CHAPTER I

INTRODUCTION

1.1 Introduction

Energy in its different forms is the basic input for life and is equally essential for the improvement of the quality of life. Since our conventional sources of energy or the fossil fuels are running short, it is extremely important to work harder for the development, improvement and upgradation of renewable sources of energy together with protection, conservation and judicious use and management of existing conventional sources.

Within the framework of finding and using the alternative energy sources, one often faces the problem of energy storage. One of the most convenient techniques is electrochemical storage. The work presented in this thesis is ultimately conducted in the context of chemical storage in the form of Li-ion polymer battery. The main advantage of this battery is that it combines a high energy density, a high cell voltage and recharge ability. This means that the energy is stored effectively that the battery can be used in many applications and that it can be used over and over again. Besides, these batteries are comparatively reliable and safe [1, 2].

The battery generally comprises (Fig.1.1) of an anode consisting of lithium intercalated graphite with a low electrochemical potential and a transition metal oxide cathode with a high potential and both can reversibly intercalate and release lithium ions [3]. Between the anode and cathode there is
a polymer electrolyte which can act as a separator. Under discharge, the electrons travel from the anode to the cathode. At the same time, Li\(^+\) ions are extracted from the anode; pass through the polymer electrolyte and into the cathode. The task for the electrolyte is merely to facilitate this Li ion transport.

**Fig.1.1.** A lithium polymer battery

Polymer electrolytes have attracted considerable attention for batteries in recent years. The path breaking studies of Wright and Armand [4, 5] on polymer electrolytes in the 1970s have opened an innovative area of materials research with potential applications in the power sources industry. The biggest advantage of polymer electrolytes is their usage in rechargeable lithium batteries in place of conventional liquid electrolytes. Due to their high molecular weight, they exhibit macroscopic properties that behave like a true solid at an atomic level. Local relaxation provides liquid like degrees of freedom that are not significantly different from those of conventional liquid. Unlike the conventional solid electrolytes, polymer electrolytes can be prepared into flexible thin films of required size and shape. The flexibility of polymer
electrolytes accommodates the volume changes of electrodes, which typically occur during the charge-discharge cycles of the electrochemical device.

A significant barrier in the development of solid polymer electrolytes is low ionic conductivity of these electrolytes due to the low segmental mobility of polymer chain. In this regard, most research works have been directed in extemporizing new polymer electrolytes that exhibit high ionic conductivity at ambient temperature via various approaches, such as blending [6], copolymers [7], comb-branched polymers [8] and cross-linked polymers [9]. All these enhancements have been achieved either by reducing the crystallinity of polymers or by lowering the glass transition temperature. Much research effort has been applied to find host polymer, dopant salt and additives for fast ion transport.

1.2 Polymers

Polymers are the chief products of modern chemical industry. They form the backbone of the modern civilization because of their extraordinary range of properties. In almost all walks of life, starting from household utensils, clothes, furniture etc. to automobiles to space aircrafts, polymer is extensively used. Some of the things are provided by nature as such while most of the others are fabricated from natural resources by the people of different skills. The field of synthetic polymers or plastics is currently one of the fastest growing material industries. The interest in engineering polymers is driven by their manufacturability, recyclability, mechanical properties and lower cost as compared to many alloys and ceramics.
A polymer (Fig.1.2) is a material whose molecules contain large number of atoms linked by covalent bonds, which makes polymers macromolecules. Polymers consist mainly of identical or similar units joined together. The unit forming the repetitive pattern is called a "mer" or "monomer".

![Fig.1.2 Representation of polymer chain](image)

- is a Monomer unit and (---) represents a covalent bond

Usually the differences in polymer properties result from how the atoms and chains are linked together in space. Polymers that have a 1-D structure will have different properties than those that have either a 2-D or 3-D structure. Several key parameters determine the properties of a polymer and they are given below.

