interfacial contacts in batteries.

In 1973, Peter V.Wright and co-workers [3] at the university of Sheffield in England reported a very significant finding that poly (ethylene oxide and potassium thiocynate (K.SCN)) form a crystalline stoichiometric polymer-salt complex. Two years later, Wright [3] demonstrated that these materials have modest electrical conductivity at temperatures above the room temperature. More extensive measurements on these systems were reported in 1979 by Michel Armand [4] at the laboratories Energetique Electrochimique in Grenoble, France. He showed that the solvent free polymer-salt complexes might be excellent electrolytes for high energy density, all solid state batteries. These discoveries brought about revolutionary changes in the field of battery electrolytes and in the last two decades or so researches have paved way for a large number of these new/improved solid state electrolytes called polymer electrolytes.

The polymer electrolytes differ sharply from the other solid state ionic materials with respect to the mode of charge transport and the value of the ionic conductivity, which is of the order of 100 to 1000 times lower than that for the latter materials. This drawback is compensated by a number of advantageous characteristics of the polymer electrolytes; for example, the
electrolytes can be formed into very thin films of large surface area giving high (100 wdm$^{-3}$) power levels; thin films minimize the resistance of the electrolyte, which is essential for a battery. It does not add weight and does not occupy much space and can therefore enhance the energy stored per unit weight of a battery. Further, from the point of view of electrochemical applications, the flexibility of the polymer electrolytes is important in that volume changes in the cell can be accommodated during cycling with physical degradation of the interfacial contacts which is often observed in crystalline or vitreous solid electrolytes. This means that unlike hard inorganic electrolytes, polymer electrolytes can deform under stress and hence can maintain interfacial contact with electrodes. As with solid inorganic electrolytes, the absence of water or reactive functional groups in the polymer electrolytes makes them compatible with the reactive electrodes used in high energy-density batteries. All these interesting characteristics make the polymer electrolytes extremely promising materials for use as electrolytes in solid state secondary rechargeable batteries.

Generally, in these batteries Lithium alloy is used as the negative electrode, and an ion-insertion compound, such as Titanium disulfide is used as the positive electrode. When the battery is discharged Lithium is oxidized at the Lithium/polymer electrolyte interface, transported as Li
through the film, and inserted. The process is reversed when the cell is recharged.

The performance data of the laboratory cells indicate that if they can be successfully scaled up, commercial solid state cells should be able to store two to five times as much energy per unit weight and volume as a conventional lead-acid car battery. Further, they could also deliver energy at the rates needed for powering an automobile successfully. The thin film polymer electrolyte battery also might replace nickel-cadmium and lead acid rechargeable cells in other applications where weight is critical such as in power sources for portable electrical and electronic equipment and in backup power for computers. So today the polymer electrolytes are much sought after and the study of electrolytes has emerged as the major field of intense research.

Polymer electrolytes may be defined as the solid ionic conductors formed by the dissolution of salts in suitable high molecular weight polymers. So the most fascinating and useful polymer electrolytes synthesised and studied in the recent past are polymer-salt complexes that have significant ionic conductivity. These materials consist of some alkaline metal salts dissolved in a solid polar polymer (usually called as polymer host) such as Poly Ethylene Oxide (PEO), Poly Acrylo Nitrile (PAN), Poly Methyl Metha Acrylate (PMMA), Poly Ethylene Glycol (PEG)
and Poly Vinyl Chloride (PVC). In polymer electrolytes, no low molecular weight solvent is present: these materials act as a solid on the macroscopic scale, however, microscopically the polymer chains can exhibit liquid behaviour i.e., segmental motion, under appropriate conditions; for example the PEO has a glass transition temperature (Tg) of -60°C and melting point (Tm) of 65°C [5]. Below Tg, the polymer chain exhibits no segmental motion: above Tg and below Tm, both the crystalline and amorphous regions are present and there is significant segmental motion of the polymer chains. Above Tm, the crystalline regions are completely absent and there is a relatively high degree of segmental motion. It has now been widely accepted that the majority of ionic conduction takes place in the amorphous regions and not in the crystalline regions. Thus the polymer-salt complexes must be operated under conditions where crystallinity is low and segmental motion is high [6]. It could be noted that not all the polymers are completely crystalline; in fact many polymers are completely amorphous. Polymers exceptionally with very low $T_g$ are suitable candidates for polymer electrolytes and extensive research on them is being carried out.