- Chemical Composition
- Molecular Weight Distribution
- Topology
- Isomerism
- Morphology

### 1.3 Characteristics of Polymers

- Low Density
- Low coefficient of friction
- Good corrosion resistance
- Good mouldability
- Excellent surface finish can be obtained
- Can be produced with close dimensional tolerances
- Economical
- Poor tensile strength
- Low mechanical properties
- Poor temperature resistance
- Can be produced transparent or in different colours

1.4 Classification of Polymers

Polymers are classified based upon

- Sources
- Structure
- Molecular Forces

1.4.1 Classification of Polymers based upon Sources

Depending on the source, the polymers are classified into two classes:

- Natural Polymers
- Synthetic Polymers

**Natural Polymers:** The polymers obtained from nature i.e. from plants and animals are called Natural Polymers. These include starch, cellulose, proteins, nucleic acids and natural rubbers.

**Synthetic Polymers:** The polymers synthesized from low molecular weight compounds are called Synthetic Polymers. Typical examples are polythene, PVC, Nylon and Terylene.
1.4.2 Classification based upon Structure

On the basis of structure, polymers are divided into three types:

- Linear Polymers
- Branched Chain Polymers
- Three-dimensional Network Polymers

**Linear Polymers:** In these polymers, the monomers are joined together to form long straight chains of polymer molecules. Some important examples of linear polymers are high density polythene, nylon, polyesters etc.

**Branched Chain Polymers:** In these polymers, the monomer units not only combine to produce the linear chain but also form branches along the main chain. Some examples are low density polythene, glycogen etc.

**Three-dimensional Network Polymers:** In these polymers, the initially formed linear polymer chains are joined to form three dimensional network structures.

1.4.3 Classification based on Molecular Forces

- Elastomer
- Fibers
- Thermoplasts
- Thermosets

**Elastomer:** Polymer chain is held up by weakest attractive forces. They are amorphous polymers having high degree of elasticity.

**Example:** Synthetic rubber.
Fibers: These are the polymers which have quite strong inter particle forces such as H - bond. They have high tensile strength and high modulus.

Example: Nylon 6, 6

Thermoplasts:

- Thermoplastic polymers soften when heated and harden when cooled. Simultaneous application of heat and pressure is required to fabricate these materials.
- On the molecular level, when the temperature is raised, secondary bonding forces are diminished so that the relative movement of adjacent chains is facilitated when a stress is applied.
- Most Linear polymers and those having branched structures with flexible chains are thermoplastics.
- Thermoplastics are very soft and ductile.

Example: The commercial available thermoplasts are Polyvinyl Chloride (PVC), Polymethyl methacrylate (PMMA) and Polystyrene.

Thermosets:

- Thermosetting polymers become soft during their first heating and become permanently hard when cooled. They do not soften during subsequent heating. Hence, they cannot be remolded/reshaped by subsequent heating.
- In thermosets, during the initial heating, covalent cross-links are formed between adjacent molecular chains. These bonds anchor the chains together to resist the vibration and rotational chain motions at high
temperatures. Cross linking is usually extensive, in that 10 to 15% of the polymer units are cross linked. Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation.

- Thermoset polymers are harder, stronger and more brittle than thermoplastics and have better dimensional stability.
- They are more usable in processes requiring high temperatures.
- Thermosets which cannot be recycled and do not melt, are usable at higher temperatures than thermoplastics, and are more chemically inert.
- Most of the cross linked and network polymers which include Vulcanized rubbers, Epoxies, Phenolic are thermosetting.

### 1.5 Polymer morphology

Molecular shape and the way in which molecules are arranged in a solid are important factors in determining the property of polymers. The behaviour of polymers can better be understood in terms of their morphology. Depending on their chemical structure and processing conditions, they may have amorphous and/or crystalline morphology. The crystalline morphology is observed mostly in polymers with linear and regular structures. Irregularities or branching in the molecular chains cause an amorphous structure. The morphology of amorphous polymers consists of a random array of polymer chains, the interactions of which determine the properties [10]. The fluctuation of properties is minimal because of the uneven packing of the chains. On the other hand, semi crystalline polymers may have very complex textures. They are two-phase systems in which the crystallites disperse in the amorphous
matrix. The fraction of the polymer that is fully crystalline is known as the crystallinity (or the degree of crystallinity). The crystallites are nucleated from the melt at a definite range of temperature and they grow. The aggregates of crystallites form spherulites, which show birefringence and can be observed by optical microscopy under polarized light.