To act as a successful polymer host, a polymer or the active part of a copolymer should generally have a minimum of three essential characteristics namely: 1) Atoms or groups of atoms with sufficient electro donor power to form coordinate bonds with cations of the salts. 2) Low barriers to bond-
rotation so that segmental motion of the polymer chains can take place readily, and 3) A suitable distance between coordinating centres to facilitate the formation of multiple intra polymer ion bonds.

1.2 Formation of Polymer-Salt Complex

With the recent upsurge of interest in polymer electrolytes, a large number of complexes have been reported between polymers and ionic salts. Strictly, some of these ought to be classified as solutions of salts in polymeric solvents. However, it is to be noted that, the term complex is applied rather loosely when referring to polymer electrolytes. It is generally taken to mean the material formed when the polymer host interacts with the salt to form a new polymer system. The polymer is acting as Nucleophilic ligand (Lewis-base) and the cation as an electrophilic (Lewis acid) in a manner similar to the formation of coordination complexes and solutions with small ligands.

The polymer electrolytes, are complexes of alkali metal salts, denoted by MX, with polymer hosts. Both the precursor salt and the host polymer are solids, so that the complex-forming reaction

\[ mMX + (-RY-)\text{n} \rightarrow (MX)\text{m .(-RY-)}\text{n} \quad (1) \]

where \((-RY-)\) denotes the polymer repeat unit, is a solid/solid reaction. As with most other reactions of this type, the kinetics of (1) are unfavourable, even when the complex is stable. Although other schemes for accelerating
(1) have been employed, including intimate grinding/mechanical mixing [7] by far the most common method has been to dissolve or suspend both the MX salt and the host polymer in a common solvent and then evaporating the solvent to get the polymer electrolyte in bulk or thin film form [8]. Acetonitrile, Tetra Hydro Furan(THF) and methanol have been the solvents most commonly used. If the polymer-salt complex is partly crystalline; both the morphology and the transport properties of the electrolyte material produced may vary with choice of solvent.

Clearly, reaction (1) will be thermodynamically favourable ($\Delta G^o$ negative) only if the Gibbs energy of Solvation of the salt by the polymer is large enough to overcome the lattice energy of the salt. In general, one then expects a close relationship between the ability to form homogeneous complexes and the ability of the monomer to dissolve the salt. It has been shown that for a given polymer host a fairly sharp demarcation line may be established between salts that can and cannot form complexes [9]; the latter simply have too large lattice energies as indicated in Table-1.1. The formation of a complex corresponds to competition between solvation energy and lattice energy of the salt according to the scheme

\[
\left\{ \text{Lattice energy of the salt} \right\} + \left\{ \text{lattice energy of polymer} \right\} + \left\{ \text{Solvation energy} \right\} + \left\{ \text{lattice energy of the complex} \right\}
\]
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* The numbers reported are the lattice energies of the salts (in kJ/mol). “yes” indicates polymer-salt complex formation and “no” indicates the lack of complex formation. The stair-step line indicates the division between complex formation and separate phases.

Striver et.al. [10] have shown the existence of an upper limit of the lattice energy of the salt, close to 850 KJ/mole for lithium derivatives, leading to complex formation. Lower the lattice energy of the salt, the easier the complex formation. In addition to the lattice energy considerations, a number of other criteria that determine the possibility of forming complexes can also be given. These include the following [10, 11-14].
(1) Concentration of polar (basic) groups on the polymer chain - a high concentration for solvating the salt effectively.

(2) Not too high a cohesive energy of the polymer but quite high a flexibility, as indicated by a low glass transition temperature, so that reorientation of the local coordination geometry, to achieve effective solvation, may be achieved.

Most polymer electrolytes are based on oxygen-containing monomers, including ethers in poly (ethylene oxide) and poly (propylene oxide) and polysiloxanes, carbonyl in poly (vinylpyrrolidone) or poly (ethylene succinate), and hydroxyls in poly (vinyl alcohol). Other Lewis base groups have also been employed, including nitrogen in poly (ethylenimine) and sulfur in poly (alkylene sulfides). In general, Lewis base character on the complexing host polymer species is required to coordinate the cation of the salt and thus to provide a favourable Gibbs energy for polymer-salt complex formation.

1.3 Solvation of Lithium anions in aprotic solvents

A salt is dissolved in a solvating polymer matrix through direct interaction of the cation and electron pairs borne by a heteroatom generally O or N, yielding a conducting solid electrolyte. Most suitable choice of
anions for aprotic, low dielectric constant dipolar polymer based polymer are those to the right in the series given below:

\[ F \gg Cl > Br > I \approx SCN > ClO_4 \approx CF_3SO_3 > BF_4 \approx AsF_6 \]

This means that large anions are the most suitable ones for solvation in aprotic polymers. These large anions, with delocalized charge are very weak bases, and possess low ion-dipole stabilization energies. In addition, their lattice energies are relatively low and have little tendency to form tight ion pairs. These anions may be soft (\( I \)) or hard (\( ClO_4^- \)) bases.

1.4 Selection of suitable Lithium Salts

One of the ways of enhancing the conductivity of polymer electrolytes is to modify the polymer hosts or to use different types of polymer hosts. However, there is another way of enhancing the ionic conductivity by changing the nature and/or concentration of the Lithium salts. The influence of the nature and concentration of the incorporated salt on the electrolyte is complex. Essentially polymer electrolytes are formed when a salt, consisting of a polarizing cation and a large anion of delocalized charge to minimize the lattice energy, is dissolved in a polymer. The salt affects the conductivity through crystalline complex formation, intermolecular cross-linking of the polymer chains, and the degree of the
salt dissociation. In particular, the anion has a major influence on phase composition and conductivity.

Many factors are to be considered for the selection of suitable Lithium salts for the polymer electrolytes. The most relevant performance factors are conductivity, thermal stability, electro chemical stability at both the anode and cathode, solubility, and cycling efficiency in rechargeable systems.

Several research groups have been pursuing the development of improved Li salts for well over the last twenty years, but there are surprisingly few, if any, known which adequately meet the above requirements. This is essentially due to the numerous mutually exclusive chemical demands created by imposing the various concurrent performance requirements. For instance, to achieve high conductivity the salt must be highly dissociated. It appears that this property can only be satisfied by compounds with electrostatic interactions i.e. spatially very large anions. Very large anions tend to have very high mass and consequently produce dense and viscous electrolytes. In such dense and viscous electrolytes, ionic migration will be impeded.

It was recognized early that Li salts having large anions are the most suitable for forming polymer electrolytes. When the anions are large as in
the case of complex ions, substantial delocalisation of the negative charge occurs with low lattice energy of the salts. Large anions also reduce ion-ion interactions. Li salts with large anions and low lattice energies such as LiClO$_4$, LiBF$_4$ and LiCF$_3$S0$_3$ provide significantly higher conductivity than small anion salts such as LiCl, which have high lattice energies. Thus the lower the lattice energy, the higher is the electrolyte conductivity [15].

1.4.1 Advantages of the presence of Large Anions in Lithium Salts

1. it gives rise to more charge carriers.
2. Improves the mobility of charge carriers
3. Reduces ion-ion interaction and consequently reduces polymer-electrode interface wherein the formation of passivation film or dendrite growth occurs.
4. Improves ion-solvent interaction for favouring perfect polymer salt complex.

Armand and Elkadi [16] have proposed criteria for solubility, the selection of Li salts based on the electrochemical stability and reducing conductivity and for redox stability measurements for polymer electrolytes in Lithium Batteries and so far LiClO$_4$, LiBF$_4$ and LiCF$_3$S0$_3$ are the only common Li salts that fulfil the electrochemical stability criterion. These Li salts are widely used for complexing with polymers to produce polymer electrolytes of significant conductivity.
1.4.2 Transference Number

As pointed out earlier, one of the important properties of a polymer electrolyte is the ionic conductivity. Another important property of a polymer electrolyte is the lithium ion transference number ($t_{Li^+}$), which ideally for lithium battery applications should be unity. A value of $t_{Li^+}$ lower than 1 would mean that concentration gradients tend to develop at electrode/electrolyte interface leading to limiting currents. Thus, both the parameters ionic conductivity and lithium ion transference number are important in order to select a polymer electrolyte for a practical lithium battery. The maximum power obtainable in a lithium cell can be related to the conductivity of the electrolyte, whereas, the maximum limiting current that can be drawn from the cell and the cycleability of the cell can be related to the $t_{Li^+}$.