1.6 Transitions in Polymers

Amorphous polymers exhibit two distinctly different types of mechanical behaviour. Some, like polymethyl methacrylate and polystyrene are hard, rigid, glassy plastics at room temperature while others like polybutadiene and polyethyl acrylate are soft, flexible, rubbery materials at room temperature.

There is a temperature, or range of temperatures, below which an amorphous polymer is in a glassy state and above which it is rubbery. This temperature is called the glass transition temperature $T_g$, and it characterizes the amorphous phase. It is especially useful since all polymers are amorphous to some degree, they all have a $T_g$.

1.6.1 Molecular Motions in Amorphous Polymers

The molecular motions occurring inside an amorphous polymer influence the glass transition temperature. The important motions are:

1. Translation motion of entire molecules (permits flow)
2. Cooperative wriggling and jumping of segments of molecules (permits flexing and uncoiling leading to elasticity)
3. Motions of a few atoms along the main chain or side groups on the main chain
4. Vibrations of atoms about equilibrium position

The glass transition temperature is the temperature at which there is only enough energy for motions (3) and (4) to occur. Below the glass transition temperature processes (1) and (2) are frozen out. This makes the material "glassy" below $T_g$ and "rubbery" above $T_g$.

1.6.2 Crystalline melting temperature

In general, the crystalline polymer does not possess any glass transition temperature. On the other hand at a sufficiently low temperature, molecular mobility (associated with segmental mobility) sets in almost abruptly, making the long range order simultaneously. The polymer now passes from the crystalline state directly to the liquid state. The temperature at which this transition takes place is called the melting temperature.

Several structural parameters affect the crystalline melting temperature of a crystalline polymer.

- The higher the molecular weight of the polymer, the higher the melting temperature.
- Regularity in the chain backbone also leads to higher melting temperature.

1.7 Polymer electrolyte

Polymer electrolytes consist of salts dissolved in polymers (for example, polyethylene oxide, PEO) and represent a unique class of solid coordination compounds. Polymers are generally electrical insulators and their properties
(thermal, electrical and mechanical) can be modified by complexation with a salt and dispersal of a second phase. Polymer electrolytes are usually formed from thermoplastic elastomers. Because of the rigid structure, they can also serve as the separator.

Since polymer electrolytes must function as both separator and electrolyte, a number of properties are critical for their successful use in lithium or lithium ion batteries. From an electrochemical point of view, the polymer electrolytes must satisfy the following requirements.

- High ionic conductivity
- High cationic transference number
- Good dimensional stability
- High electrochemical stability and chemical compatibility with both Li anode and cathode material and
- Good mechanical stability.

Various approaches are developed to meet the above requirements.

- Blending of two polymers [6, 11]
- Adding plasticizers to polymer electrolytes [12, 13]
- Adding fillers to make composite polymer electrolytes [14, 15]
- Cross-linking two polymers [7, 9]
- New polymer synthesis [16, 17]
1.8 Formation of salt-polymer complexes

The dominant class of polymer electrolytes is formed using neutral polar polymer complexed with uni-univalent metal salt MX, where M is normally an alkali metal and X fairly a soft anion. To form these, we write schematically

\[
\begin{align*}
\text{AB} - B_{\text{y}} + MX & \rightarrow \text{AB} - B_{\text{y}} \cdot MX \\
\end{align*}
\]

where AB denotes the polymeric sub unit. In all cases the sub unit contains the Lewis base. Therefore one of the dominant energetic interactions involves the salvation or complexation of the cation \( M^+ \) by the basic component of the polymer.