1.5 Stability of Polymer electrolytes

The electrochemical stability of an electrolyte is one of the essential parameters for the rechargeable lithium batteries. The instability in the electrolyte is known to bring out irreversible reactions and capacity fading in the battery [17]. The stability commonly expressed as ‘electrochemical stability window’ or simply as electrochemical window or potential window of the polymer electrolyte (in volts as units) should be the same as that of
the electrode potential or higher so that over potentials during recharging are compensated by the higher stability window. For example, for a 4V lithium battery a window of at least 4.5V vs. Li/Li\textsuperscript{+} in the polymer electrolyte is required for compatibility with lithium-ion intercalating electrode materials.

Thermal and mechanical stabilities of a polymer electrolyte during charge/discharge cycles are vital for a safe and durable battery. During charge and discharge, heat will be generated in the battery which increases the surface area of an existing passive layer at the electrode surface [18]. This heat can also melt and degrade the polymer electrolyte within the battery and cause internal short circuits. Increase in temperature due to environmental factors during storage increases the self-discharge reactions in the battery and shortens its life. So the mechanical and thermal stability of the electrolyte are vital for safe and durable batteries.

1.6 Some general techniques for mechanical stability and/or ionic conductivity enhancement

a) Polymer type and conductivity enhancement

The early investigations on polymer electrolytes were mostly on PEO, salt complexes. The PEO is a linear polymer, which has a fairly high degree of crystallinity. As the ion transport occurs primarily in the amorphous phase, the high degree of crystallinity of most of these PEO
complexes is an unwelcome complication and only low ionic conductivity results. A very promising linear Polyether that does not have the problems of crystallinity consists of medium-chain Poly (ethylene glycols), PEG linked by methylene groups. By this mechanism the OC2H4 repeat units of PEO are interrupted by OCH2 units, thus preventing crystallization. However, the branched poly (ethylimine), though closely related to PEO, is an amorphous material and is therefore generally superior to the crystalline linear counterpart PEO as a host for polymer electrolyte formation.

The realization that high conductivity in polymer electrolytes is dependent on local thermal motion of polymer segments led to the exploration of comb polymers as hosts for polymer electrolyte formation. The general concept is to utilize a flexible backbone and attach to these short-chain polar oligomers capable of complexing alkali metal salts. These ideas led to the synthesize and characterisation of polyphosphazene, polysiloxane, and polyitaconate comb polymers containing short-chain polyether side chains [19-24].

From a practical standpoint even the amorphous linear polymers are inconvenient because they tend to flow at somewhat elevated temperatures. This nuisance can be remedied in fundamental studies by proper design of cells for electrical measurements, but it is a serious drawback for potential commercial applications where long-term dimensional stability is required.
Cheradarae and co-workers [25] provided a solution to this problem by the synthesis of network polymers consisting of cross-linked poly (ethylene glycols) [8, 25-27]. If the degree of cross linking is kept low or if flexible cross-links are employed, segmental chain motion is not significantly impaired and salt complexes of these network polymers have conductivities that are superior to those of the crystalline linear polymers [8,28]. Cross-linked siloxane and phosphazene comb polymer electrolytes are found to have good mechanical properties with little sacrifice in conductivity (20cj. It has also been shown that amorphous materials with high conductivity can be prepared by radiation cross-linking poly (ethylene oxide)-salt complexes above their melting point [30].

b) Polymer blends

Multi component polymer systems and polymer-polymer blends have attracted considerable attention recently because of their potential use as practical engineering materials. Miscibility of the components has a profound influence on the macroscopic properties of multi component polymers. Thermodynamic considerations for miscible blends show that both nucleation and crystallization growth rates will be reduced by the presence of a non-crystallisable component. This results from the reduction of chain mobility and the changes in chemical composition during crystallization.
Polymer blends are essentially used to achieve good mechanical properties. In these materials the two polymers involved in the blend exist as a physical mixture of separate phases held together by physical forces and not by chemical bonds. Since the Polymer blend based electrolytes are generally developed to improve the structural integrity of Polymer Electrolytes, the polymer blends usually consist of a polar polymer providing the conductive paths, and a more rigid structural polymer such as polystyrene, PVA, for improving the mechanical stability. However, it must also be mentioned that at times of polymer blending is resorted to in order to improve the ionic conductivity of polymer electrolytes.