Three parameters are important for the control of salt/neutral molecular interactions

- Electron pair donicity
- Acceptor number
- Entropy term

Donor number measures the ability of the solvent to donate electrons to solvate the cation and considered as a Lewis acid, on the other hand the acceptor number quantifies the possibility for anion [base] salvation.

The only salt forming complexes are those with a large delocalized anion requiring little salvation. The criterion is the same but even more stringent than for aprotic solvents like propylene carbonate (PC), since the polarity of these molecules implies an appreciable acceptor number.
The entropy term depends on the optimal spatial disposition of the solvating units. The formation of the complex corresponds to competition between salvation energy and lattice energy of the salt, according to the scheme

\[
\text{Lattice energy of the salt} + \text{Lattice energy of the polymer} = \text{Salvation energy} + \text{Lattice energy of the complexes}
\]

Shriver et. al [18] have shown the existence of an upper limit of the lattice energy of the salt, close to 850 kJmole\(^{-1}\) for lithium derivatives leading to complex formation. In a nutshell the criteria for the formation of salt-polymer complexes may be summarized as follows [18, 19].

- Salt dissolves in a solvent only if the associated energy and entropy changes produce an overall reduction in free energy of the system
- In polymer there exists polar groups and it can be expected that polymers behave as solvents and dissolve salts to form stable ion-polymer complexes
- It is possible when the interaction between the ionic species and the coordinating groups on the polymer chain compensate for the loss of salt lattice energy

### 1.9 Characteristics of the components of polymer electrolyte

The requirements of the polymer electrolyte’s components to obtain an efficient electrolyte are given below
1.9.1 Polymer
A successful polymer host has the following characteristics:

- Atoms or group of atoms with sufficient electron 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
- A suitable distance of separation between coordinating centers for enabling the formation of multiple intra polymer ion bonds.

1.9.2 Salt

Last four decades, many alkali salts consisting Li⁺, Na⁺, K⁺, Ag⁺, Mg⁺, NH₄⁺ cations were mixed with the polymers (PEO), (PPO) etc. in the preparation of polymer electrolytes.

The following features are required for lithium salts as electrolytes

- Solubility in a given solvent (at least up to conductivity maximum)
- High ionic mobility (conductivity)
- Electrochemical stability in wide potential window (at least 0–4V vs. Li)
- Chemical stability against all other cell elements (solvent, electrodic materials, charge collectors etc.)
- Thermal stability (up to 70 °C)
- High transference number and
- Low association rate at high concentrations.

The small ionic radius of the Lithium ion can provide high volumetric capacity and the electrochemical potential for the Lithium system is 3.01V for
Li/Li$^+$ ion. Thus Lithium ion conducting polymer electrolyte has been widely studied due to their potential use in rechargeable high energy density batteries [20, 21].

1.9.3 Plasticizer

- Plasticizers are relatively low molecular weight, nonvolatile (mostly liquids) materials which have a capacity to alter the physical properties of a polymer to render it more useful as film forming agents.
- The function of plasticizer is to make the polymer more pliable and soft and thereby enhancing flexibility and plasticity to the films.
- Plasticizers are added in order to reduce the glass transition temperature ($T_g$).
- Plasticizers interpose between every individual strand of polymers and thereby causing breakdown of polymer-polymer interactions.
- The tertiary structure of the polymer is modified into more porous, flexible and with less cohesive structure.

The plasticizer should have the following characteristics

- It should have a high dielectric constant ($\varepsilon$), so that it can dissolve salts to sufficient concentration.
- It should be fluid (low viscosity), so that facile ion transport can occur.
- It should remain inert to all cell components, especially the charged surfaces of the cathode and the anode, during cell operation.
- It should remain liquid in a wide temperature range. In other words, its melting point ($T_m$) should be low and its boiling point ($T_b$) high.
• It should also be safe (high flash point $T_f$), nontoxic and economical.

1.9.4 Solvent

A solvent is a liquid or gas that dissolves a solid, liquid or gaseous solute, resulting in a solution. It should be capable of dissolving the polymer, salt and should be miscible with the plasticizer. Commonly used solvents are organic solvents. They usually have a low boiling point and evaporate easily or can be removed by distillation leaving the dissolved substance behind.

1.9.5 Ceramics

Ceramics are crystalline inorganic materials that are generally stable upto high temperature and remain chemically inert [22]. The dispersion of ceramic filler in polymer electrolytes was first suggested by Western and Steele to improve the mechanical strength of the polymer electrolyte [14].

1.10 Classification of polymer electrolyte systems

Since the introduction of polymer electrolyte in the 1970’s, many types of polymer have been extensively investigated. The polymer electrolyte systems could be classified into three categories, namely,

- Poly electrolytes
- Solvent swollen polymer electrolytes
- Solvent free polymer electrolytes

1.10.1 Polyelectrolytes

Polyelectrolytes are polymers which have their own ion-generating groups chemically bound to the macromolecular chain and the presence of a counter-ion maintains the electro neutrality of the salt. These classes of
materials are either positively or negatively charged ions covalently attached to the polymer backbone and therefore only the unattached counter ions have long range mobility. The conductivity of the polymers is very low ($10^{-10}$-$10^{-15}$ Scm$^{-1}$) in dry conditions but hydrated polyelectrolytes achieve high conductivity in the presence of high dielectric constant solvent (e.g. water). In hydrated polyelectrolytes, ionic transport takes place through the aqueous medium in which the polymer is dispersed. Slade et. al [23] reported high ambient temperature conductivity of $10^{-2}$ Scm$^{-1}$ in hydrated Nafion.

### 1.10.2 Solvent swollen polymer electrolytes

In solvent swollen polymers, solvents (aqueous /non- aqueous) swell the basic polymer host [like poly(vinyl alcohol) or poly (vinyl pyrrolidone)]. The dopant ionic solutes like H$_3$PO$_4$ are accommodated in the swollen lattice which permits the ionic motion in solvent rich swollen region of the polymer host. These materials are, in general, unstable and their conductivity depends on the concentration of the solvent in the swollen region. The properties of such polymers depend on the pre-treatment, structure of the sample, temperature, relative humidity etc.

**Examples:** Nafion, complexes of poly (vinyl alcohol) (PVA) with H$_3$PO$_4$ [24] poly(silamine) with H$_3$PO$_4$ [25], PEO with NH$_4$HSO$_4$ [26].

### 1.10.3 Solvent free polymer electrolytes

The polymer - salt complexes are formed by complexes between salts of alkali metals and polymer containing solvating heteroatoms such as O, N, S etc. The most common examples are complexation between poly (ethylene
oxide)(PEO) and alkali metal salts. The polymer salt complexes are further divided into a) solid polymer electrolytes b) blend polymer electrolytes c) Gel polymer electrolytes d) Composite polymer electrolytes.

**a) Solid polymer electrolytes**

In solid polymer electrolytes, the polymer host itself is used as a solid solvent along with lithium salt and does not contain any organic liquids. The polymer serves as solid solvent due to their high molecular weight. They exhibit macroscopic properties that behave like a true solid at an atomic level. Local relaxation provides liquid like degrees of freedom that are not significantly different from those of conventional liquid. Polymer electrolytes have emerged as potential ionic materials for application in different electrochemical devices due to some special properties like good electrode–electrolyte contact, ease of preparation in different forms, good mechanical and adhesive properties [27, 28]. They can be formed into thin films of large surface area giving high power. The flexibility of the films allows space-efficient batteries to be constructed [29].

**b) Blend polymer electrolytes**

Blend is a mixture of two or more polymers. Blending of two polymers was initiated from the idea of Rhoo et.al [30] demonstrating the advantage of the blend over the individual polymer which lacks the obtained desirable properties from the blend. Mixing of polymers is a well established strategy for the purpose of obtaining materials with combined superior properties or avoiding the need to synthesize novel structures constitutes an attractive
research area. As many emerging applications are of limited volume and require specific property profiles not suitable for broad application utility, polymer blend technology is often the only viable method to deliver the desired material. These polymer blends have some unique properties that are different from the basic polymers from which these have been produced.