c) Plasticizers

Plasticizers are low molecular weight non-volatile substances, mostly liquids, which when added to a polymer, improve its flexibility, processibility and hence its utility. The plasticizer substantially reduces the brittleness of many amorphous polymers because its addition even in small quantities markedly reduces the glass transition temperature ($T_g$) of the polymer. This effect is due to a reduction in cohesive forces of attraction between polymer chains. The plasticizer molecules, being relatively small in size compared to polymer molecules: penetrate into the polymer matrix and establish polar attractive forces reducing the cohesive forces between the polymer chains and increasing the segmental mobility, thereby reducing
the $T_g$ value. The larger the number of chain end segments, the larger will be effective segmental motion and lower will be glass transition temperature ($T_g$). The extent of reduction in $T_g$ with the addition plasticizers depends on factors such as solubility parameters, polarity and density of plasticizers. The decrease in glass transition temperature results in softening of the polymer backbone and increasing its segmental motion. Such segmental motion produces voids or free volume which enables the easy flow of ions through the material. Further the plasticizers have high dielectric constant which in turn dissociates the salt more easily generating increased number of ionic carriers. In addition, the low viscosity of the plasticizers reduces the viscosity of the polymer electrolyte thereby facilitating the ionic mobility in the polymer backbone. To sum up, plasticizers enhance the ionic conductivity in polymer electrolytes with a reduction in the glass transition temperature of the polymer electrolyte. Low molecular weight polythene and polar organic solvents are the two types of commonly used plasticizers. Examples of such plasticizers are: Ethylene Carbonate (EC), Propylene Carbonate (PC), Di Butyl Phthalate (DBP), Di Octyl Phthalate (DOP) and Di Ethyl Phthalate (DEP).

1.7 Major requirements for Device Applications

As mentioned earlier, the development of high energy density batteries with large potential windows and shelf life is intimately linked
with the development of suitable polymer electrolytes. Apart from batteries practical applications of the polymer electrolytes include Electrochromic devices, modified electrodes/sensors, solid-state reference electrode systems, super capacitors, thermoelectric generators, high vacuum electrochemistry and electrochemical switching.

The polymer electrolytes intended for device applications must satisfy the following essential requirements:

1. conductivity between $10^{-4}$ and $10^3$ S/cm in the ambient temperature range of $-40^\circ$C to $70^\circ$C.
2. good dimensional stability.
3. good thermal stability.
4. chemical compatibility with the electrodes/conductors over the whole ambient temperature range; and
5. in addition, for battery application, an ability to afford Li recycling (recharge) at an efficiency of greater than 99% is also essential.

This means that when polymer electrolytes are developed, they are to be characterised to assess their suitability for the end-use in mind and so intense research is going on in synthesising/developing new polymer electrolytes and analysing them/improving the characteristics of the already developed polymer electrolytes for various applications.
1.8 Ion Transport mechanism - Some basic theories for polymer electrolytes

I.Sol Transport theories

Different theories have been proposed for understanding the charge (or ion) transport mechanism in polymer electrolytes. This theoretical development is to provide a set of models using which interpretations of the experimental data can best be made for understanding phase diagram behaviour, conductivity as a function of stoichiometry, temperature and frequency; and for understanding Spectroscopic data and NMR phenomena [31J and their dependence on chemical properties such as polymer chain length, cross linking, and counter ion.

1.8.2 Empirical Equations: VTF and WLF Equations

Historically, the VTF equation was [32] developed to deal with the viscosity properties of super cooled liquids. It was written as an empirical relationship for the viscosity, in the form

$$\eta = C \exp\left[+B/(T-T_0)\right] \quad \text{where } C \propto T^{1/2}$$

When combined with the Stokes-Einstein relationship for diffusion namely

$$D = \frac{kT}{6\pi\eta r} \quad \text{(3)}$$

where $k$ is Boltzmann's constant and $r$, a radius for diffusion, the equation (3) becomes
It is to be noted that $T_0$ is an empirical fitting parameter, and also that the equation (3), which is used to relate diffusion and viscosity, applies to diffusive motion of spheres in continuous media, not necessarily to Coulombically charged carriers in a coordinating inhomogeneous solvent characterized by a wide distribution of relaxation times. In fact, the original notation for $T_0$ was $T_x$, which signified [33] that it is to be identified as the temperature at which relaxation times become infinite. $T_0$ normally is roughly 50K below the glass transition temperature.