To improve the processing behaviour for end use, one polymer blending with another polymer is a common practice. The exploitation of certain unique set of properties of individual polymer for the benefit of the overall properties of a multi component system forms the basis of polymer blending. Hence blending of polymers has resulted in the development of polymeric materials with desirable combination of properties.

Polymer blends are developed in such a way that they remain structurally stable during manufacturing, cell assembling, storage and usage as well as to prevent leakage from the cell container or without the cell. Many blend electrolytes have been reported based on PEO-PAN [31], P (VdF-HFP)-PVAc [32], PVC-PMMA [33] and so on.

**c) Gel polymer electrolytes**

Gel electrolyte is a two-component system, viz., a polymer matrix swollen with a liquid electrolyte. It combines the positive attributes of both the liquid (high ionic conductivity) and solid polymer electrolytes (elimination of leakage problems). The ion conduction in these electrolytes takes place through the liquid electrolytes where the host polymer mostly provides the structural support. Addition of plasticizer increases the chain flexibility, reduces
crystallinity, decreases the glass transition temperature and hence increases the conductivity. And these electrolyte systems have a relatively high ionic conductivity (up to $10^{-3}$ to $10^{-4}$ S/cm) at room temperature. However, an improvement in conductivity is adversely accompanied by degradation in solid-state configuration and a loss of compatibility with the lithium electrode [22], particularly when the fraction of plasticizers is too high.

d) Composite polymer electrolytes

Dispersing ceramic fillers (solid plasticizers) such as Al$_2$O$_3$, TiO$_2$, SiO$_2$, BaTiO$_3$ in the polymer matrix, produces composite polymer electrolytes. This approach was first introduced by Weston and Steele [14]. Ceramic filler is used to reduce the glass transition temperature and crystallinity of the polymer and thus allows the amorphous polymer to maintain the liquid-like characteristic at the microscopic level. Ceramic fillers that are frequently used have particle sizes in the range of about several ten nanometers up to several micrometers. Smaller the particle sizes of the oxides, larger the conductivity enhancement [34]. The inorganic filler also acts as a support matrix for the polymer, so that even at high temperature, the composite remains solid. However, at the microscopic level, it maintains a liquid-like structure, which is important for sufficient conductivity. The nano sized BaTiO$_3$ incorporated PEO composite electrolyte exhibits ionic conductivity of the order of $10^{-3}$ Scm$^{-1}$ and good electrochemical stability (4.0V).
1.11 Ion transport in polymer electrolytes

Ionic conductivity $\sigma$, is expressed as

$$\sigma = n e \mu$$

where $n$ is the number of mobile ions, $e$ is the electronic charge and $\mu$ is the ionic mobility. In solvent-free polymer electrolytes, the charged carriers are in the form of single cations, single anions, or the ion clusters. The conductivity of charge carriers present in an electrolyte generally depends upon the concentration of salt containing the mobile species as well as on the extent up to which the salt is dissociated. The mobility of the charge carriers is determined by their environment and it is a function of the interaction with polymer and other ions, the nature of the charge carrier, the flexibility of polymer segment, etc. [35, 36]. Ionic conduction is achieved by the movements of ions associated with polymer segment [37]. Berthier et al [38] established that significant ionic mobility in polymer electrolytes is a property of an amorphous phase above the glass transition temperature.

It is believed that the motion of ions is associated with motion of polymer segment and the cations could be transferred via the polymer segmental motions by making and breaking the coordination bonds between cations and polymers under electrical field [37]. Ionic conduction in polymer electrolytes can take place in two ways viz., intrachain and interchain hoping as shown in Fig.1.3.
Generally, both cation and anion are in mobile state in polymer electrolytes. The movement of the mobile ion depends upon the ionic radii of the counter ion. In most polymer electrolytes, the anions are large \[39\] and delocalized, being the dominant mobile charge carriers, while the cations are essentially coordinated to the host \[40\]. Above \(T_g\), the segments of the polymer are in rapid motion. This indicates the importance of polymer segmental motion in ion transport.
Ionic conduction is again the function of the transference number. The transference number of ion ‘i’ in an electrolyte is defined as

\[ t_i = \frac{\sigma_i}{\sigma} \]

where \( \sigma_i \) is the conduction due to the ion i, and that of the electrolyte including any contribution from electronic conductivity, \( \sigma_e \). Thus \( \sigma \) is defined as

\[ \sigma = \sigma_i + \sigma_e + \sum_j \sigma_j (j \neq i) \]

where the last term is the sum of the conductivity due to all mobile ions. Because an ideal electrolyte passes no electronic current, \( \sigma_e = 0 \). Mobile ions other than working ion i encounter blocking ions resulting in an ion pile-up at the electrode/electrolyte interface lowering the voltage across the electrolyte of the cell. Ideally, therefore, the working species should alone contribute to conductivity, leaving \( \sum_j \sigma_j = 0 \). Thus \( t_i = \sigma_i / \sigma \) for ideal electrolytes. The influence of ion-ion and ion-polymer as well as ion – plasticizer interactions on the ion transport in solid electrolytes has been an important subject of study in recent years [41, 42].

1.12 Ionic transport and its temperature dependence

(Empirical Relationships of the Conductivity Temperature Dependence)

The ionic conductivity in polymer electrolytes is generally thermally activated and it increases with temperature. The empirical relationships, Arrhenius law equation (1), Vogel-Tamman-Fulcher (VTF) equation (2) have been developed to fit extensive ionic conductivity data of various polymer electrolytes at different temperatures,
\[ \sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right) \] \hspace{1cm} (1)
\[ \sigma = AT^{-\frac{1}{2}} \exp \left( -\frac{B}{T-T_0} \right) \] \hspace{1cm} (2)

where \( A \) is a constant that is proportional to the number of carrier ions; \( B \) denotes the pseudo-activation energy associated with the motion of the polymer; \( k \) is the Boltzmann constant; \( E_a \) is the activation energy; \( T_0 \) is a reference temperature (normally associated with the ideal \( T_g \) at which the free volume is zero, or with the temperature at which the configuration entropy becomes zero) [43].

Arrhenius law equation as shown in equation (1) is a basic relationship, which describes the linear relationship of the ionic conductivity against the reciprocal absolute temperature. However, nonlinear behaviour of some polymer electrolytes have been reported which can be explained by VTF mechanism. It describes the transport properties in a viscous matrix and is explained by free volume theory. Conductivity on polymer chain mobility can be generally associated with the free volume of the polymer. A small amount of unfilled volume is associated with the end of a polymer chain. This volume is called the free volume. As temperature increases, the free volume increases. Larger the free volume, greater is the ability of the chain to rotate, hence the ion transport becomes more rapid. For a given mass of polymer, the amount of free volume will depend on the number of chain ends, hence the number of chains and hence the degree of polymerization. The temperature dependence of ionic conductivity of solid polymer electrolytes has been analyzed by Ratner in detail [19].
In general, however the conductivity vs. temperature behaviour of the salt polymer complexes may be described by any of the following pattern

- VTF behaviour throughout the temperature range available
- Arrhenius behaviour at low temperature and VTF behaviour at high temperature
- Arrhenius behaviour throughout, but with two different activation energies, high $E_a$ close to $T_g$ and smaller $E_a$ at higher temperatures.
- VTF behaviour in the temperature range slightly above $T_g$, but Arrhenius behaviour at higher temperatures.
- Behaviour which is unlike either Arrhenius or VTF at all temperatures.

1.13 Major advantages of polymer electrolyte

The polymer electrolytes play an important role in solid polymer electrolyte battery:

- It is a lithium ion carrier and as noted earlier, can be formed into thin films to improve the energy density.
- It acts as a electrode spacer, which eliminates the need to incorporate an inert porous separator.
- It is a binder, which ensures good electrical contact with electrodes.
- It avoids the gas formation during operation (charge and discharge).
References