**Williams, Landel** and Ferry [33J (WLF) went considerably further; they were concerned not only with viscosity, but also with the relaxation processes which characterize any glass-forming material. They considered a quantity $a_x$, often called the shift factor, which is just the ratio of any mechanical relaxation process at a temperature $T$ to its value at some reference temperature $T_s$. The ratio $b_x$ of electrical relaxation times appears to be identical to $a_x$ for the systems which WLF considered. Then, if for each polymer system a different reference temperature $T_s$ is chosen, and $\Delta T$
is expressed as a function of \((T-T_s)\), the functional form of \(a_r\) turns out to be nearly universal for all polymers. That is, if \(\log a_r\) is plotted against \((T-T_s)\), a universal curve is obtained for all polymers. The curve fits well over roughly 100K, from \(-50K<(T-T_s)<50K\), and since empirically \(T_s-T_g \approx 50K\), the curve fits from near \(T_g\) to about 90K above \(T_g\). Having obtained this remarkable empirical fit, Williams, Lander and Ferry attempted to derive an analytical form for it. To do so, [33] they first adopted the VTF equation in the form (2), and defined

\[
\log a_r = \text{const.} + \log \left[ \frac{\eta(T)}{\eta(T_g)} \right]
\]  

(6)

it follows that, to within an additive constant,

\[
\log a_r = \left[ \frac{-C_1(T-T_s)}{(C_2 + T - T_s)} \right]
\]  

(7)

Equation (7) is often called the WLF relationship. If it is to work (based on VTF), then

\[
C_2 = T_s - T_o
\]  

(8)

where \(T_o\) is the VTF temperature of reference [as in equation (2)] and analogously \(T_s\) may be taken as WLF reference temperature. Empirically, it is found that

\[
C_2 \approx 102K
\]  

(9a)

\[
C_1 \approx 8.9 = \beta/k
\]  

(9b)
Combining equation (9a) with the statement that \( T_s \) is normally about \( T_g + 50K \), and it is expected that \( T_o \equiv T_g - 50K \), which, again, is often found to be quite accurate. Finally, it is possible to rewrite the WLF equation (7) using \( T_g \) rather than \( T_s \); and obtain

\[
\log a_1 = \frac{-17.44(T-T_g)}{51.6 + T - T_g}
\]  

(10)

Often the WLF equation is coupled with the empirical observation known as Walden’s rule [34]

\[
D_\eta = \text{const} / r_i
\]  

(10a)

or equivalently with the Stokes - Einstein relationship (3). If in addition the Nernst-Einstein relationship (5) is used, then the temperature dependence of the conductivity in the WLF form [35] can be written as

\[
\log \left[ \frac{\sigma(T)}{\sigma(T_s)} \right] = \frac{C_1(T-T_s)}{C_2^+(T-T_s)}
\]  

(11)

To a good first approximation, \( \sigma T = \sigma_o e^{R\eta(T-T_s)} \) and equation(11) holds quite well for a series of polymer electrolytes. On the basis of this, Cheradame's group has argued that WLF behaviour is the rule in polymer electrolytes and, therefore, that the fluidity (inverse viscosity) of the polymer chain segments largely determines the conductivity.
The WLF form of equation (11) was, in fact, originally [35] based on the empirical VTF form [36] of \( \sigma T = \sigma_0 e^{-B/(T - T_o)} \), with \( \sigma_0 = AT^{1/2} \) but written for the fluidity (\( \eta^{-1} \)) rather than for \( \sigma T \). The equivalence of equation (11) to the VTF form is obvious and this provides an identification of the parameters as

\[
C_2 = T_s - T_o \tag{11a}
\]

\[
C_1 = B/K(T_s - T_o) \tag{11b}
\]

where the constants \( C_1 \) and \( C_2 \) refer to equation (11) which represents the equation for mechanical shift factor.

The WLF and VTF equations themselves are empirical generalizations, rather than the result of any theoretical approach. However, they describe the thermal dependence of the conductivity of the polymer electrolyte quite well. In an attempt to understand how the conductivity mechanism works, initially quasi-thermodynamic theories, [37-42] have been applied with some success to deal with the transport properties of polymer electrolytes. These theories are based on considerations involving the critical role of the glass transition temperature \( T_g \) and of the so-called "equilibrium" glass transition temperature \( T_o \). Above \( T_g \), the polymeric material becomes macroscopically rubbery rather than glassy, [37-42] mechanistically; this is understood by considering that a local environment of any given polymer chain becomes liquid-like above the glass transition
temperature. Therefore, it is only the thermal energy in excess of the glass transition temperature that provides actual mobility of the local polymer chain segments. In this sense, it is not surprising that the Arrhenius behaviour, involving inverse temperature, is replaced by the VTF behaviour involving the inverse of \((T - T_0)\) for polymer electrolytes. The concept of equilibrium glass transition temperature \(T_0\) is based on the kinetic feature of \(T_g\) depending on the rate of cooling, and it can be taken as the temperature at which all "free volume" vanishes or at which all polymer segmental motion disappears or at which the excess configurational entropy treats \(T_0\) in terms of volume is called the free volume theory \(f\, 37,38\).

1.8.3 Free-volume theory

The WLF arguments, as discussed earlier, stress two important results: first that WLF behaviour is found to be universal for many disordered systems, including glasses and pure polymers (not necessarily polymer complexes); it holds independently of the relaxation time distribution. Second, the WLF behaviour is based only on empirical observations, including viscosity measurements and the VTF form of equation (2). While it is consistent with free-volume theory, it does not require free-volume (or any other) theory.
In practice, the application of free-volume ideas to polymer electrolytes consists largely of using the WLF equation (7) for the physical properties (viscosity, storage modulus) and the VTF equation (2) for conductivity. However, as discussed earlier, the WLF and VTF equations are empirical and do not depend on free-volume theory for their derivation. Thus even if WLF and VTF equations are very accurate for a given set of measurements, there is no guarantee that the system's behaviour is governed by free-volume behaviour. Since, however, the free-volume concept is easily understood, elegant in its simplicity, and widely discussed as a theoretical framework for understanding conductivity in polymer electrolytes, it is briefly discussed below.

A clear formulation for free-volume theory as given [43] by Cohen and Turnbull in 1959; originally deals with the basic elements of the model, and has served as the basis for more elaborate treatments. They consider a liquid of hard spheres, and use straightforward statistical mechanics for calculating the most probable distribution) to derive a probability distribution for void volumes of various sizes. They assume, following the Stokes-Einstein relationship, that viscosity is proportional to inverse diffusion coefficient ($\eta \propto D$), and then study the viscosity. Batschinsky [44] had long ago suggested that viscosity of many liquids is nearly independent of temperature at constant volume and therefore the
fluidity ($\dot{\gamma}$ = \eta^{-1}, the inverse viscosity) increases linearly with free volume, and Cohen and Turnbull developed this relationship in their model.

The basic assumption of the Cohen and Turnbull treatment is that diffusion is not activated but rather occurs as a result of the redistribution of free volume within the liquid. The molecules are assumed confined within their cages, except when a hole is opened which is large enough for the molecule to jump into; the contribution a molecule with thermal velocity $u$ makes to the diffusion coefficient is then

$$D(v) = g a(v) u$$  \hspace{1cm} (12)

with $g$, a geometric factor and $a(v)$ a cage diameter. But $D(v)$ has no contribution unless $v$ (the free volume) exceeds a critical free volume $v^*$, so that

$$D = \int D(v) p(v) dv$$  \hspace{1cm} (13)

with $p(v)$ the probability of observing the free volume $v$. Maximising the number of ways of distributing the free volume (that is, maximising the entropy) subject to conservation of total free volume and of number of molecules leads to

$$p(v) = \frac{\gamma}{v_f} \exp(-\gamma v/v_f)$$  \hspace{1cm} (14)

where $\gamma$ is a Lagrange parameter. Using equation (14) in equation (13) finally gives, for the diffusion coefficient,

$$D = g a^* u \exp(-\gamma v^*/v_f)$$  \hspace{1cm} (15)

where $a^*$ is roughly the molecular diameter.
The modelling ideas underlying equation (12) imply that if solute molecules (or in the case of solid state ionics, ions or ion-pairs) are far smaller than solvent (Polymer) species, their diffusion rate will be fixed by, and be the same as, the solvent, since only when solvent cage holes appear can solute move.

The final step in using equation (15) is to expand \( v_f \) rather around the temperature 'at which the free volume disappears'. Thus they write

\[
v_f = \alpha \bar{v}_M(T-T_o)
\]

(16)

with \( \bar{v}_M \) signifying the mean molecular volume over the range \((T-T_o)\) and \( \alpha \), as before the difference in thermal expansion coefficients between liquid and glass over the same range. They also include pressure dependence; using \( \Delta P \) to indicate pressure increment, \( \beta \) the mean compressibility, and \( v_p \) the mean molecular volume over the interval \((0, \Delta P)\), they finally write the free volume as

\[
v_f = \alpha \bar{v}_M(T-T_o) - \beta v_p \Delta P
\]

(17)

and ignoring the pressure dependence and instead of expanding \( v_f \) about \( T_o \) (the temperature at which the free volume goes to zero), expanding it about the glass transition \( T_g \), the equation (16) becomes

\[
v_f = v_b [0.025 + \alpha(T-T_g)]
\]

(18)

where \( v_b \) is the molar volume at \( T_g \) and the 0.025 factor comes from the WLF treatment. If the two expansions (18) and (16) are to agree, then
\[ T_o = T_g - 0.025/\alpha \]  \hfill (19)

Finally, using the value of \( \alpha \) given by WLF relation, \( T_o \) is given by

\[ T_o \approx T_g - 50K \]  \hfill (20)

This approximate relationship between the equilibrium glass transition temperature \( T_o \) at which the free volume disappears, and the thermodynamic glass transition temperature \( T_g \) at which endotherms are seen is often quoted in the literature as an empirical result from WLF equation/treatment. \( T_o \) deduced from measured mechanical properties generally lies quite close to 50K below \( T_g \) is another demonstration of the power of the WLF treatment. It must be remembered that discontinuities in \( \alpha(T) \) and in \( C_p(T) \) are rate-and history-dependent rather than truly thermodynamic.

When the equation (16) is substituted into the equation (15), the free-volume expression for the diffusion coefficient becomes

\[ D = g\alpha^* u \exp[-\gamma v^*/\alpha \bar{v}_M(T-T_o)] \]  \hfill (21)

With the further arguments (from equipartition) that \( u \sim T^{1/2} \), and the use of Nernst-Einstein result (5), the free-volume theory leads to the equation

\[ \sigma = \sigma_o \exp[-B/(T-T_o)] \]  \hfill (22)
The quasi-thermodynamic theoretical constructions based on VTF and WLF equations or upon the free-volume offer substantial advantages: they describe temperature dependence of several of the transport properties, including conductivity, viscosity, and diffusivity, quite well over a fairly broad temperature range and they provide easy interpretations of several of the relevant theoretical parameters including the equilibrium glass transition temperature and the critical free volume $v^*$ for segmental motion.

To conclude this chapter, it can be said that the prospect of major uses for polymer electrolytes has stimulated much basic research on polymer electrolytes. Some of the areas under study are the factors that govern the formation of polymer-salt complexes, the structure of these complexes and ionic transport mechanism. With the basic and applied research complementing each other, the field of polymer electrolytes has advanced by leaps and bounds within the last two decades for diverse applications and because of its pre-eminence, the fields of polymer electrolytes continues to be a fertile and major intense field of research. Eventhough some of the polymer electrolyte systems based on PEO, PAN, PMMA, PEG, PVdF and other polymers have exhibited fairly improved room
temperature conductivity, researches are continuing to improve the ionic conductivity of polymer electrolytes by various ways including using new types of polymers and polymer blends.

In this direction an attempt has been made in the present work to develop a few polymer electrolytes based on the low cost and easily available Poly Vinyl Chloride (PVC) polymers, characterise them with a view to assess their suitability as electrolytes for Lithium battery applications and understand the structure of these electrolytes and the ion transport mechanism in them.
References


8. A particularly elegant and extensive series of investigations has been report by H. Cheradane and Co-workers. They employ network based on short-chain PEO and PPO, cross-linked with various agent, especially isocyantes. The materials are prepared by dissolving the salt in the poly ether sometimes with added, solvent, cross-linking the material with isocyanate in a reaction catalysed by Sn^{4+}, and drying the resulting membrane.


